STRUCTURAL STUDIES OF BINUCLEAR COBALT(III) CYANO COMPLEXES

Thesis by

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"There is something in such laws that takes the breath away. They are not discoveries or inventions of the human mind, but exist independently of us. In a moment of clarity, one can at most discover that they are there and take them into account. Long before there were people on the earth, crystals were already growing in the earth's crust. On one day or another, a human being first came across such a sparkling morsel of regularity lying on the ground or hit one with his stone tool and it broke off and fell at his feet, and he picked it up and regarded it in his open hand, and he was amazed."

M. C. Escher
"Approaches to Infinity"

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ABSTRACT

The crystal structures of six closely related binuclear cobalt(III) complexes have been determined by single crystal X-ray diffraction methods, in order to study the effects of the pentacyano system upon the bonding to various bridging ligands. Studies pertinent to dioxygen bridging ligands include the bis(pentacyanocobalt(III)) structures $K_5\{(CN)_5CoO_2Co(CN)_5\}\cdot H_2O$ and the double salt $K_8\{(CN)_5CoO_2Co(CN)_5\}(NO_3)_2\cdot 4H_2O$, as well as the bis(pentaamminecobalt(III)) structure $\{(NH_3)_5CoO_2Co(NH_3)_5\}(SCN)_4$. In all cases, the dioxygen ligands (peroxo and superoxo) are found to bridge the two cobalt atoms in the asymmetric, staggered arrangement, and both planar and nonplanar structures are noted. The structures of two molecules of the type pentacyanocobalt(III)pentaammine-cobalt(III) are determined, with the bridging ligands cyanide and thiocyanate. These compounds are $(CN)_5CoNCCo(NH_3)_5\cdot H_2O$ and $(CN)_5CoSCNCo(NH_3)_5\cdot H_2O$. The preparation and structure of the compound $K_6\{(CN)_5CoSSO_2Co(CN)_5\}\cdot 6H_2O$, containing the new bridging ligand thiosulfite (SSO_2^{2-}) are reported. This ligand bridges the two cobalt atoms through its two sulfur atoms, and has a geometry similar to that of normal coordinated sulfites. Coordination to cobalt is <u>trans</u> planar.

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CHAPTER I. INTRODUCTION

A. The Cyanide Ion

As this thesis is concerned with the cyanide ion as a ligand in several binuclear cobalt(III) complexes, a brief discussion of the characteristics of this ligand are in order. The CN^- group may be described simply in the Lewis formalism as $:C\equiv N:$, or equivalently in molecular orbital symbolism as $KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi 2p)^4$. In either case the net bond order is three. Perhaps the most useful model for thinking of the cyanide ion in terms of coordination to transition metals employs 2s-2p hybridization of the atomic orbitals of both atoms, leading to σ_z lone pairs in sp orbitals localized on the C and N atoms. Other filled orbitals are of π symmetry and bonding character. The lowest energy empty orbitals are the degenerate $\pi^*_{x,y}$ orbitals. A diagrammatic representation of the chemically important cyanide orbitals is given below, with filled orbitals shaded.

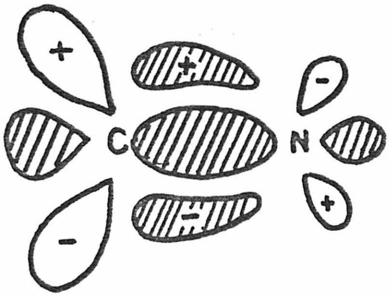


Figure I-1

Relative orbital energies calculated by a semi-empirical SCF MO procedure indicate that the highest energy filled MO is the "lone pair" with σ_z symmetry localized mainly on the carbon atom, which is to be expected due to the higher electronegativity of nitrogen. The next lower sigma orbital is that localized on nitrogen, with the degenerate π_x, π_y orbitals between. Metal orbitals of proper symmetry to overlap with σ_z ligand orbitals are nd_σ, $(n+1)s$ and $(n+1)p\sigma$, and as it turns out for cobalt, the metal d orbitals in particular are of favorable energy for overlap.

The electronic structure described above leads to chemical properties of the cyanide ion which make it both interesting and complicated in its role as a ligand. The high energy lone pair localized on the carbon atom causes the ion to be strongly basic, and thus gives it good sigma donor properties. It is thus expected that monodentate (usually referred to as "terminal" in this thesis, with no intended reference to possible effects upon the experimenter's health) cyanide ligands will be coordinated in a linear fashion through the carbon atom, as is more definitely true for carbonyls. Such bonding is usually assumed and has always been confirmed by recent experiments designed to differentiate between carbon and nitrogen bonded terminal cyanide. Indirect evidence has been interpreted in this manner, for instance the fact that methylation of complex cyanides yields methyl isocyanides. As the precision of the X-ray diffraction experiment has increased, it has become possible to differentiate between the similar electron densities around carbon and nitrogen, and more directly prove the bonding mode. While "reasonable" refined thermal parameters and residual electron densities during refinement are usually taken as such proof, recently electron population parameters have been used to distinguish the carbon and nitrogen atoms.[2] Neutron diffraction has also been a useful tool. No bona fide stable N-bonded terminal cyanide has ever been confirmed. One of two isomers of $\{Co(CN)_2trien\}^+$ which were reported to contain N-bonded cyanide[3] has very recently been shown by X-ray diffraction to contain the cyano ligands in the normal, C-bonded mode,[4] and it is quite likely that the other isomer does also.

Strong ligand-metal σ bonding causes the donor atom of the ligand to become more electropositive and become more receptive to metal-ligand π bonding (π back-bonding) from the metal $d\pi$ orbitals if the ligand possesses orbitals of π symmetry. This type of bonding might also be expected to be favorable because it distributes negative charge away from the metal which would otherwise be accumulated there due to σ donation. Carbon monoxide is the ideal such ligand, being a neutral species with the lowest energy empty orbitals being of π symmetry. Cyanide is expected to have π-accepting properties also, since it is isoelectronic with CO, however its negative charge should lower its relative electronegativity and somewhat decrease its π accepting properties.

Evidence concerning π-bonding in cyano complexes is somewhat confusing and not wholly conclusive. Perhaps the most compelling reason to believe is based simply on chemical properties. Efficient σ-bonding ligands which cannot accept π donation from the metal (Cl^-,OH^-, etc.) do not form stable complexes with metals in low oxidation states, while such stabilization is typical of good π-accepting ligands such as ϕ_3P, CO, and RNC. Cyanide is known to form many complexes with metals in low oxidation state, although they are in most cases chemically less stable than the analogous carbonyl complexes. Substantial metal-ligand π bonding is also consistent with the high position of cyanide on the "spectrochemical series," as the crystal field splitting energy, Δ_0, is increased through stabilization of the t_2g orbital caused by delocalization into π^* cyanide orbitals. Infrared spectra have been used to evaluate the M-C and C-N bond orders, but suffer from several drawbacks, including the fact that the σ donation and π acceptance have opposite effects on k_{C-N} (the force constant of the C-N bond), such that changes in this value with degree of π bonding are small.

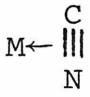
X-ray diffraction data, the usual solution to controversial bonding questions, have not unambiguously solved the problem of π bonding in cyano complexes for primarily two reasons. One of these was best put by Griffith in an excellent review of cyanide complexes of transition metals,[5] "Values of metal-ligand bond distances do not provide impressive evidence for π-bonding owing to lack of information on the length that the bond would have if it were exclusively σ in character." The other problem is that changes in bond lengths, particularly C-N, between complexes suspected of exhibiting appreciable and little π bonding will be small, and many X-ray studies of cyano complexes are of insufficient precision to detect such changes. Few determinations have placed the C-N distance with an esd of smaller than 0.01 Å. Even in more precise determinations, intermolecular interactions may tend to obscure the information sought.

Another interesting feature of the cyanide ligand is its ambidentate nature. Lone pairs, localized on both the carbon and nitrogen atoms, are available for donation, and the energy difference between them is not as great as in CO. While terminal cyanides are always C-bonded (vide supra) or isomerize quickly when formed as the isocyanide,[6] cyano complexes can serve as ligands, coordinating to another transition metal through the nitrogen atom. The cyanide in these compounds serves as a bridging ligand, and such $M-C\equiv N-M'$ bridges are quite common in polymeric metal cyano complexes, although rare in discrete binuclear complexes which are chemically stable. The history of cyano-bridged complexes dates back to the beginning of coordination chemistry. Interestingly, the first known coordination complex was prepared in 1704 by a German artist seeking a dye, and this compound, Prussian Blue, contains polymeric cyano bridges.[7] Diesbach heated animal wastes with Na_2CO_3 in an iron vessel, and obtained $Fe_4\{Fe(CN)_6\}_3$, a cubic polymer containing Fe^{II} and Fe^{III} linked together by CN^-. Structural studies of Prussian Blue and related compounds have been vigorously pursued, but understanding has been hampered by difficulty in obtaining crystals, interstitial inclusions, disorder of the cyano group, and the difficulty in distinguishing C from N even in an ordered structure.

Discrete binuclear complexes with cyano bridges are a great deal less common, as mentioned before. At the time of this writing, to the knowledge of the writer, only seven have been reported, of which two are questionable. Before the work described in this thesis, the crystal structure of only one of these[8] had been determined.

A useful tool in the detection of bridging cyano groups is infrared spectroscopy.[9] Terminal cyanides display an IR absorption in the region of 2110-2140 cm^{-1}, while bridging cyanides absorb at higher frequencies, within a range of about 2200-2230 cm^{-1}. This effect is presumably caused by a constraint placed upon the motion of the cyanide group by the second metal atom.

The presence of filled π orbitals in the bonding scheme of the cyanide ion suggests their use as donors, leading to edge-on π-complexes similar to π-olefin complexes:



$$M \leftarrow \begin{matrix} C \\ ||| \\ N \end{matrix}$$

No simple complexes of this type are known, which is reasonable, since the cyanide carbon atom is a far better donor than the π system. One might expect that blocking the carbon atom with an alkyl group would allow edge-on coordination, and several acetonitrile complexes of Re^{III} are considered candidates for this type of bonding due to the absence of the usual C≡N stretching mode in their IR spectra.[10,11] The crystal structure of one of these complexes, $ReCl_3(PPh_3)_2NCCH_3$, has been worked out, and the acetonitrile was found to coordinate in the linear σ fashion through the nitrogen atom.[12] It seems likely that the other related compounds in question are bonded in the same manner.

B. The Dioxygen Ligand

The term "dioxygen" will be used here in a rather general sense, referring to all ligands or potential ligands consisting entirely of two oxygen atoms bonded together, regardless of oxidation state of the group. The term molecular oxygen should be understood to mean the neutral, naturally occurring molecule O_2, and peroxo and superoxo refer to the anions O_2^{2-} and O_2^-, respectively. These distinctions in many cases get to be academic, as in metal complexes the actual oxidation state of the ligand may become nebulous.

Dioxygen has been described as an "exotic"[13] ligand, which is a quite descriptive allusion to the fact that even more than for cyanide, the electronic structure of the ligand allows a number of possibilities of bonding modes for coordination to transition metals. Its role as a ligand is, however, very fundamental and important, since it is as a ligand that dioxygen is involved in biological metabolism and transport.

Historically, this molecule was important in the development of the now quite popular and useful molecular orbital theory, since its ground state is a triplet $^3\Sigma_g^-$, a fact which could not be explained by previous theories of coordinate bonding. The electronic configuration of the ground state is $KK(\sigma_s^b)^2(\sigma_s^*)^2(\sigma_z^b)^2(\pi_{x,y}^b)^4(\pi_{x,y}^*)^2$, and thus the molecule is paramagnetic with two unpaired electrons and has a net bond order of two. Hybridization of s and p orbitals is probably not a useful model for thinking about the oxygen molecule. While there can be no doubt that this sort of mixing is a useful concept when applied to carbon compounds, it should be noted that the s-p orbital energy separation in molecular oxygen is almost 120kK, three times that of carbon,[14] and hybridization is probably a rather poor approximation to the true bonding situation in O_2. Thus all bonding interactions should be thought of in terms of the unhybridized molecular orbitals.

While in triply-bonded molecules such as CO and N_2, the $\sigma 2p$ atomic orbitals are largely nonbonding and thus are available for donation to transition metal d orbitals, we would not expect to observe this type of coordinate bonding for the doubly-bonded O_2, in which the $\sigma 2p$ orbitals are highly bonding and localized between the oxygen centers. This orbital has a much lower energy in molecular oxygen than in the triply-bonded molecules, and is probably much too low in energy to be important in bonding interactions. Further population of the π_g^* orbitals in the dioxygen anions O_2^- and O_2^{2-}, with resultant lengthening of the O-O internuclear distance, would be expected to further lower the energy of the $\sigma 2p$ orbital while having little effect upon the energy of the $\pi_u 2p$ orbitals, which have about the same energy in both the dioxygen molecule and the triply-bonded molecules.

These properties lead us to expect a "bent" end-on geometry for coordination of dioxygen ligands to transition metals. The bent M-O-O unit allows strong σ-donor interactions between the in-plane π^* orbital with the d_{z^2} orbital of the metal and π interactions between the out-of-plane π^* orbital and the $d_{xz,yz}$ orbitals of the metal. For a complexed peroxide ion, which has filled π^* orbitals, these interactions would be described as σ donation and π donation, whereas for superoxide, which has unfilled π^* orbitals, π-back bonding (π-acceptor) interactions are possible.

Upon complexation, the formerly degenerate π^* orbitals of dioxygen split in energy, that lying out of the M-O-O plane being of higher energy and thus containing the unpaired electron if there is one. Another metal may engage this unit in exactly analogous bonding, forming a staggered M-O-O-M unit with each degenerate π^* orbital being involved in bonding with both metal centers, assuming a planar unit. For a non-planar M-O-O-M unit (specifically one with a 90° torsion angle) each dioxygen π^* orbital would be involved in σ bonding with one of the metal centers and in π bonding with the other. The limiting cases are diagrammed in Figure 2, and the bonding in any form with a torsion angle intermediate between 90 and 180 degrees cannot be thought of in such simple terms.

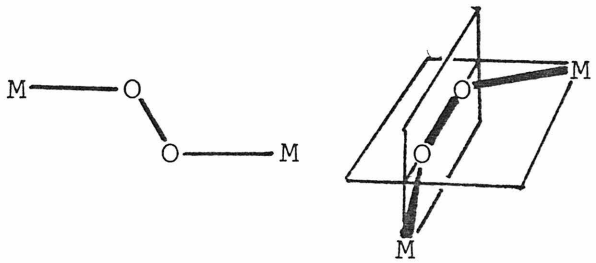


Figure I-2

The π_b orbitals of dioxygen may also act as σ donors, leading to an "olefinic" type of bonding. The geometry of this kind of complex is shown in Figure 3; in the ideal case the two oxygen atoms are equidistant from the metal. This geometry also allows π interactions with the π^* orbitals of dioxygen.

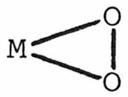


Figure I-3

Finally, linear coordination of the dioxygen ligand should be considered. If the $\sigma 2p$ orbital is ruled out on energetic grounds, as has been discussed previously, then the π^* and πb orbitals are the only energetically favorable possibility in a linear M-O-O unit, and with them only π donor or acceptor interactions are possible. This bonding is expected to be weak by comparison to σ-donor interactions, and thus such complexes are expected to be unstable. It is quite disturbing that an example of linear coordination of the dioxygen ligand is, in fact, known. The $\{(CN)_5CoO_2\}^{3-}$ ion has been shown, by a crystal structure determination, to have a nearly linear Co-O-O unit, with this angle being 175(2)°.[15] Bond distances within the ion suggest its formulation as a superoxo complex of Co(III). The bonding in this complex is somewhat obfuscatory, since the Co-O bond seems to be about as strong as in the corresponding μ-superoxo dimer which will be described in this thesis, in which σ donation is certainly very important. Clearly, our present understanding of the role of dioxygen as a ligand is inadequate.

We have, then, at least four modes of coordination of dioxygen to metals which have been demonstrated to exist. Other unconfirmed possibilities can also be imagined. The so-called 1:1 complexes (one metal atom to one dioxygen ligand) come in three varieties. 1) The symmetric complexes are five coordinate (when dioxygen is considered as monodentate) complexes of Rh, Ir, Pt, and Co.[16-19] The O-O distances vary quite a lot in these compounds, and it is difficult to assign the oxidation state of either the metal or the dioxygen group in many of them. These compounds have recently been discussed in several reviews and will not be discussed in depth here. 2) Asymmetric 1:1 complexes (bent end-on) are known to result from oxygenation of square planar complexes of Co(II) and Fe(II) with tetradentate ligands in the presence of a coordinating base. Very recently, X-ray structural data have begun to become available for these model compounds for heme proteins, but disorder and high thermal motion of the dioxygen ligand are common problems, and the precision of the derived geometries has thus far been uniformly low. It appears that the cobalt complexes are best described as Co(III)

superoxo complexes with the Co-O-O angle of about 126°.
3) The only known example of linear bonding is the previously-described $(CN)_5CoO_2{}^{3-}$ ion.

Binuclear complexes, the real subject of this discussion, are a great deal more common than any of the previously mentioned 1:1 compounds. The only established geometry for these complexes is the "staggered" asymmetric mode depicted earlier. The symmetric, π-bonded configuration also seems possible in dimers, and indeed was erroneously thought to be documented by an X-ray structure which exhibited disorder. This quite unfortunate situation will be discussed in detail in the succeeding section. Finally, due to the recent surprising appearance of the linear monomer, the linear dimer can, with a somewhat perverted imagination, be considered as a possibility. We might expect that the μ-superoxo decacyano complex would be a prime candidate for this sort of bonding if any imaginable complex would, but as will be reported in this document, that complex is staggered.

C. The Thiocyanate Ion

The SCN^- anion, well known as a "pseudohalide" ligand in classical coordination chemistry, has received recent interest in its role as an ambidentate ligand. It has been the principal species of interest in the investigation of linkage isomerism, due to its ability to coordinate to metals through either the nitrogen atom (isothiocyanate) or sulfur atom (thiocyanate) or both. Several pairs of compounds have been characterized in which thiocyanate coordinates to the same system through either terminal atom, and in all cases, one linkage is more stable than the other. Complexes have recently been isolated which contain in the same molecule both thiocyanate and isothiocyanate linkages.

The molecular orbitals of the thiocyanate ion which are important to coordination are described by DiSipio, et al., who performed an MO calculation to determine the relative energy levels.[20] They are similar to those found in cyanide except for an extra orbital (labelled 2π). This orbital is the highest filled level and is essentially nonbonding, localized on the sulfur atom. The lowest unfilled orbital (labelled 3π) is considerably higher in energy than the cyanide π^* orbital, and therefore less suited to π-acceptance. The two highest filled σ orbitals are probably best thought of as nonbonding sp hybrids localized on the end atoms. Bonding to metals is expected to be primarily σ donation from the sp lone pair on nitrogen, leading to a linear M-NCS group, and/or σ donation from the 2π lone pair on the sulfur atom, leading to a bent M-SCN linkage. Some π-accepting character of the M-S bond, utilizing the 3π orbital might be expected, although weak. Gutterman and Gray,[21] in a spectroscopic examination of complexes of the type $(CN)_5CoX$ where X is a triatomic ligand, found no evidence of participation of π-acceptor orbitals of the triatomic ligand in the metal-ligand bonding.

Structural data for thiocyanate complexes and ionic thiocyanate are somewhat confusing. If the canonical structure S-C≡N is assumed, distances of approximately 1.79 Å for S-C and 1.15 Å for C≡N would be expected. Actual results exhibit quite a bewildering variation. While practically all thiocyanate groups determined by X-ray diffraction are reasonably linear, S-C distances vary over the range of 1.55 to 1.76 Å, and C-N distances vary over a range of 1.13 to 1.34 Å.[22] This wide variation is no doubt partly due to the low precision (and perhaps accuracy) of much of the work; however, even when only the more precise determinations are considered, the observed ranges are still considerably wider than what one might expect. Although the bonding within the thiocyanate ion is expected to rearrange considerably upon complex formation, present data do not distinguish well between one set of distances for ionic thiocyanates and another for complexed ligands; considerable overlap exists, and conclusions regarding electron rearrangements must await more structural data.

The bonding mode of thiocyanate to transition metals is an interesting story which is not yet understood in its entirety, although trends are clear, and accurate predictions can be made. Apparently the stability of the thiocyanato and isothiocyanato linkages are inherently close together, such that subtle effects upon the electron distribution at the metal can easily exchange the order of stability. Generally, the nitrogen end of SCN^- is thought of as a hard base in the Pearson sense, and the sulfur end is thought of as a soft base. Thus thiocyanate would be expected to coordinate to hard acids such as Co(III) through the nitrogen atom and to soft acids such as Pd(II) through the sulfur atom. This sort of prediction holds up well throughout the periodic table as long as thiocyanate is the only ligand, but breaks down when other ligands are involved. Soft ligands can "soften" a hard metal such that thiocyanate will prefer to bond via the sulfur atom; for instance, $(CN)_5CoSCN^{3-}$ is more stable than its linkage isomer. An inverse effect causes $(NH_3)_5CoNCS^{2+}$ to be more stable than its linkage isomer. This rule works nicely except that for soft metals, exactly the opposite effect is noted. Soft bases such as alkylphosphines cause N-coordination in Pd(II) and Pt(II) complexes while hard bases such as NH_3 cause S-bonding. Steric and other environmental constraints have also been shown to affect the thiocyanate bonding mode, such that the subject is not at all transparent. In the borderline area in particular, other effects probably greatly outweigh the symbiotic relationships, which are themselves not well understood. Thiocyanate continues to be an intriguing ligand.

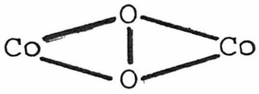
D. Binuclear Cobalt Complexes

1) Cobaltammines:

The ammine ligand has been classically of primary importance in the development of the chemistry of binuclear cobalt complexes. The first dicobalt complex was obtained by Fremy in 1852, when he synthesized a brown product by exposure of ammoniacal cobalt(II) solutions to air.[23] Fremy formulated this complex as a μ-peroxodicobalt(III) ion, and as it turned out, many years of investigation into the new field led to not only a wealth of new complexes, but to a complete confirmation of Fremy's original formulation. Extensive efforts during the late 19th and early twentieth centuries by Jorgensen, Vortmann, Werner, and others led to the synthesis and characterization of a staggering number of binuclear cobalt ammine complexes containing a wide variety of ligands and up to three bridges. The classic paper in this field was published in 1910 by Werner, summarizing his work and that of a large number of students.[24]

Much of the work, both in Werner's time and in recent times, has centered around the complexes containing an O_2 bridge. These complexes have become a subject of renewed interest because an understanding of the bonding of dioxygen to transition metals is fundamentally important to the subject of oxygen transport and metabolism by metalloproteins. Dioxygen-bridged complexes formed by direct oxygenation may be fairly easily oxidized by a one-electron oxidation without destruction of the dioxygen bridge. Werner realized that two different sorts of dioxygen-bridged complexes existed, but the bonding theories of his time did not allow for an understanding of the nature of the oxidized complex, and thus the terminology peroxocobalt(III,III) and peroxocobalt(III,IV) was contrived to distinguish the two. This formulation, of course, implies that the two cobalt centers are nonequivalent or are equivalent only by a resonance between the Co(IV) and Co(III) forms. Much more recently, in the mid-1960's, the problem of assigning formal oxidation states to the cobalt atoms was cleverly avoided by reference to the magnetic properties of these compounds. The paramagnetic ions of type $\{L_5CoO_2CoL_5\}^{5+}$ were for a time termed as "paramagnetic peroxo" complexes, and the analogous 4+ ions were termed "diamagnetic peroxo". Only through the full power of X-ray crystallography and EPR measurement were the complexes understood. It is now understood and accepted that the (4+) complexes are ordinary Co(III,III) compounds containing a peroxo bridge, and the (5+) compounds are actually Co(III,III) compounds containing a superoxo bridge. In both cases, the two cobalt atoms are identical with respect to oxidation state and electron configuration.

The geometric configuration of the bridging dioxygen group in these complexes has been a subject of as much controversy as the assignment of oxidation states to the metal atoms and ligands. A very unfortunate combination of circumstances led to their misformulation for a period of time in the early 1960's. Vlček,[25] on the basis of a molecular orbital calculation, predicted that the O-O group in the superoxo complex should be oriented perpendicular to the Co-Co axis, with π overlap, as is the case in certain 1:1 complexes. The first salt of this ion chosen for an X-ray crystallographic determination exhibited, as ill fortune would have it, a sort of disorder which caused the overall electron density in the area of the bridging group to resemble somewhat the perpendicular arrangement which had been proposed and was therefore perhaps expected.[26] Partially as a result of low precision, the diffraction data were interpreted by Vannerberg and Brosset to indicate the incorrect perpendicular bonding arrangement



This misinterpretation unfortunately found its way into several books and papers written shortly thereafter, such that older discussions of this subject must be read with caution. The true configuration of this ion was elucidated by a crystallographic study of the monosulfate tris(bisulfate) salt in 1966 and a redetermination of the original pentanitrate structure by Marsh and Schaefer the following year.[27,28] The structure of the diamagnetic (4+) ion was suggested by an inaccurate crystal structure determination by Vannerberg in 1965 of the tetrathiocyanate salt[29] and completely established by Schaefer in 1968 in a precise determination of the disulfate tetrahydrate.[30] The structures of the two ions are similar, both containing the bridging ligand in the asymmetric, staggered configuration

The superoxo complex was found in both determinations to be essentially planar, with an O-O distance of about 1.31 Å and a Co-O-O angle of about 118 degrees. The peroxo complex exhibited an O-O distance of 1.47 Å and a Co-O-O angle of about 113 degrees. While the cation in the sulfate structure was found to contain a torsion angle of 146°, the same ion in the apparently unsatisfactory tetrathiocyanate structure was rigorously planar. This discrepancy was not taken too seriously until a redetermination of the thiocyanate salt (one of the subjects of this thesis) proved the original formulation to be essentially correct. The factors which we now believe to account for this difference, based not only on the redetermination but also on the results of several similar structural studies, will be discussed at length in a later portion of this document.

2) Cobalt cyano complexes

Aqueous solutions of Co(II) and the cyanide ion in a ratio of 1:5 or smaller probably contain the ion $Co(CN)_5^{3-}$, which is an exceedingly good reducing agent. While the chemistry of cobalt pentacyanide is extremely interesting and complex in many respects, this discussion will be limited to its role in the formation of binuclear complexes. A large number of two-electron oxidizing agents are capable of forming bridged species of the type $(CN)_5Co-L-Co(CN)_5^{n-}$. The simplest, which does not really "belong" in the same class with the rest, is the solid state dimer of the pentacyanocobalt(II) ion, $\{Co_2(CN)_{10}\}^{6-}$, in which the bridging group is simply an electron-pair bond formed between the metal ions. The structure of this complex has recently been determined by two X-ray studies of the hydrated barium salt.[31,32]

The formation of the other members of this series may be visualized as a two-step process, in which the neutral ligand L first engages in an oxidative addition reaction with the $Co(CN)_5^{3-}$ ion to form $(CN)_5Co(III)-L^-$. Since the ligand L is a two-electron oxidizing agent, this complex may oxidatively add to another molecule of $Co(CN)_5^{3-}$ to form the bridged complex $(CN)_5Co(III)-L(2-)-Co(III)(CN)_5^{6-}$. In reality, the ligand L need not be a neutral species to begin with, such that the final charge on the binuclear ion may vary.

Perhaps the most important of the complexes of this sort is that in which the ambidentate, oxidizing ligand L is molecular oxygen. The oxygenation of $Co(CN)_5{}^{3-}$ was first described by Haim and Wilmarth,[33] who also found that the diamagnetic product $(CN)_5CoO_2Co(CN)_5{}^{6-}$ can be easily oxidized by a one-electron oxidant (oxygen itself seems to be a sufficiently good oxidizing agent) to form the superoxo complex. The brown peroxo ion is stable only in strong alkaline solution, while the magenta superoxo (5-) ion is stable in solution over a wide range of pH. Prior to the work described in this thesis, the configuration of neither of these ions was definitely known; however, they were both widely assumed to have the staggered, asymmetric dioxygen bonding mode, primarily by analogy to the corresponding decaammine complexes and by ESR examination of the paramagnetic compound.[34] There has been some discussion of the possibility that the π acceptor nature of the cyanide ion would alter the electron distribution around the cobalt atom in such a way as to cause the dioxygen to bond in the symmetrically bridged mode in the decacyano ions, even though the decaammine ions were finally demonstrated not to have this type of bonding.

It is worthy of note that, strictly speaking, the superoxo ligand does not fall into the category described, for the μ-superoxo complex cannot be made directly by oxidation of the $Co(CN)_5{}^{3-}$ ion. In order to form this complex, the dioxygen ligand must be reduced to peroxo by two-electron oxidative addition and then reoxidized back to the superoxo state. The $(CN)_5CoO_2Co(CN)^{5-}$ ion can, however, be synthesized in an alternate manner which turns out to be much more convenient than the oxidation of the μ-peroxo decacyano ion. The μ-superoxo decaammine ion can be synthesized in pure form very easily and in good yield. Its reaction with cyanide ion is amazingly fast at room temperature, forming almost quantitatively the μ-superoxo decacyano ion without destruction or alteration of the superoxo linkage.[34] The mechanism of this metathesis reaction has not been investigated, but it seems likely that it involves some sort of redox intermediate reactions, since its rate is many orders of magnitude faster than the replacement of ammine by cyanide in the hexamminecobalt(III) ion or in several binuclear complexes containing bridging ligands of invariable oxidation state (i.e., cyanide).

Other ligands which form ligand-bridged complexes of the form $(CN)_5Co{-}L{-}Co(CN)_5^{n-}$ are Cd(II),[35] Hg(II),[35] Tl(I),[36] $SnCl_2$,[37], SO_2,[37] acetylene,[38] C_2F_4,[39] p-benzoquinone,[40], Se_2,[41], S_2, SSO_2^{2-},[41], and (perhaps) N_2O_2.[42] It seems clear that many other two-electron oxidants may form such dimers, but the reactions simply have not been performed. Previous to the work described in this thesis, the crystal structures of none of these compounds had been determined. Some are more interesting than others. For instance, the dicobalt decacyanide dimer stabilizes the S_2^{2-} ion, which is not known to exist as the free ion, and thus provides a way in which a "nonexistent" ion can be studied structurally.

3) The system $(NH_3)_5Co\text{-}L\text{-}Co(CN)_5$

Molecules of type pentaamminecobalt(III)-L-pentacyanocobalt(III) are ideally suited for the structural study of ambidentate ligands L. The existence of these species is very recent, the first being reported in 1969.[43] These investigators prepared the cyano-bridged compound by a thermal dehydration reaction. Thermal dehydration of salts of the aquopentaamminecobalt(III) ion yields products in which a variety of anions replace water in the inner coordination sphere:

$$\{(NH_3)_5CoOH_2\}X_3 \xrightarrow{\Delta} \{(NH_3)_5CoX\}X_2 + H_2O$$

By using the complex anion $Co(CN)_6^{3-}$ as the anion X, they were able to synthesize the cyano-bridged binuclear compound. Another similar reaction led to the synthesis of the linkage isomer of this complex. The successful synthesis of the $(NH_3)_5CoCN^{2+}$ ion[44] led to the isocyano-bridged compound by substitution of this ion for water in $(CN)_5CoOH_2^{2-}$:[45]

$$(CN)_5CoOH_2^{2-} + (NH_3)_5CoCN^{2+} \longrightarrow (CN)_5\ CoNCCo(NH_3)_5 + H_2O$$

More recently, both linkage isomers with $L{=}SCN^-$ have been prepared by exactly analogous reactions upon both isomers of $(NH_3)_5Co(SCN)^{2+}$.[46] No other compounds of this series have yet been reported, although several other promising ambidentate ligands are available.

These compounds were initially interesting in investigation involving internuclear interactions in binuclear complexes. Their electronic spectra exhibit no hint of such interaction, as they correspond very closely to the sum of the spectra of two isolated Co(III) atoms in the appropriate ligand environments. In fact, the observation that the UV-VIS spectra did not conform to the average environment of the two cobalt atoms was an important consideration in their initial characterization as asymmetric binuclear complexes with "unmixed" ligands. An X-ray structure determination confirmed the characterization of the cyano-bridged compound $(NH_3)_5CoNCCo(CN)_5$.[8]

These complexes, as mentioned earlier, are nice systems for the structural (bonding) study of ambidentate ligands, for several reasons:

a) They stabilize ordinarily unstable linkages by coordination of the free end of the ambidentate ligand. For example, the Co-NC linkage isomerizes very quickly to Co-CN in terminal complexes; however, species such as $(NH_3)_5Co$-NC are quite stable as a fragment of a binuclear complex.

b) In effect, two systems can be studied at once. For instance, the $(NH_3)_5Co\text{-}XY\text{-}Co(CN)_5$ system gives us information about both $(NH_3)_5Co\text{-}XY$ and $(CN)_5CoYX$.

c) The complexes are neutral species when the bridging ligand is monoanionic, as most are. For an X-ray crystallographic study, no messy counterions obscure the information sought, and the number of atoms is kept to a minimum.

d) In general, if the -XY- linkage exists, there is probably a good chance that the -YX- linkage will also exist, as the difference between the stabilities of the two linkage isomers is considerably smaller than for nonbridging ligands. For any given ambidentate ligand, both isomers can usually be studied.

e) Most known complexes of this sort crystallize well, probably due to the good possibilities for hydrogen bonding.

In this thesis, the crystal structures of two more of the complexes in this system are described, the isocyano complex and the thiocyanato complex. The structure of the isocyano molecule is very revealing when compared to that of the cyano molecule. The thiocyanato structure is interesting in itself; however, the structure of its linkage isomer has not been determined.

CHAPTER II. EXPERIMENTAL

A. Synthesis of Compounds, Crystal Preparation, and Preliminary Characterization

1) $K_8\{(CN)_5CoO_2Co(CN)_5\}(NO_3)_2 \cdot 4H_2O$

The μ-peroxo decacyano ion was prepared by rapid bubbling of oxygen through a solution containing $Co(CN)_5{}^{3-}$ at 0^o C.[33] Cobaltous nitrate and potassium cyanide were used in the preparation reported to yield $K_6\{Co_2O_2(CN)_{10}\} \cdot H_2O$. The crude product, when examined microscopically, appeared to contain thin, brown flakes which were transparent when moist but became opaque upon drying. Smaller deep orange crystals which remained transparent upon drying and colorless KNO_3 were also present. Recrystallization was accomplished by addition of ethanol to a solution of the crude product in 1 M KCN at 0^o C.; the transparent orange crystals were the least soluble solid, and were collected as the major product. Iodometric determination of peroxide content of the orange product yielded consistently lower values than would be expected for any hydrate of $K_6\{Co_2O_2(CN)_{10}\}$; repeated recrystallization did not substantially affect the peroxide analysis. Density measurements (performed by flotation in a CCl_4-$CHBr_3$ mixture) and cell dimensions determined from Weissenberg photography indicated a unit cell which could not possibly contain an integral number of formulas of any conceivable hydrate ($<13H_2O$) of the potassium salt. The UV-visible spectrum of these crystals dissolved in 1 M KOH was identical to that reported for $K_6\{Co_2O_2(CN)_{10}\}$.[47] It was obvious that these crystals contained, among other (unknown) species, the binuclear ion of interest, and since they are a great deal more stable than the simple potassium salt (presumably the brown flakes which fell apart upon drying), were deemed suitable for a structural study.

Growth of diffraction-quality crystals was nontrivial, but successfully accomplished by careful control of the ethanol-water proportions in a solution at 0° C. Crystals were washed with ethanol and ether and air dried. Oscillation and Weissenberg photography indicated systematic absences $h0\ell$ with ℓ odd and $0k0$ with k odd, which are uniquely consistent with monoclinic space group $P2_1/c$. A crystal of dimensions 0.11 x 0.44 x 0.15 mm, elongated along b, was chosen for intensity data collection and mounted with its b axis inclined approximately ½ degree from the diffractometer ϕ axis.

2) $K_5\{(CN)_5CoO_2Co(CN)_5\}\cdot H_2O$

The zinc salt of the $\{(CN)_5CoO_2Co(CN)_5\}^{5-}$ ion was prepared from $\{Co_2O_2(NH_3)_{10}\}(SO_4)(HSO_4)_3$ by replacement of ammine ligands with cyanide ligands on the pre-formed CoO_2Co unit, a reaction which goes remarkably easily at room temperature.[34] Using the insoluble orange zinc salt as a starting material, extensive efforts were made to crystallize the binuclear anion with a variety of cations, including K^+, Na^+, NH_4^+, Ca^{2+}, Ba^{2+}, $(C_4H_9)_4N^+$, and $\{CoO_2(NH_3)_{10}\}^{5+}$. All attempts yielded powders or more often intractable oils except for potassium, which, with difficulty, could be coerced to form rather poor but single crystals, magenta in color. Crystals were grown from aqueous solution by addition of a 1:1 mixture of methanol and ethanol at 0°, followed by slow cooling to -15°. Repeated attempts to grow high quality crystals were made, but the tendency to oil or to form small, dendritic crystals was pronounced. Large crystals which sometimes formed could not survive the trauma of being removed from the mother liquor and warmed to room temperature, even if the warming was performed at rates so slow as to tax the patience of the experimenter to experience the joys of reciprocal lattice photography. Thin, bladelike crystals could be removed intact, and whereas they were rather small and pathologically shaped for the purposes of precise X-ray diffraction, they yielded clean diffraction patterns, and the structure was determined using them.

Preliminary Weissenberg photography of the reciprocal lattice indicated a triclinic lattice, and a Delaunay reduction procedure[48] exposed no higher symmetry. The Delaunay-reduced triclinic cell was chosen for structure solution and refinement (vide infra); however, intensity data were collected in the unreduced cell as originally indexed on photographs, due to the benefits of aligning the crystal precisely around the long axis, with consequent ease in locating and indexing reflections in diffractometer coordinates. The matrix which transforms the "film" axes into the Delaunay cell axes (and therefore also the film reciprocal indices into the indices in the Delaunay cell) is:

$$\begin{pmatrix} -1 & 1 & 0 \\ 1 & -1 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

Density determinations performed by flotation in a CCl_4-$CHBr_3$ mixture established the number of formula units of $K_5\{(CN)_5CoO_2Co(CN)_5\}\cdot H_2O$ as three, a rather unusual number. A crystal of approximate dimensions 0.55 x 0.03 x 0.09, elongated along the real c axis, was chosen for intensity data collection and placed in a capillary for protection from atmospheric humidity (the compound is somewhat deliquescent) and mounted with its long axis coincident with the diffractometer ϕ axis.

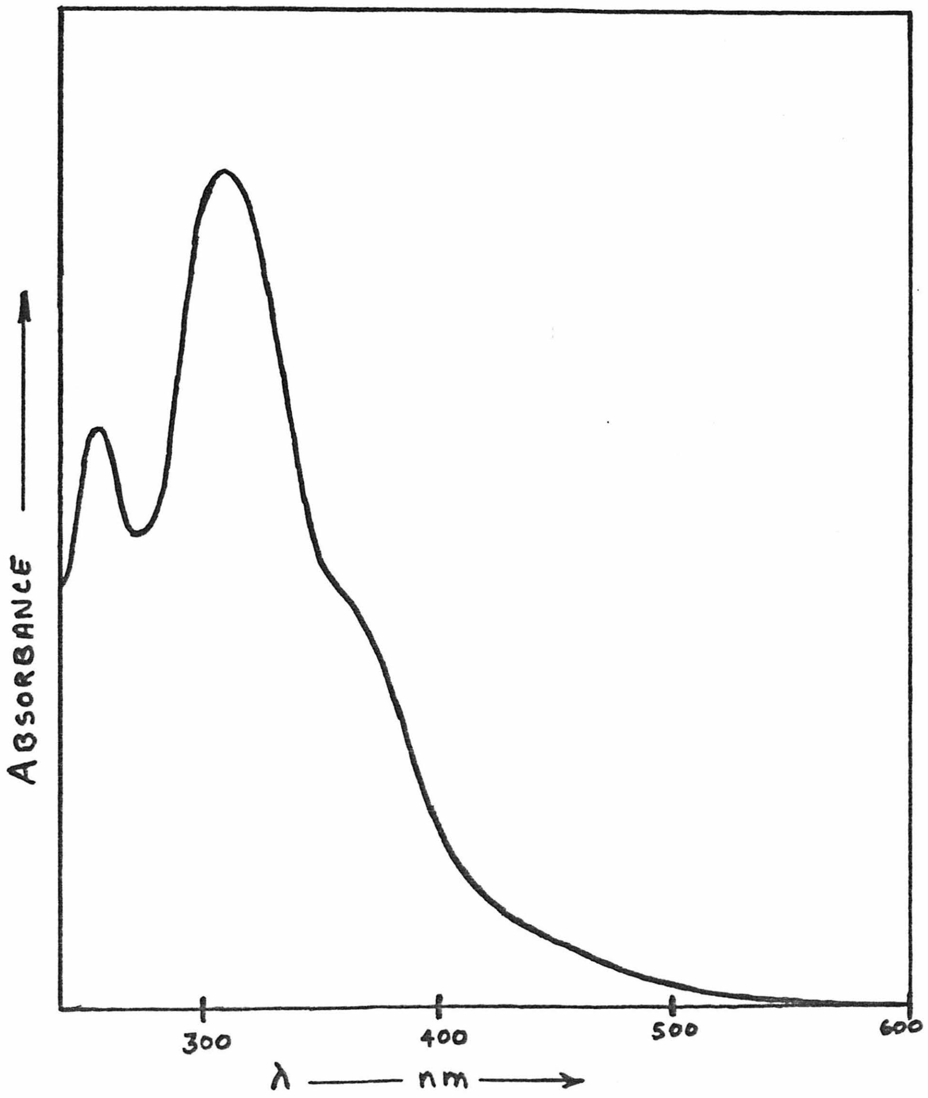
3) $K_6\{(CN)_5CoSSO_2Co(CN)_5\}\cdot 6H_2O$

The recently reported procedure for the preparation of the $\{Co_2S_2(CN)_{10}\}^{6-}$ anion was carried out,[41] using elemental sulfur in the oxidation of $Co(CN)_5{}^{3-}$. Sources of cobaltous and cyanide ions were cobaltous acetate and KCN. The orange-brown product is quite soluble in water and tends to form a dark brown, almost black oil. Spectroscopic experiments indicate that this product contains appreciable amounts of at least one other cobalt cyano complex which this experimenter has not isolated. Workers in another laboratory have isolated from this reaction a complex which appears to contain one sulfur atom per two cobalt atoms, as judged by elemental analysis.[49]

Recrystallization, which is difficult due partially to the extreme solubility of this complex in water, was attempted using a variety of cations and solvent systems, with some success at good crystal formation using an ethanol-water mixture with barium counterion at -15^{o}. One recrystallization attempt using potassium ion in an ethanol-water solvent system was allowed to sit for approximately eight weeks at -15^{o}, yielding large, well-formed, dark orange prismatic crystals growing amid a ground mass of polycrystalline material, yellow to brown in color. The large crystals were obtained in pure form by the Pasteur method (discriminatory crystal-picking). A UV-VIS spectrum of this material (Figure II-1) indicated that it is not the μ-dithio complex. Unit cell dimensions, space group information, and a density determination suggested that the anion is dimeric, and indicated a possible formulation such as $K_6\{Co_2S_2(CN)_{10}\}\cdot 8H_2O$. Eventual successful refinement demonstrated the compound to be $K_6\{(CN)_5CoSSO_2Co(CN)_5\}\cdot 6H_2O$. Weissenberg photographs indicated systematic absences $hk\ell$ with $h+k$ odd and $h0\ell$ with ℓ odd, consistent with monoclinic space

Figure II-1

UV-VIS spectrum of the μ-thiosulfito complex.



groups C 2/c and Cc. Qualitative examination of the intensity distribution on films led to the judgment that the centric space group was more likely, and the space group was assumed to be C 2/c. Preliminary work was done in space group I 2/a, since the crystals were elongated along an axis in this setting, and the monoclinic angle β is conveniently extremely close to 90°. Twinning was commonly observed in these crystals; however, several large single crystals were found. A crystal of approximate dimensions 0.45 x 0.30 x 0.26 mm was mounted with its long dimension (<u>a</u> in I 2/a or $\bar{1}01$ in C 2/c) coincident with the ϕ axis of the diffractometer.

4) $\{(NH_3)_5CoO_2Co(NH_3)_5\}(SCN)_4$

Synthesis of the compound was effected by dissolving one gram of $Co(SCN)_2$ in 50 ml of water, adding 27.8 ml of 15 M NH_4OH, and refrigerating the solution exposed to the atmosphere at 0° C. for several hours. Dark green to black needles were separated from the mother liquor by filtration and were washed with ether. These were large and of nearly square cross-section. Cleavage normal to the needle axis is fairly good, such that crystal fragments almost cubic in shape were easily obtained. Oscillation and Weissenberg photographs indicated an orthorhombic lattice with systematic extinctions $0k\ell$ with $k+\ell$ odd and $h0\ell$ with $h+\ell$ odd. These absences are consistent with space groups Pnn2 or Pnnm, and the centric space group reported in the original investigation[29] was assumed. Eventual refinement proved the appropriateness of this choice. A density determination was made by flotation in a CCl_4-$CHBr_3$ mixture. A crystal of approximate dimensions 0.24 x 0.22 x 0.22 mm was mounted on a diffractometer with its c axis roughly aligned with the instrumental ϕ axis. This crystal had been covered with three coats of epoxy cement applied under a stream of argon to retard decomposition which was observed to occur with other crystals of this compound. The complex is decomposed, evolving oxygen when placed in water, and it is likely that atmospheric humidity is responsible in part for decomposition upon standing.

5) $(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$

A sample of this compound was supplied by A. Haim as a finely divided yellow powder. Several methods of recrystallization were attempted in order to produce crystals which retained their integrity upon drying, and thus several crystalline modifications were isolated and partially characterized. Recrystallization from an ethanol-water mixture yielded tetragonal crystals of space group $P4_2$ with cell dimensions a=8.08, c=14.66 Å. Intensity data for this modification were collected on a diffractometer by M. U. Wimbrow and B. L. Trus;[50] however, the crystal underwent anisotropic decay during measurement, and the data obtained were not of suitable quality to allow even the general features of the structure to be determined.

This decay was probably spontaneous loss of solvent which is not necessarily related to irradiation in the X-ray beam.

Prismatic crystals were obtained from an aqueous acetic acid solution, and were found to be orthorhombic with approximate cell dimensions a=11.4, b=10.7, c=14.5 Å. Systematic extinctions do not uniquely determine the space group of this form, but considerations of density and point symmetry limit the possibility to $Cmc2_1$ or C2cm. These crystals spontaneously lost solvent within minutes after removal from mother liquor, and no further work was done with them.

Crystals were grown by evaporation of a solution of the compound in concentrated aqueous $NaHCO_3$. The strategy was to co-crystallize the binuclear complex with sodium bicarbonate in order to stabilize solvent hydrogen bonding interactions, and indeed this plan seemed to work, as stable, albeit quite small crystals were obtained. Weissenberg photography indicated systematic extinctions $0k\ell$ with k odd, $h0\ell$ with ℓ odd, and hk0 with h odd, uniquely consistent with space group Pbca, and unit cell parameters approximately the same as those found for stable crystals of the linkage isomer $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ grown by evaporation from neat aqueous solution.[8] This result was fortuitous but highly beneficial; instead of incorporating bicarbonate ion, a stable form of the monohydrate had been prepared which is isostructural with the known structure of the linkage isomer.

A small crystal of approximate dimensions 0.08 x 0.04 x 0.06 mm was mounted on the diffractometer with its a axis slightly inclined from the diffractometer ϕ axis.

6) $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$

A sample of the compound was generously supplied by J. G. Wardeska of East Tennessee State University in the form of an orange powder. Large, single crystals were easily grown by dissolving this powder in 0.5M $HClO_4$ at 50°, filtering the solution, and quickly cooling to 10°. Crystals were collected after 24 hours, washed with ethanol, and air dried. The well-formed crystals are elongated with rectangular cross-section. Systematic extinctions judged from Weissenberg films are $0k\ell$ with k odd, $h0\ell$ with ℓ odd, and hk0 with h odd. These extinctions uniquely determine the space group to be Pbca. A density determination performed by flotation in a CCl_4-$CHBr_3$ mixture established that the unit cell contains 8 formula units and suggested that the complex is present in the crystal as the monohydrate. The crystal chosen for data collection was elongated along c, and terminations at both ends were crumbled away to approximate a rectangular prism of dimensions 0.08 x 0.26 x 0.37 mm. It was mounted with its c axis inclined about ½ degree from the ϕ axis of the diffractometer.

B. Intensity Data Collection

Intensity data for all structures reported in this thesis were obtained under basically similar circumstances. The general procedure of data collection and reduction will be described here, and specific parameters for individual determinations will be tabulated.

All data except for measurements on $K_8\{Co_2O_2(CN)_{10}\}(NO_3)_2\cdot 4H_2O$ were collected on General Electric XRD quarter circle diffractometers automated by Datex, which are equipped with proportional counting detectors and circuitry. Measurements for the double salt mentioned above were made using a locally assembled Syntex-automated E & A full-circle diffractometer with similar counting circuits. In those cases in which CoKα radiation was used, it was filtered with iron foil, and MoKα radiation was monochromatized by a graphite crystal monochromator. Pulses generated by the scintillation counters were screened by pulse height analyzers before counting. Orientation matrices were obtained for all crystals by least-squares fits to χ and ϕ values for carefully centered reflections, and cell parameters were derived from least squares fits of 2θ values. Intensity data were measured by θ-2θ scans at constant rate on the GE machines and variable rate (proportional to peak intensity) on the Syntex machine. Backgrounds were counted for equal periods of time at each extreme of the scan, these periods being arbitrarily set on the GE machine and totalling the same as the scanning time for the variable speed scans. Scan widths varied linearly with 2θ; the slopes ($^\circ$ scan/$^\circ$ 2θ) and intercepts (width at $2\theta=0$) appear in Table 1. Reflections with 2θ values less than 4° could not be measured by the GE instruments. Several standard reflections were periodically remeasured in each case as a check of instrumental stability and crystal decay; particular reflections chosen as standards are listed in Table 1. If appropriate, linear decay corrections were applied to observed intensities, using these standards as a guide.

All net intensities were corrected for Lorentz and polarization effects, and when absorption corrections were necessary, these corrections were made by the method of Gaussian quadrature, with the integration calculated over a grid of 8 x 8 x 8 points.[51] Data were placed on an approximately absolute scale by the method of Wilson.[52] Observational variances $\sigma^2(F_0^{\,2})$ were assigned from counting statistics including a term $(0.02\ S)^2$, where S is the scan count, to allow for instrumental variations.[53] The magnitude of this "slop term" was chosen to correspond with what has been found to be appropriate through past experiences of investigators in this laboratory.

TABLE II-1. DATA COLLECTION SUMMARY

	μ-$O_2^{2-}(CN)_{10}$	μ-$O_2^{-}(CN)_{10}$	μ-$SSO_2(CN)_{10}$
Scan Range:			
Slope	.00769	.01739	.01230
Intercept	1.85°	1.50°	1.84°
Background Counting Time	Variable	30 sec.	20sec for $2\theta<40^\circ$ 40sec for $2\theta\geq40^\circ$
Scan Rate	Variable	1 °/min	2°/min for $2\theta<40^\circ$ 1°/min for 2 $\geq40^\circ$
Maximum Sin θ/λ	0.595	0.516	0.595
Check Reflections	500 $01\bar{3}$ 020 $23\bar{3}$	030, $2\bar{9}2$, $6\bar{6}0$, $\bar{4}81$ $\bar{2}23$,	511, $\bar{8}08$, $5\bar{3}1$, $3\bar{1}3$ $\overline{10}\cdot2\cdot2$,
Crystal Decay	3% in F^2	3% in F^2	9% in F
Decay Correction	Linear	Linear	Linear
Absorption Correction	None	Transmission Coefficients 0.81-0.94	Transmission Coefficients 0.59-0.66
Total Data Collected	2806	3399	5084
Total Independent Non-Zero weight data	2114	3399	5084
Basis for zero weight	$F_0^2<2\sigma(F_0^2)$	All data used	All data used
# Reflections to determine cell dimensions	19	18	12
Radiation	MoKα	MoKα	MoKα

*See discussion of refinement

TABLE II-1. (cont.)

	μ-$O_2^{2-}(NH_3)_{10}$	μ-NC	μ-NCS
Scan Range:			
Slope	.00720	.00893	.01364
Intercept	0.97°	1.11°	1.50°
Background Counting Time	30 sec	40 sec $hk\ell$ 60 sec $h\bar{k}\bar{\ell}$	30 sec
Scan Rate	2°/min	1°/min $hk\ell$ ½°/min $h\bar{k}\bar{\ell}$	1°/min
Maximum Sin θ/λ	0.545	0.543	0.595
Check Reflections	134, 612	324, 274	400,040,006,132
Crystal Decay	Negligible	Negligible	½% in F^2
Decay Correction	None	None	Linear
Absorption Correction	None	None	None
Total Data Collected	1678(2 octants)	4590(2 octants)	2703
Total Independent Non-Zero Weight Data	824	1822	2453
Basis for zero weight	$F_0^2<0$	$F_0^2<0$	assignments*
# Reflections to determine cell dimensions	13	17	20
Radiation	CoKα	CoKα	MoKα

TABLE II-2. CRYSTAL DATA

Formula	$K_8\{Co_2O_2(CN)_{10}\}(NO_3)_2\cdot 4H_2O$	$K_5\{Co_2O_2(CN)_{10}\}\cdot H_2O$
Formula Wt.	919.0	623.6
Space Group	Monoclinic $P2_1/c$	Triclinic $P\bar{1}$
Z	2	3
<u>a</u>	11.605(4) Å	11.707(9) Å
<u>b</u>	8.383(3) Å	19.423(15) Å
<u>c</u>	16.639(4) Å	7.664(7) Å
α	-	93.92(7)°
β	109.43(2)°	110.36(8)°
γ	-	94.71(8)°
Volume	1526(1) $Å^3$	1620(4) $Å^3$
ρ(expt)	1.98(1) $g\cdot cm^{-3}$	1.91(1) $g\cdot cm^{-3}$
ρ(calc)	2.000(2) $g\cdot cm^{-3}$	1.918(5) $g\cdot cm^{-3}$
λ	0.71069 Å	0.71069 Å
μ	22.3 cm^{-1}	25.7 cm^{-1}
Habit	{101}, {$\bar{1}$01}, {111}	Irregular

TABLE II-2. (cont.)

$K_6\{Co_2SSO_2(CN)_{10}\}\cdot 6H_2O$	$\{Co_2O_2(NH_3)_{10}\}(SCN)_4$	$(NH_3)_5CoNCSCo(CN)_5\cdot H_2O$
816.9	552.5	409.2
Monoclinic C2/c	Orthorhombic Pnnm	Orthorhombic Pbca
8	2	8
36.860(15) Å	13.266(2) Å	14.166(4) Å
9.241(2) Å	10.574(2) Å	14.549(4) Å
20.772(12) Å	7.940(2) Å	15.187(9) Å
-	-	-
124.10(3)°	-	-
-	-	-
5859(7) Å^{3}	1114 Å^{3}	3130(1) Å^{3}
1.83(1) g·cm^{-3}	1.63(1) g·cm^{-3}	1.77(2) g·cm^{-3}
1.852(4) g·cm^{-3}	1.647(2) g·cm^{-3}	1.736 g·cm^{-3}
0.71069 Å	1.79021 Å	0.71069 Å
21.6 cm^{-1}	83.6 cm^{-1}	24.9 cm^{-1}
$\{\bar{1}01\}$ and several $\{hk0\}$	$\{100\}$, $\{010\}$, $\{001\}$	Undetermined

TABLE II-3. COMPARISON OF CRYSTAL DATA FOR CYANO-BRIDGED ISOMERS

	Cyano	Isocyano
Formula	$(NC)_5CoCNCo(NH_3)_5 \cdot H_2O$	$(NC)_5CoNCCo(NH_3)_5 \cdot H_2O$
Formula Weight	376.86	376.86
F_{000}	1501	1501
Space Group	Pbca	Pbca
a axis	17.359(5) Å	17.399(4) Å
b axis	12.187(3) Å	12.187(2) Å
c axis	13.936(3) Å	13.931(1) Å
d_m	1.66(2) $g \cdot cm^{-3}$	1.68(2) $g \cdot cm^{-3}$
d_x	1.699 $g \cdot cm^{-3}$	1.696 $g \cdot cm^{-3}$
# of data	1791	1822
R	0.044	0.085
Goodness of fit	1.32	1.76
Crystal size	.16 x .07 x .08 mm	.08 x .04 x .06 mm

CHAPTER III. STRUCTURAL SOLUTIONS AND REFINEMENTS

Solutions to the crystal structure described cover a wide range of difficulty, ranging from the obvious structure of the cyano-bridged compound to the quite difficult and elusive structure of the superoxo-bridged compound. Details of the methods used to solve and refine each individual crystal structure will be treated separately; however, many aspects of these methods are identical and will be covered here.

Machine calculations were done using several IBM products available at Caltech over a period of time, including the 360/75, the 370/155, and the 370/158 computers. Programs within the CRYM system were used extensively, as well as ORTEP[54] and several programs created by this writer for particular purposes. The quantity minimized in all least-squares calculations was $\Sigma w(F_0{}^2-F_c{}^2)^2$, where the weights are $1/\sigma^2(F_0{}^2)$. Scattering factors were taken from the International Tables for X-Ray Crystallography[55] for the elements Co, K^+, S, O, N, and C. Neutral form factors were used in all cases except for potassium, and the real part of anomalous dispersion was taken into account for Co in CoKα and MoKα and for K^+ in MoKα radiation. Hydrogen scattering factors were those of Stewart, Davidson, and Simpson for bonded hydrogen.[56] Least-squares matrices were sometimes blocked when computer memory requirements or economic considerations required such action; those cases will be described explicitly. Refinement was terminated when shifts were small with respect to their estimated standard deviations. Definitions of indicators used in the following descriptions are $R = \Sigma |F_0 - |F_c|| / \Sigma F_0$ and goodness of fit (GOF) $= \{\Sigma w(F_0^2 - F_c^2)^2 / (m-s)\}^{\frac{1}{2}}$, where m = number of observations and s = number of refined parameters.

A. $K_8\{Co_2O_2(CN)_{10}\}(NO_3)_2 \cdot 4H_2O$

A Patterson map was calculated using data with $2\theta \leq 30^\circ$, from which the positions of the cobalt atom and four potassium ions were deduced. This is one more potassium ion than is required for charge balance with the binuclear anion, such that another monovalent anion was sought. A Fourier synthesis phased on the heavy atoms revealed the positions of all ligand atoms, the extra anion which was identified as a nitrate ion, and the oxygen atoms of both water molecules. A structure factors calculation using all nonhydrogen atoms yielded an R value of 0.29. Thus the previously uncharacterized compound was identified as $K_8\{(CN)_5CoO_2Co(CN)_5\}(NO_3)_2 \cdot 4H_2O$. This structure was refined by least-squares techniques. Hydrogen atoms were located by difference Fourier syntheses after partial refinement; their positions were refined, and their isotropic temperature factors were assigned values of B = 5.0

Table III-1

Observed and calculated structure factors for Potassium decacyano-μ-peroxodicobalt(III)ate Dinitrate Tetrahydrate. Columns are l, $10F_{obs}$, and $10F_{calc}$. An asterisk (*) indicates that the reflection was given zero weight in the refinement.

Table III-2

Positional and thermal parameters for Potassium decacyano-μ-peroxodicobalt(III)ate Dinitrate Tetrahydrate.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	81870(4)	12434(5)	1256(3)	184(2)	177(2)	183(3)	11(2)	93(2)	2(2)
K(1)	34325(8)	14834(12)	46478(7)	327(5)	606(7)	663(7)	36(4)	172(5)	−280(6)
K(2)	60061(8)	19597(12)	19228(6)	329(5)	654(6)	365(6)	47(5)	106(4)	62(5)
K(3)	182(8)	20309(10)	28758(6)	386(5)	348(5)	315(5)	−24(4)	180(4)	−3(4)
K(4)	23515(7)	34397(9)	17297(6)	368(5)	335(5)	345(5)	1(4)	172(4)	−64(4)
O(1)	96233(22)	−1493(32)	2620(19)	398(16)	379(16)	609(21)	60(13)	354(15)	69(15)
C(1)	68013(30)	23998(40)	1199(22)	285(19)	268(20)	219(21)	21(17)	129(17)	−1(16)
N(1)	59570(29)	30809(41)	1457(22)	391(19)	501(21)	416(23)	151(17)	199(18)	42(18)
C(2)	91572(30)	28795(40)	8352(22)	252(18)	241(21)	241(21)	19(16)	81(17)	71(17)
N(2)	96767(28)	38967(35)	12678(21)	404(19)	267(18)	398(21)	−50(15)	49(17)	−15(16)
C(3)	71073(30)	−2723(38)	−5907(21)	291(19)	207(19)	200(21)	35(15)	118(17)	34(16)
N(3)	64249(28)	−11697(36)	−9938(21)	401(19)	333(18)	353(20)	−11(15)	101(16)	−65(17)
C(4)	80897(28)	1554(38)	10959(23)	214(18)	185(19)	273(22)	12(14)	77(17)	−4(16)
N(4)	79843(27)	−5010(37)	16833(20)	375(19)	370(19)	317(20)	4(16)	137(16)	34(17)
C(5)	81683(27)	23996(38)	−8574(22)	177(17)	206(19)	268(21)	−20(14)	93(16)	−42(17)
N(5)	80888(28)	31091(36)	−14652(20)	396(18)	348(18)	328(21)	−13(15)	189(16)	85(17)
N(6)	44787(31)	7957(44)	30990(21)	437(21)	640(26)	282(20)	45(19)	152(17)	0(19)
O(2)	45540(30)	22437(37)	29864(20)	785(23)	507(21)	502(21)	139(17)	227(19)	84(17)
O(3)	53605(25)	−989(38)	31687(23)	422(18)	536(20)	1035(31)	130(15)	320(19)	−51(20)
O(4)	35005(26)	2164(43)	31404(20)	400(17)	1025(26)	492(21)	−8(18)	232(16)	14(20)
O(5)	12264(25)	18507(34)	48235(21)	335(14)	275(15)	598(21)	−38(13)	196(14)	−62(14)
O(6)	10887(25)	4526(37)	19111(19)	376(16)	557(18)	316(18)	176(15)	89(14)	−38(15)

	x	*y*	*z*	*B*
H(1)	717(42)	1248(53)	4752(29)	5.0
H(2)	926(40)	2624(53)	4859(29)	5.0
H(3)	731(37)	344(49)	1345(28)	5.0
H(4)	1741(39)	30(51)	2068(29)	5.0

[a] All coordinates have been multiplied by 10^5. [b] Temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. [c] All U's have been multiplied by 10^4. [d] Estimated standard deviations are given in parentheses.

which were not refined. Refinement of the full structure utilized two matrices, one containing all positional parameters, and the other containing thermal parameters and the scale factor. The total number of parameters varied in the last cycle of least squares was 215, corresponding to a data: parameter ratio of 9.80. In this cycle, no nonhydrogen atom parameter shifted more than 30% of its esd, and no hydrogen atom parameter shifted by more than 50% of its esd. The final R index is 0.043, and the final "goodness of fit" is 1.77. A three-dimensional difference synthesis calculated at the conclusion of the refinement indicated three peaks of density between 0.6-1.1 $e\text{Å}^{-3}$ in the region of the binuclear ion; however, no chemically reasonable interpretation of these peaks was apparent. The largest discrepancy between a calculated structure factor and a measured F treated as "unobserved" was slightly greater than $3\sigma(F_0)$.

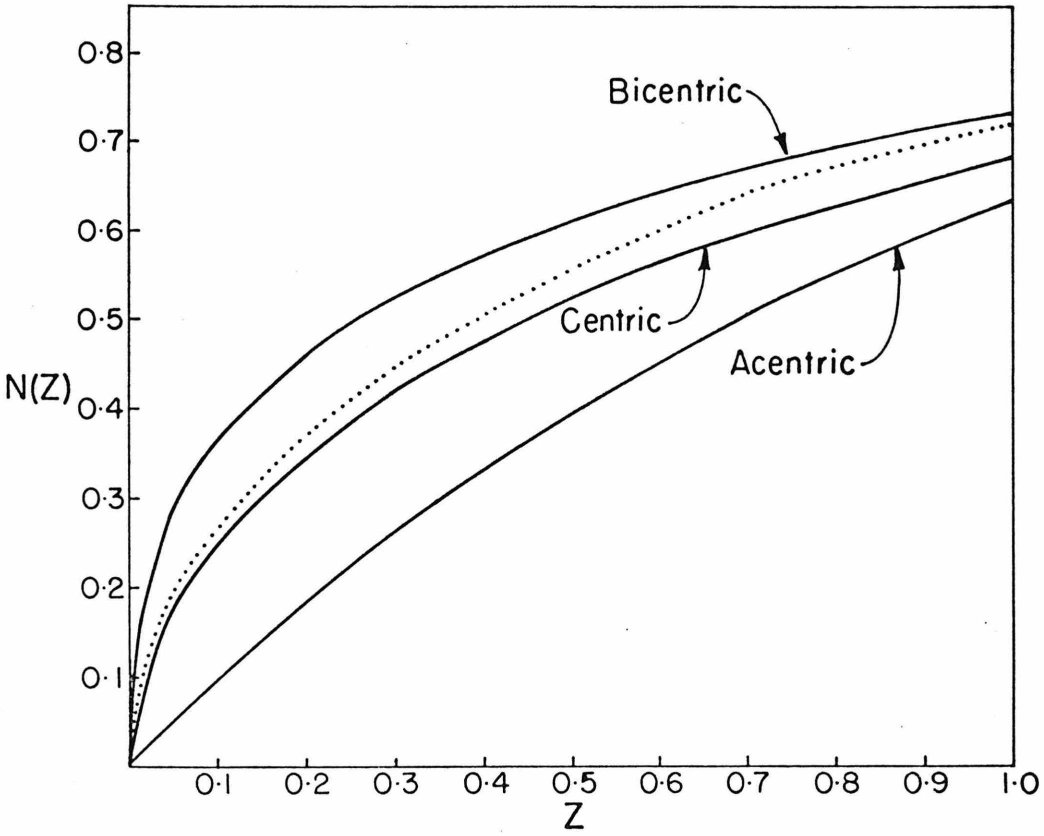
B. $K_5\{Co_2O_2(CN)_{10}\}\cdot H_2O$

Initially, extensive efforts to solve the structure by Patterson methods were unsuccessful, several apparent solutions proving to be incorrect. We then turned to direct methods. The origin was established by assigning signs to three reflections of appropriate parities having high E values and being involved in large numbers of Σ_2 relationships;

in addition, five reflections of parity type <u>eee</u> with $E > 1.5$ were assigned positive signs by Σ_1 relationships. Expansion of this starting set through Σ_2 relationships of probability greater than 0.95 yielded but 21 additional signs. Two additional reflections were given symbolic signs, but only 94 new phases were developed in terms of these signs. However, when a third symbol was introduced, a total of 368 symbolic phases were developed in addition to the 29 absolute phases. The eight E maps corresponding to all combinations of symbolic signs were calculated; none of these E maps indicated an obvious structure to us, but all eight showed a very pronounced hypersymmetry, with pseudo centers of symmetry at (1/3, 1/6, 1/6) and (2/3, 1/3, 1/3).

While hypersymmetry had previously been suspected (see Figure III-1), its nature had not been known. It was now apparent that all of the origin-fixing reflections, one of the symbolic reflections, and in fact most of the reflections with large E values fall into the subset $h - k - \ell = 3n$, and that an approximate structure can be described in terms of a subcell with a volume 1/3 that of the true unit cell. A Patterson map calculated for this subcell (that is, based on the reflections with $h - k - \ell = 3n$) was readily interpreted in terms of the positions of one cobalt atom and two potassium atoms per asymmetric unit, leading to the locations of all six cobalt atoms and twelve of the fifteen potassium atoms in the

Figure III-1



Howells, Phillips, and Rogers zero moment plots for the experimental data for Potassium μ-superoxodecacyanodicobalt(III)ate Monohydrate (dotted) and theoretical curves for the first three hypersymmetric distributions. The bicentric distribution arises from a non-crystallographically centrosymmetric motif in a centric space group.

real unit cell. This structure was consistent with one of the E maps that we had calculated earlier; from this map we assigned positions to the three remaining potassium ions, assuming one of them to lie on a center of symmetry $(0,0,\frac{1}{2})$ as required for an ordered structure.

Ideally, this structure would exhibit a higher degree of hypersymmetry than the bicentric distribution, since it consists of the bicentric arrangement with an additional, parallel motif lying on a center of symmetry and possesses a translational regularity not present in the simple bicentric pattern. The actual data lie below the theoretical curve of the bicentric distribution, because the actual deviations from the ideal structure are large. Only 12 of the 15 potassium ions lie on the hypersymmetric array, the two independent binuclear ions are decidedly nonparallel, and the conformations of the ligands in the two are quite different.

An initial structure factor calculation led to an R index of 0.45 for the 2210 reflections with $\sin^2\theta/\lambda^2$ less than 0.19. A Fourier synthesis then revealed the positions of all ligand atoms and of one water in a general position. Structure factors based on this model yielded an R index of 0.32; however, a difference map indicated that the potassium ion placed at $(0,0,\frac{1}{2})$ is, in fact, disordered about that center, occupying with equal probability two positions separated by 2.7 Å. Refinement of the structure utilized two matrices, one containing all positional parameters and the other containing all thermal parameters and the scale factor. Convergence was slow. All atoms were given anisotropic thermal parameters, except for the cyanide carbon atoms which were treated as isotropic. After many cycles of least-squares refinement, convergence was reached at an R of 0.12 and a "goodness of fit" of 2.28; however, the troublesome disordered potassium ion had unreasonably small thermal parameters. At this point, our model contained two water molecules and three units of $K_5\{Co_2O_2(CN)_{10}\}$ per cell, while the salt had been previously chemically characterized as the monohydrate.[34] By allowing the population parameter of the disordered potassium ion to refine by least squares, we concluded that the "missing" water molecule actually shares the site occupied by the disordered potassium ion; adding an oxygen atom with half population at the same position as this potassium ion caused the thermal parameters of the combined K^+ and water oxygen atom (KW) to refine to reasonable values. After a few more cycles of least-squares refinement, convergence was reached with no parameter shifting by more than ½ its esd. Final values of R and "goodness of fit" are 0.106 and 1.81 for m = 3399 reflections and s = 331 parameters respectively. Attempts to locate hydrogen atoms of the ordered water molecule were unsuccessful. A three-dimensional difference synthesis calculated at the conclusion of the refinement indicated no residual

Table III-3

Observed and calculated structure factors for Decacyano-μ-superoxodicobalt(III)ate Monohydrate. Columns are k, $10F_{obs}$, $10F_{calc}$.

$K_5[Co_2O_2(CN)_{10}]\cdot H_2O$

```
  0  K  0

 0     0 8993*

  8  K  -7

-1  278  271
 0 -113   27
 1  -57   19
 2  318  275

  7  K  -6

-6   45    8
-5  157  183
-4  284  304
-3  399  398
-2   95  144
-1   99  126
 0  279  259
 1 -126    6
 2  111  157
 3  458  404
 4 -112   45
 5  125   51
 6  124  130
 7  268  214
 8  142   65
 9  612  542
10  109  108

  8  K  -6

-7 -141   48
-6   75   70
-5  270  197
-4  275  258
-3   89   90
-2  503  489
-1  264  301
 0   23   32
 1  228  277
 2  166  158
 3  100    5
 4  381  341
 5  271  251
 6  215   96
 7  116  101
 8  116   98

  9  K  -6

-6  248  203
-5  175  173
-4  -85   45
-3   71   92
-2  161  115
-1   79   39
 0  137   65
 1  191   59
 2  287  249
 3   56   33
 4  213  123
 5  365  322
 6   62   25

 10  K  -6

-1   72  118
 0  501  496

  6  K  -5

-5  362  349
-4  262  280
-3   87  183
-2   55   49
-1  291  293
 0   71    6
 1  197  250
 2 -107   53
 3  144  116
 4  629  554
 5  239  148
 6   30  106
 7  419  354
 8  115  104
 9  234  138
10  461  408
11  253  211
12  211  179
13   84   42

  7  K  -5

-6  257  238
-5  300  304
-4  198  265
-3  -56   36
-2  175  202
-1  478  555
 0  218  184
 1  215  173
 2  590  614
 3  139  138
 4   93   57
 5  294  288
 6  447  383
 7  350  336
 8  410  348
 9  165  116
10  180  103
11  160   73
12  218  196

  8  K  -5

-7   46   20
-6  324  350
-5  106   10
-4  106   48
-3  439  494
-2  -55   32
-1  202  210
 0   91   86
 1  383  367
 2  -81   45
 3   89   45
 4 -103   18
 5  100   53
 6  315  260
 7  252  197
 8  121  138
 9   50  118
10  113   42

  9  K  -5

-8  309  267
-7  135   58
-6  502  456
-5  352  284
-4   77   97
-3  415  421
-2  257  271
-1  137  168
 0  300  293
 1  584  535
 2  315  319
 3  210   58
 4  304  326
 5  113   25
 6   70   38
 7  548  513
 8  -79    3
 9  -93   29

 10  K  -5

-7  144  127
-6  170  188
-5  148  131
-4  380  402
-3  460  461
-2   84   71
-1  290  287
 0  110  157
 1   77   42
 2  293  261
 3  113   93
 4  121   59
 5 -149   54
 6   99  111

  5  K  -4

-4  650  685
-3  110   25
-2  102  134
-1  175  197
 0   98  137
 1  336  335
 2   95   10
 3  408  445
 4  141   11
 5   88   90
 6  182   65
 7  -88   52
 8  301  299
 9  203  200
10  165  133
11  145  114
12  214  109
13  156  110
14  203  223

15  -94   71

  6  K  -4

-5  231  271
-4  637  681
-3  422  445
-2  137   98
-1  203  223
 0  197  242
 1  430  460
 2  453  447
 3  526  501
 4  403  410
 5  179  201
 6  676  648
 7  111  169
 8  262  222
 9  792  749
10  -57   20
11  159  109
12  115   85
13  -48   49
14  259  249

  7  K  -4

-6  302  344
-5  234  270
-4  581  606
-3  213  247
-2  615  646
-1  816  855
 0  133  204
 1  150  213
 2  182   76
 3  301  300
 4  506  479
 5   82   47
 6  205  207
 7   47   67
 8  -86   49
 9  204  243
10   88  102
11  159   64
12  119    3
13   54  105

  8  K  -4

-7  209  216
-6  593  588
-5  194  212
-4  137  153
-3  267  284
-2  239  267
-1  195  224
 0 -111   64
 1   52   63
 2  148  149
 3  481  406
 4  163  114
 5  546  525
 6   94   70
 7   52   73
 8  594  604
 9  436  418
10  254  216
11  332  348
12  -52    5

  9  K  -4

-8  429  435
-7  445  392
-6   84   84
-5  276  316
-4  293  303
-3  335  346
-2  300  292
-1  360  342
 0  496  516
 1  126  160
 2  -59   44
 3  173  170
 4  497  483
 5  162   98
 6  239  295
 7  407  403
 8  137  114
 9   78   21
10 -122   21

 10  K  -4

-9  -47   56
-8  180  149
-7  167  131
-6  162  143
-5  302  351
-4  132  102
-3  196  148
-2  110   34
-1  117  133
 0   88  134
 1   46   62
 2  242  254
 3  141   72
 4  283  239
 5  231  192
 6  -71   11
 7  183  208
 8  -24   48

 11  K  -4

-6  153  106
-5  345  276
-4  -70  111
-3  -76   55
-2  261  216
-1  215  209
 0  430  456
 1  240  202
 2   86  115
 3   19  117
 4   28   61

  4  K  -3

-3  114   79
-2 1353 1513
-1  454  489
 0  448  492
 1  504  543
 2   76  133
 3  188  177
 4  185  160
 5  498  461
 6  778  746
 7  137   91
 8   35   12
 9  157  118
10  161   91
11  177  209
12  -67   98
13   77    1
14   65    5
15  220  276
16  189  202
17 -122   51

  5  K  -3

-4  508  546
-3  164  178
-2  282  307
-1  539  582
 0  226  218
 1  427  462
 2   31    7
 3  -66   56
 4  699  695
 5  448  428
 6  -91   33
 7  481  475
 8  108  155
 9  336  333
10  418  421
11  834  838
12  484  505
13  409  440
14   92   73
15  261  282
16  225  215

  6  K  -3

-5  132  170
-4   23   60
-3  143  153
-2  467  531
-1  469  519
 0  435  487
 1  166  194
 2  300  293
 3  232  235
 4  -23   19
 5  313  310
 6 1347 1309
 7  524  521
 8  248  207
 9  101   66
10  442  432
11  135  181
12  202  160

13  454  436
14  241  166
15  231  271

  7  K  -3

-6  243  268
-5  105   90
-4  300  276
-3  468  490
-2  120   84
-1  182  182
 0  124    6
 1  499  532
 2  -63  123
 3 -191   40
 4  194  181
 5   74   68
 6  389  396
 7  264  264
 8  259  233
 9  176  158
10  267  303
11 -118   33
12  460  468
13  186  184
14  -65   30

  8  K  -3

-7   91  102
-6  339  355
-5   97   33
-4  269  244
-3  309  308
-2 -122   19
-1  456  479
 0  503  511
 1  394  404
 2  808  813
 3   73   83
 4  402  418
 5  204  218
 6  178  230
 7  644  686
 8  241  317
 9   62   99
10  206  257
11  -67   73
12  149  160

  9  K  -3

-8  319  298
-7   62   19
-6  374  354
-5  113  123
-4  122  129
-3 1040 1023
-2  226  242
-1  325  366
 0  271  240
 1  171  131
 2  304  278
 3  192  210
 4  175   79
 5  -57   21
 6  182  174
 7 -107   18
 8  210  231
 9  136   93
10  157   88
11  115  110

 10  K  -3

-9 -109   93
-8  447  453
-7  203  183
-6   62   31
-5   82    1
-4  185  179
-3  163   30
-2  119   52
-1  117   71
 0  122   16
 1  251  270
 2  140   66
 3  183  191
 4  -84   52
 5  140  130
 6  157  157
 7  407  422
 8  241  241

 11  K  -3

-7  232  273
-6   72   15
-5   62    8
-4   58  153
-3  148  112
-2  138  108
-1  163  121
 0  113   81
 1  142   76
 2  140  158
 3 -161   69
 4  -72   86
 5  451  451

  3  K  -2

-2  642  703
-1  606  747
 0   99   72
 1   55  159
 2  -59   13
 3  527  510
 4  405  383
 5  815  793
 6  286  236
 7  450  436
 8 1315 1307
 9  560  570
10  320  304
11  182  175
12  444  468
13  274  255
14   22   45
15  338  388
16   86  106
17  167  150
18  235  321

  4  K  -2

-3  129  105
-2  675  711
-1  169  153
 0  958 1043
 1  205  228
 2  176  147
 3 1886 1929
 4   97  111
 5  225  235
 6  691  654
 7   78  167
 8  171  160
 9  235  202
10   39   27
11  221  254
12  499  488
13  149   56
14  305  336
15   74   72
16  119   92
17  117  169

  5  K  -2

-4  246  260
-3   53   50
-2   68   76
-1  106  164
 0   66   63
 1 1158 1244
 2  354  375
 3  779  809
 4 1120 1140
 5  464  460
 6  525  538
 7  466  501
 8  586  607
 9  379  386
10   98   21
11  215  240
12  198  161
13  183  192
14  520  512
15  -69   12
16  238  252

  6  K  -2

-5  153  127
-4 1018 1062
-3   64   89
-2  265  279
-1 1191 1289
 0  287  321
 1  219  225
 2  130  148
 3  223  245
 4  305  312
 5  443  498

 6  530  560
 7   64   67
 8  378  391
 9  406  409
10  131   33
11  257  281
12  175  228
13  193  256
14  432  479
15   92   80

  7  K  -2

-6 1061 1085
-5  334  332
-4  153  125
-3  310  332
-2  101   30
-1  441  429
 0   37   35
 1  153  193
 2 -113   28
 3  542  570
 4   98  141
 5  414  473
 6  136  155
 7   75   82
 8  238  250
 9  917  984
10  261  317
11  316  335
12  210  258
13  233  249
14  237  236

  8  K  -2

-7  387  412
-6   85  114
-5  386  405
-4  126  125
-3   53    7
-2  511  540
-1  345  338
 0  248  238
 1  -96   42
 2  -23   10
 3  169  182
 4 1037 1120
 5  129   79
 6  178  197
 7  516  551
 8  181  227
 9  153   82
10  110   36
11  181  180
12 -158   43
13  175  151

  9  K  -2

-8   42   88
-7  497  530
-6   44   43
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 -14   -79    56
 -13   351   331
 -12   165   182
 -11   346   354
 -10   116    95
  -9   139   112
  -8   355   329
  -7   402   414
  -6   121    50
  -5   920   877
  -4   413   384
  -3   169    89
  -2   740   719
  -1   525   514
   0  1348  1228
   1   920   834
   2    84   125
   3   723   701
   4   869   831
   5   980   916
   6   491   456
   7   486   470
   8   566   567
   9   -62     6
  10   364   377
  11   -34    75
  12   264   285
  13   167   143
  14   162   143
  15   214   168

    -1   K   4

 -17  -106    29
 -16   156   130
 -15   133   111
 -14    83   124
 -13   237   236
 -12    51    23
 -11    76   119
 -10   828   798
  -9   -86    50
  -8    66    62
  -7   934   963
  -6   103    98
  -5   586   611
  -4   853   890
  -3   518   560
  -2    52   145
  -1    92   113
   0   380   427
   1    59   111

   2   527   441
   3   452   422
   4   227   193
   5   795   723
   6   129   187
   7   553   514
   8   201   269
   9    33    55
  10   296   284
  11   166   175
  12   -16    45
  13   347   357
  14   173   166
  15   147    66

     0   K   4

 -17   -47    11
 -16    97     2
 -15   353   316
 -14   -78    17
 -13    23    73
 -12   305   293
 -11   267   222
 -10   545   545
  -9   276   277
  -8   101    89
  -7    46    54
  -6   310   355
  -5   371   399
  -4   365   462
  -3   164   200
  -2   175   194
  -1   118    85
   0   612   634
   1   116    63
   2    36    97
   3   252   252
   4   217   162
   5    76    90
   6   659   602
   7   553   504
   8   624   576
   9   123   106
  10   173   139
  11   122    76
  12   227   253
  13   364   353
  14    60    47

     1   K   4

 -16  -107    65
 -15   413   370
 -14   167   189
 -13   230   134
 -12    41    10
 -11   330   300
 -10   530   513
  -9   404   416
  -8   325   310
  -7   121    69
  -6   420   419
  -5  1021  1067
  -4   118   162
  -3   -87    60
  -2   370   433
  -1    19    11
   0   -69    95
   1   132   163
   2   134    73
   3   206   220
   4   157   149
   5   314   307
   6   144   169
   7   -50   112
   8   626   595
   9   269   254
  10   215   204
  11   257   143
  12   142   180
  13   248   259
  14   218   165

     2   K   4

 -16   294   248
 -15   202   224
 -14   246   275
 -13   158   144
 -12    70    42
 -11   106    99
 -10   302   319
  -9   111    51
  -8   195   203
  -7   665   706
  -6   106   112
  -5    88    16
  -4   258   284
  -3   237   292
  -2   344   409
  -1   136   123
   0    93    43
   1   497   537
   2   545   567

   3    23    26
   4   776   785
   5    85   158
   6    43    73
   7   484   459
   8   694   590
   9   320   341
  10    99    85
  11   101   110
  12   143   155
  13   162   102

     3   K   4

 -15   -69    73
 -14   207   140
 -13    33     4
 -12   220   203
 -11    21    57
 -10   -19     9
  -9   547   542
  -8    91    53
  -7   294   324
  -6   466   525
  -5   164   140
  -4   175   250
  -3   898   954
  -2   474   515
  -1   425   461
   0   242   252
   1   183   209
   2   575   589
   3   934   924
   4   454   469
   5   199   216
   6   112    74
   7   478   509
   8   240   250
   9    74    29
  10   298   279
  11   -33    35
  12   183   190

     4   K   4

 -14   394   381
 -13  -161     1
 -12   147   168
 -11   124   112
 -10   177   187
  -9   220   199
  -8   654   684
  -7    11    44
  -6   376   417
  -5   408   413
  -4   -89    71
  -3   124   172
  -2   493   519
  -1   110   212
   0  -127    41
   1  -115    87
   2   265   248
   3   115     2
   4   363   311
   5    35    80
   6   145   172
   7   458   435
   8    79    22
   9   257   207
  10   272   289

     5   K   4

 -12   169   173
 -11   140   215
 -10    80    32
  -9   369   358
  -8   162   124
  -7    79    94
  -6   196   195
  -5   201   215
  -4   299   313
  -3     7   128
  -2   231   157
  -1   779   767
   0   113    89
   1    54   139
   2   333   336
   3   108    94
   4   168   188
   5   445   468
   6   228   253
   7   133   143
   8  -139    30

     6   K   4

 -10    78    16
  -9   126   161
  -8    28    53
  -7   216   157
  -6   844   855
  -5    49   105
  -4    86     2
  -3   127   164

  -2    53    31
  -1   186   187
   0   271   238
   1   114   159
   2   147   157
   3   242   232
   4    56   119
   5   251   186

     7   K   4

  -6   244   274
  -5  -170    41
  -4   139    50
  -3   206   157
  -2   404   390
  -1   270   220
   0   212   199
   1    98   116

    -9   K   5

   9    40     2

    -8   K   5

   8    62    35
   9    97   124
  10    92    17
  11   227   219

    -7   K   5

   7   182   180
   8   217   146
   9   118   118
  10   -91    19
  11   298   214
  12   112   117

    -6   K   5

   6   246   233
   7   441   442
   8   252   202
   9    48    62
  10   192   148
  11   148   154
  12   203   165
  13  -152    42

    -5   K   5

 -14   -62    35
 -13    78    77
 -12  -118    46
 -11    97    28
 -10   111    26
  -9   242   144
  -8   246   139
  -7   237   191
  -6   712   604
  -5   168   147
  -4   365   301
  -3   146   215
  -2    29    12
  -1   242   243
   0   626   666
   1   267   273
   2   645   697
   3   191   226
   4   192   214
   5   308   307
   6   694   694
   7   543   538
   8    79    74
   9   113    10
  10   125   114
  11    84    52
  12     1    33
  13   271   246

    -4   K   5

 -14  -127    77
 -13   -15    44
 -12    79    40
 -11   374   284
 -10   -56    46
  -9   127   104
  -8   591   550
  -7   -23    77
  -6    60    64
  -5   602   501
  -4   197   161
  -3   540   469
  -2   585   558
  -1   171   174
   0   225   253
   1   538   587
   2   396   400
   3    70    43
   4   297   317
   5   369   396
   6   227   215

   7   315   320
   8   109   141
   9   173   149
  10    68    36
  11    63    63
  12   214   165
  13   231   207

    -3   K   5

 -15    41    81
 -14   100    91
 -13   185   191
 -12   147   151
 -11   213   187
 -10   118    89
  -9   160   132
  -8   417   364
  -7   344   291
  -6   442   363
  -5   521   476
  -4   119    61
  -3    24    22
  -2   619   526
  -1   122    65
   0   151   148
   1   215   250
   2  1043  1030
   3    66   126
   4    78   113
   5   386   422
   6   107    67
   7   221   229
   8   625   592
   9   108   157
  10   209   224
  11   -45   110
  12   264   193
  13   -95    11

    -2   K   5

 -15   190   168
 -14   141   151
 -13   314   253
 -12   102   107
 -11   191   155
 -10    28   129
  -9   539   534
  -8   209   167
  -7   176   117
  -6   558   541
  -5   127   117
  -4   193   145
  -3  1215  1283
  -2   159   131
  -1   -50    35
   0   508   513
   1   263   215
   2   229   233
   3   410   394
   4   332   337
   5   306   293
   6   -69    59
   7   481   463
   8   275   279
   9   412   329
  10   355   336
  11   -64    62
  12   192   138
  13   148   112

    -1   K   5

 -15    35    22
 -14   342   287
 -13   131    88
 -12    15    39
 -11  -104    15
 -10    97    32
  -9   -96    61
  -8   705   674
  -7   163   141
  -6    99    94
  -5   118   171
  -4   -87    48
  -3   316   389
  -2   144   105
  -1   156   200
   0   431   421
   1   331   306
   2    64    46
   3   531   467
   4   174   196
   5   245   199
   6   559   533
   7   181   198
   8    74    66
   9   129   150
  10   294   266
  11   162   179
  12    91    94
  13   151    87

     0   K   5

 -15   115   110
 -14    15     1
 -13   127     9
 -12   131    45
 -11   -84    10
 -10   141     9
  -9    37    95
  -8   254   292
  -7   693   712
  -6    92    82
  -5   349   400
  -4   320   376
  -3   321   343
  -2   310   377
  -1   603   691
   0   106   142
   1   181   209
   2   390   349
   3   229   241
   4   195   153
   5   839   760
   6   327   270
   7   103   147
   8    92    12
   9   289   233
  10   102    60
  11    18   102
  12    91   100

     1   K   5

 -14  -148    15
 -13   -75    81
 -12   384   360
 -11   112    36
 -10    37    23
  -9    56   136
  -8    82    54
  -7   248   254
  -6   649   691
  -5   101    31
  -4    35    21
  -3   137   162
  -2    74   137
  -1   157   278
   0   695   725
   1   329   336
   2   165   217
   3   230   251
   4    44    85
   5   139    72
   6   130   136
   7   150    96
   8   140    51
   9   352   327
  10   142    29
  11   167   214

     2   K   5

 -13   116    51
 -12   239   252
 -11   186    97
 -10    58    54
  -9   145   130
  -8    16    79
  -7   172   163
  -6    77   142
  -5    67    27
  -4  -133    45
  -3   256   294
  -2   483   529
  -1   148    81
   0    51    69
   1   667   691
   2   -40    36
   3    71    30
   4   454   447
   5   185   197
   6   379   421
   7   308   301
   8   272   261
   9   -28    93
  10   284   270

     3   K   5

 -12   124    60
 -11    93    54
 -10    30    68
  -9    55    12
  -8   139   121
  -7   452   476
  -6   112     3
  -5    45    23
  -4   848   932
  -3   106    15
  -2    47    92
  -1   345   393
   0   161   174
   1   201   254
   2   370   387
   3   130   120
   4   -65   113

   5   102    86
   6   176   246
   7   334   346
   8   313   276

     4   K   5

 -10   150    19
  -9   431   425
  -8    99    61
  -7   113    82
  -6   101    46
  -5    95   108
  -4   254   311
  -3    29    31
  -2   182   139
  -1   112     0
   0   390   445
   1   -84    32
   2   207   217
   3   132   133
   4   147    53
   5   291   301
   6   496   497

     5   K   5

  -8   177   220
  -7   129    14
  -6    74   111
  -5   605   644
  -4    57   101
  -3    78    36
  -2   355   363
  -1   205   153
   0    75    44
   1   524   543
   2   157   188
   3  -174    27

    -8   K   6

   8   349   336

    -7   K   6

   7  -115   106
   8   125   137
   9    85    66

    -6   K   6

 -11   176   133
 -10   221   151
  -9   205   133
  -8   154   114
  -7   115   134
  -6   164   158
  -5   126    16
  -4   144   167
  -3   226   119
  -2    29    95
  -1   223   272
   0   172   202
   1   210   206
   2   -81    12
   3   138   200
   4   398   401
   5   127    75
   6   110    36
   7   113   137
   8   -38    61
   9   164   198
  10   196   188

    -5   K   6

 -12   139   109
 -11   251   127
 -10   178   160
  -9    56    30
  -8    43    11
  -7   152   169
  -6    73    56
  -5   131     3
  -4   282   195
  -3   125    57
  -2   150    22
  -1   818   800
   0    67    62
   1    48    52
   2   226   214
   3    73    28
   4   127    96
   5   318   298
   6   197   168
   7    81    86
   8    57   130
   9   380   334
  10   154   140

    -4   K   6

 -12   505   385
 -11    89    70

 -10   122    95
  -9   296   240
  -8   126    59
  -7   156   101
  -6   791   639
  -5   290   167
  -4    14    79
  -3   125    33
  -2   -23    67
  -1   174   134
   0    70    74
   1  -104    38
   2   318   363
   3   345   370
   4    79    13
   5   620   632
   6   -57     7
   7   247   206
   8   -55   113
   9   395   358
  10  -137     0
  11  -124   104

    -3   K   6

 -13   294   280
 -12   127     7
 -11   357   298
 -10   110   162
  -9   -36     8
  -8   404   315
  -7    58    16
  -6   420   409
  -5   220   258
  -4    28    65
  -3   184   137
  -2   579   594
  -1    98    70
   0   208   210
   1   578   498
   2    75    34
   3   310   280
   4   609   573
   5   209   244
   6    66    93
   7   512   489
   8   368   329
   9   131    17
  10   -61    18

    -2   K   6

 -13   248   222
 -12    61    77
 -11    86    97
 -10   545   504
  -9   160   169
  -8   159   197
  -7   279   246
  -6   118    27
  -5   114    23
  -4   359   419
  -3   189   235
  -2   108     2
  -1   367   343
   0   178   264
   1   217   210
   2   619   512
   3   367   321
   4   252   197
   5   405   325
   6  -115    46
   7   115   117
   8    80    31
   9   153   123
  10    95   102

    -1   K   6

 -12   109    42
 -11   160   132
 -10   314   299
  -9   168   109
  -8   -35    12
  -7   142    99
  -6   148   126
  -5   106   174
  -4    76    18
  -3   256   254
  -2   257   269
  -1    42   113
   0   693   679
   1   176    61
   2  -101    16
   3   286   263
   4    77    86
   5    79   156
   6   441   398
   7   154    96
   8  -139    40
   9   122   119

     0   K   6

 -12   163   115

 -11   344   306
 -10    65   101
  -9    74    94
  -8   112    81
  -7    16    52
  -6   210   198
  -5   550   555
  -4    86    45
  -3    88    89
  -2   394   436
  -1    90    32
   0    65    56
   1   300   290
   2    24   135
   3   -71    53
   4    24     0
   5    34    45
   6   265   301
   7   254   201
   8   186   222

     1   K   6

 -11   -92    48
 -10   363   334
  -9    60   109
  -8    96    75
  -7   155   215
  -6   155    81
  -5   102    97
  -4   116    53
  -3   -82    67
  -2   192   234
  -1  -127    81
   0   112     6
   1   205   246
   2   261   322
   3    36    19
   4   535   526
   5   127    85
   6   169    28
   7   247   241

     2   K   6

  -9   330   340
  -8    26    64
  -7   271   280
  -6   117   162
  -5   -97    91
  -4   137   159
  -3   449   530
  -2    96    23
  -1   181   182
   0   257   289
   1   -65    66
   2   132    59
   3   709   759
   4   194   184
   5   141    71

     3   K   6

  -7  -113   142
  -6    48     4
  -5   153   118
  -4  -164    56
  -3   -49    93
  -2   466   499
  -1   -99   109
   0   195   174
   1   153    17
   2   166   166

    -7   K   7

  -5   130    95
  -4   356   302
  -3   137   108
  -2   102    94
  -1    78    97
   0   -92    30
   1  -116    21
   2    85    13
   3    76    48
   4   137   139

    -6   K   7

  -7  -119    92
  -6   253   180
  -5   188   160
  -4   210   191
  -3    50    78
  -2   117    18
  -1    93    21
   0   247   225
   1    73    28
   2   239   253
   3   119   186
   4    97    80
   5   -70    31

    -5   K   7

  -8   342   315
  -7   168   136
  -6   -77    25
  -5   349   326
  -4   128    30
  -3   -53    34
  -2    65   140
  -1   -91    24
   0    69   106
   1   362   306
   2   165    86
   3   316   296
   4   174   125
   5   160   133
   6    64    56

    -4   K   7

  -8    65    83
  -7   166   153
  -6   173    89
  -5    78   106
  -4   153    27
  -3   108    67
  -2   205   179
  -1     9     8
   0   166    64
   1   114   114
   2   541   492
   3   -80   112
   4   162    17
   5   204   265
   6   -96    42

    -3   K   7

  -9   332   302
  -8    72    10
  -7    48    54
  -6   182   145
  -5    81   109
  -4   196   134
  -3   530   529
  -2   115    24
  -1   136    61
   0   160   154
   1   106    66
   2   143     3
   3   294   252
   4    79    48
   5   116    59
   6    56    56

    -2   K   7

  -8   452   408
  -7   -66    32
  -6   149   169
  -5   240   199
  -4   142   195
  -3   189   183
  -2    58    16
  -1    59    44
   0   164   152
   1   146   133
   2    45   132
   3   170   164
   4   121    92
   5   130   117

    -1   K   7

  -7   332   290
  -6   -43    77
  -5   139   181
  -4   122   171
  -3    68    87
  -2  -108    64
  -1   171   176
   0   106    16
   1   -73   163
   2   305   216
   3   131     0
   4   201   126

     0   K   7

  -6   279   257
  -5    98    89
  -4   131    49
  -3   126    58
  -2   -55    39
  -1   169   121
   0   312   291
   1   -78    57
   2   171   217
```

Table II-4 Positional and Thermal Parameters[a]

Atom	X	Y	Z	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1C)	20950(16)	3252 (9)	10540(26)	268(12)	363(12)	334(14)	-24 (9)	42(10)	-3(10)
Co(1A)	44973(16)	32752 (9)	18697(27)	251(12)	409(12)	385(14)	-15 (9)	45(10)	-29(10)
Co(2A)	87377(15)	35264 (9)	37270(27)	218(11)	363(12)	345(13)	14 (9)	27(10)	-16(10)
K(1)	9864(29)	42114(16)	6209(46)	587(25)	482(22)	484(26)	88(18)	127(21)	55(19)
K(2)	23489(32)	25462(16)	63843(48)	770(27)	435(22)	473(25)	81(19)	191(21)	-56(19)
K(3)	42232(42)	8316(23)	69346(76)	948(36)	929(33)	1572(50)	86(27)	459(35)	-563(33)
K(4)	-1775(31)	17428(16)	92343(51)	530(23)	437(22)	695(29)	41(18)	110(21)	68(20)
K(5)	67461(30)	15529(17)	35821(51)	503(24)	519(23)	614(28)	-34(18)	-5(21)	10(20)
K(6)	33344(29)	49052(16)	63346(51)	461(22)	423(21)	721(29)	-33(17)	185(21)	-57(20)
K(7)	66852(31)	37902(19)	78526(57)	492(25)	915(30)	796(33)	-92(22)	128(23)	-48(25)
K W	-356(53)	6328(34)	43552(91)	644(44)	1462(62)	803(52)	-45(42)	69(39)	100(46)
O(1C)	343 (9)	263 (5)	-86(15)	55 (7)	65 (8)	72 (8)	1 (5)	12 (7)	40 (7)
C(1C)	3767(13)	418 (7)	2075(20)	3.64(0.34)					
N(1C)	4816(12)	484 (7)	2724(22)	46(10)	91(11)	139(15)	-10 (8)	4(10)	56(11)
C(2C)	2095(12)	838 (7)	-968(20)	3.40(0.33)					
N(2C)	2051(10)	1156 (6)	-2235(17)	63 (9)	45 (8)	47 (9)	-4 (6)	8 (7)	9 (7)
C(3C)	2162(12)	-504 (7)	-269(20)	3.68(0.34)					
N(3C)	2195(13)	-1040 (6)	-1031(19)	115(12)	57 (9)	71(11)	15 (8)	32(10)	-4 (8)
C(4C)	2007(13)	1130 (7)	2450(21)	4.02(0.35)					
N(4C)	1804(14)	1605 (6)	3285(19)	150(14)	37 (8)	77(11)	-9 (8)	64(11)	-8 (8)
C(5C)	2058(12)	-179 (7)	3046(21)	3.52(0.33)					
N(5C)	1989(11)	-479 (6)	4290(20)	63 (9)	74(10)	83(12)	2 (7)	17 (9)	30 (9)
O(1A)	6244 (8)	3604 (4)	3010(13)	41 (6)	45 (6)	59 (7)	9 (5)	-2 (6)	-16 (6)
O(2A)	7028 (8)	3197 (5)	3137(13)	39 (6)	60 (7)	56 (8)	18 (5)	12 (6)	-11 (6)
C(1A)	2826(12)	3022 (6)	742(18)	2.77(0.29)					
N(1A)	1775(10)	2872 (5)	-42(16)	29 (7)	53 (8)	53 (9)	-3 (6)	6 (7)	4 (7)
C(2A)	10408(12)	3731 (6)	4315(18)	2.67(0.29)					
N(2A)	11443(10)	3833 (5)	4599(16)	30 (7)	43 (7)	64 (9)	-7 (6)	8 (7)	-18 (7)
C(3A)	4771(11)	2437 (7)	748(18)	2.73(0.30)					
N(3A)	4933(10)	1940 (5)	-18(17)	63 (9)	38 (8)	57 (9)	-2 (6)	2 (8)	-11 (7)
C(4A)	4493(12)	3688 (7)	-253(20)	3.27(0.33)					
N(4A)	4526(11)	3938 (6)	-1580(20)	68(10)	76(10)	82(12)	14 (8)	30 (9)	26 (9)
C(5A)	4112(12)	4137 (7)	2722(19)	3.51(0.32)					
N(5A)	3826(10)	4674 (6)	3061(18)	47 (8)	42 (8)	79(10)	0 (6)	12 (8)	-11 (7)
C(6A)	4528(13)	2855 (7)	4030(22)	3.99(0.35)					
N(6A)	4640(13)	2605 (8)	5429(20)	86(11)	127(12)	55(11)	11 (9)	13 (9)	15(10)
C(7A)	9116(11)	2722 (7)	4921(19)	2.84(0.30)					
N(7A)	9365(10)	2213 (6)	5634(17)	53 (9)	60 (9)	55(10)	-25 (7)	-9 (7)	13 (7)
C(8A)	8836(11)	4060 (6)	5901(19)	2.89(0.30)					
N(8A)	8825(10)	4383 (6)	7243(16)	49 (8)	51 (8)	47 (9)	-2 (6)	12 (7)	-7 (7)
C(9A)	8419(12)	4312 (7)	2382(19)	3.16(0.31)					
N(9A)	8222(10)	4761 (6)	1383(16)	56 (8)	47 (8)	42 (9)	0 (6)	10 (7)	-5 (7)
C(10A)	8625(12)	3041 (7)	1454(21)	3.50(0.33)					
N(10A)	8531(12)	2805 (6)	-39(20)	89(11)	75(10)	68(11)	32 (8)	16 (9)	-9 (9)
O(4)	6358(11)	1668 (6)	7090(17)	124(11)	108(10)	85(10)	10 (9)	35 (9)	-3 (8)

---

[a] Heavy atom (Co and K) coordinates have been multiplied by 10^5. Light atom coordinates have been multiplied by 10^4. Anisotropic temperature factor is of form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)]$. Heavy atom thermal parameters have been multiplied by 10^4. Light atom U's have been multiplied by 10^3. Estimated standard deviations are given in parentheses.

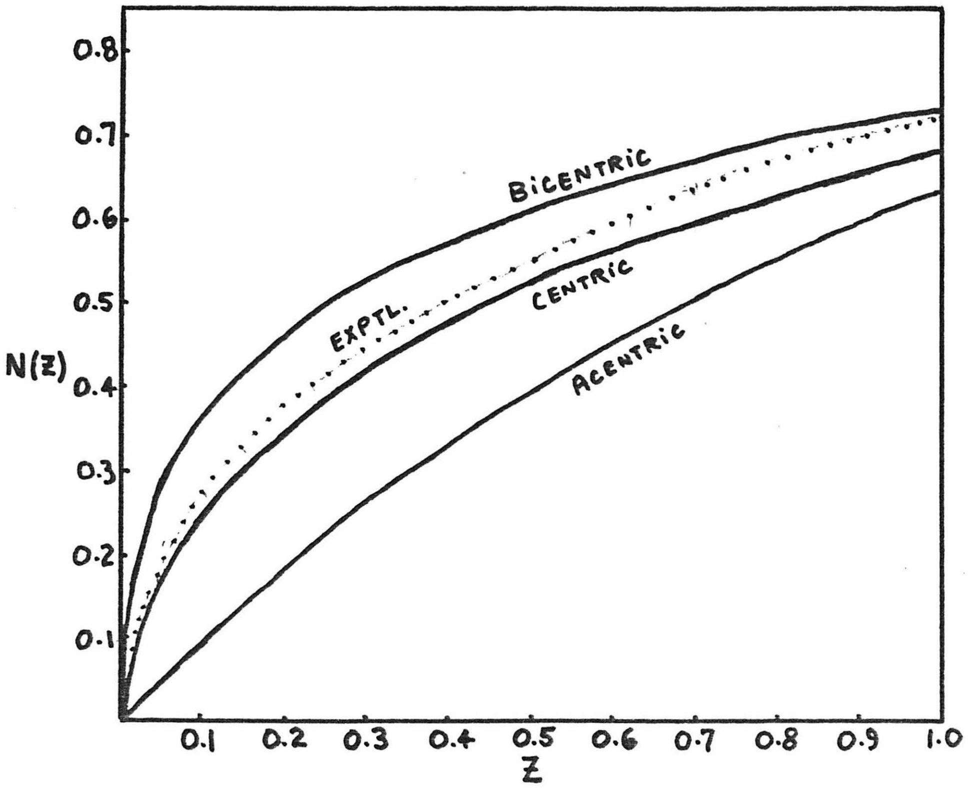
peaks greater than 0.7 eÅ^{-3}.

C. $K_6\{Co_2SSO_2(CN)_{10}\}\cdot 6H_2O$

Due to the unavailability of a diffractometer, an attempt was made initially to solve this structure from film data. A total of 651 intensity data were crudely estimated from seven Weissenberg films (0kl-6kl in I2/a), from which a Patterson map was calculated. A reasonable model was deduced from Patterson-Fourier iterations, but it eventually proved to be incorrect. When diffractometer data became available, a new Patterson map was calculated from them, and some improvement in resolution over the film Patterson was noted. The structure was solved using the new data. Based upon the hypercentricity of the intensity distribution (Figure III-2), the space group was initially assumed to be the centric C2/c; however, it was not possible to find an ordered arrangement of the heavy atoms (2Co, $6K^+$, 2S) in this space group. A pseudocentric model in space group Cc was tried, which led to the location of all ligand atoms (including the unexpected sulphito oxygen atoms) and several water molecules. This model was refined by least squares to an R factor of 0.117 and a goodness of fit of 5.2, at which point convergence was imminent with the ten heavy atoms having anisotropic temperature factors. The model, besides exhibiting a poor GOF,

Figure III-2

Zero moment plots for theoretical distributions and experimental data (dotted) for Potassium μ-thiosulfitodecacyanodicobalt(III)ate Hexahydrate.



contained several disconcerting features which pointed to the fact that it was incorrect. Co-C distances varied over a broad range which taxed credibility, and some Co-C-N angles varied from linearity by almost 40 degrees. Isotropic temperature factors of the ligand atoms were totally unreasonable, and the pseudocenter relating the two dicobalt ions in the asymmetric unit was disturbingly close to exact. Although two of the potassium ions and several of the water molecules of this acentric model do not fit a centric model, the evidence indicated that a disordered model in space group C2/c was more likely to be correct. A structure factors calculation based upon the ordered part of the centric model in space group C2/c yielded an R factor of 0.22. This model contained a half-integral number of potassium ions per asymmetric unit as a result of K(1) lying on a twofold axis at (0, y, ¼), and a Fourier synthesis revealed an additional potassium ion K(7) half populated in a general position.

Refinement of this model, which was performed using three least-squares matrices, resulted in reasonable geometry and temperature factors, confirming the appropriateness of the centrosymmetric space group. One matrix contained all positional parameters, and temperature factors were placed in two matrices of approximately equal size. The scale factor was contained within the same matrix as the anisotropic temperature factors of the heavy atoms. Twelve positions,

TABLE III-6. PARAMETERS FOR $K_6\{(CN)_5CoSO_2Co(CN)_5\}\cdot 6H_2O$

	X	Y	Z	POP	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	0	1259(28)	¼		335(12)	581(16)	365(13)	0	137(11)	0
K(2)	8997(5)	17425(19)	98772(10)		339(8)	529(11)	484(10)	-26(8)	231(8)	97(9)
K(3)	22910(7)	6655(29)	73991(14)		503(12)	1076(20)	898(17)	11(13)	285(12)	410(15)
K(4)	42838(7)	7220(23)	69084(12)		764(14)	660(13)	639(13)	31(11)	468(12)	82(11)
K(5)	-523(7)	16132(32)	44440(13)		663(14)	1365(23)	599(14)	27(15)	356(12)	-109(15)
K(6)	33441(5)	24250(22)	73383(10)		466(10)	610(12)	562(11)	-35(10)	327(9)	-118(10)
K(7)	24676(16)	3495(64)	49069(30)	0.50	568(25)	1104(40)	687(30)	11(28)	94(23)	-59(30)
Co(1)	15056(3)	23945(10)	52407(5)		308(5)	296(5)	271(5)	-7(4)	184(4)	-12(4)
S(1)	13286(6)	26611(20)	61332(11)		537(11)	338(10)	396(10)	-58(9)	349(9)	-48(9)
C(1)	7045(16)	3039(57)	56297(28)		494(30)	585(35)	418(30)	-144(27)	322(27)	-180(27)
C(2)	14439(17)	-2834(58)	66783(33)		611(35)	509(35)	746(40)	201(29)	507(33)	196(31)
S(2)	10999(5)	8231(19)	63590(10)		321(9)	310(9)	349(9)	15(8)	244(8)	-1(8)
Co(2)	9515(3)	15019(10)	72314(5)		269(5)	330(5)	248(5)	-3(4)	152(4)	-8(4)
C(1)	16681(23)	24905(81)	45300(40)		468(42)	399(42)	392(40)	-53(38)	272(36)	-44(37)
N(1)	17775(25)	26266(89)	41181(41)		879(55)	898(60)	659(48)	-190(49)	634(47)	-126(47)
C(2)	20833(21)	29422(72)	60371(38)		330(37)	319(39)	348(39)	-17(30)	193(34)	-14(31)
N(2)	24347(20)	32402(74)	65219(37)		390(37)	574(45)	507(42)	-30(34)	182(34)	-14(36)
C(3)	16820(23)	4479(81)	54502(42)		375(39)	436(46)	420(43)	-29(35)	259(36)	-40(36)
N(3)	18038(22)	-7289(77)	55722(44)		590(45)	470(45)	789(54)	71(38)	369(43)	-33(41)
C(4)	9268(22)	18313(76)	44333(39)		381(39)	399(42)	341(40)	0(34)	245(35)	-34(33)
N(4)	5813(20)	15186(76)	39355(34)		474(39)	653(46)	321(35)	-90(36)	175(32)	-121(34)
C(5)	13465(23)	43722(79)	50345(38)		434(41)	382(43)	277(37)	-29(35)	200(33)	-27(33)
N(5)	12553(24)	55501(72)	49074(41)		770(52)	378(43)	609(48)	126(37)	290(43)	56(36)
C(6)	8030(23)	19502(79)	79452(40)		436(41)	437(44)	325(39)	-105(34)	225(35)	-58(33)
N(6)	6865(23)	22027(75)	83387(37)		819(50)	594(47)	498(41)	-150(39)	497(41)	-175(36)
C(7)	15452(24)	12492(88)	80290(43)		414(43)	509(51)	383(43)	70(38)	122(37)	24(38)
N(7)	19053(24)	11180(101)	85016(48)		500(47)	1037(73)	720(57)	152(48)	10(44)	-92(53)
C(8)	8230(21)	-4676(79)	72782(38)		365(38)	446(45)	293(36)	28(34)	215(32)	-11(33)
N(8)	7238(20)	-16340(68)	73018(36)		560(40)	393(39)	489(40)	-15(33)	322(35)	38(32)
C(9)	3555(21)	17872(75)	64044(38)		330(37)	388(41)	336(38)	36(32)	219(33)	-45(32)
N(9)	-22(19)	18935(81)	59316(37)		293(34)	844(56)	486(41)	69(35)	182(33)	-71(38)
C(10)	10586(21)	34745(78)	72332(38)		354(37)	391(41)	322(37)	17(34)	227(32)	16(35)
N(10)	11265(22)	47111(71)	73056(39)		721(47)	450(42)	641(45)	-34(36)	524(41)	-64(36)
O(1W)	49229(20)	511(76)	16443(37)		732(42)	882(49)	755(45)	-113(39)	423(39)	126(40)
O(2W)	28411(30)	5722(133)	19808(75)	0.50	165(49)	784(91)	980(99)	-123(55)	115(59)	281(78)
O(3W)	2558(6)	0(21)	312(11)	0.40	6.86(0.42)					
O(4W)	7403(37)	35037(130)	8706(56)	0.80	1475(93)	1621(104)	957(76)	-358(85)	822(75)	-528(76)
O(5W)	30707(50)	18364(176)	3694(87)	0.50	981(113)	1085(125)	826(109)	-70(98)	627(99)	-284(96)
O(6W)	21692(35)	29819(133)	1529(73)	0.50	403(67)	784(90)	754(88)	-187(63)	236(65)	408(75)
O(7W)	18900(25)	32354(90)	15670(40)		1087(60)	1232(68)	656(48)	-344(54)	229(45)	134(48)
O(8W)	2933(35)	41996(142)	48323(68)	0.80	1148(84)	2059(129)	1550(104)	196(86)	1067(85)	-119(95)
O(9W)	2275(11)	3332(40)	1064(21)	0.15	4.46(0.77)					
O(10W)	3372(14)	1024(47)	891(25)	0.15	5.71(0.98)					
O(11W)	795(15)	3548(55)	976(28)	0.20	4.90(1.17)					
O(12W)	391(15)	4222(54)	4848(28)	0.20	6.36(1.18)					

All coordinates except those for isotropic atoms ($\times 10^4$) have been multiplied by 10^5. All U's have been multiplied by 10^4. Estimated standard deviations are given in parentheses. Anisotropic temperature factor is of form $\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}\ell^2c^{*2}+2U_{12}hka^*b^*+2U_{13}h\ell a^*c^*+2U_{23}k\ell b^*c^*)\}$.

Table III-5

Observed and calculated structure factors for Potassium Decacyano-μ-thiosulfitodicobalt(III)ate Hexahydrate. Columns are l, $10F_{obs}$, $10F_{calc}$.

$K_6[(CN)_5CoSSO_2Co(CN)_5]\cdot 6H_2O$

0	0	L
0	031327*	
-43	1	L
11	-113	100
12	342	367
13	418	491
14	312	324
15	371	385
16	464	406
-42	0	L
8	78	196
10	161	76
12	569	630
14	669	691
16	-83	82
18	937	925
-42	2	L
9	564	482
10	303	315
11	118	188
12	205	195
13	-90	26
14	992	1058
15	494	469
16	366	306
17	599	626
-41	1	L
7	625	611
8	119	202
9	177	227
10	-182	45
11	611	608
12	278	283
13	305	401
14	262	51
15	695	680
16	298	260
17	41	218
18	929	892
19	475	501
-41	3	L
9	261	317
10	-196	23
11	-69	170
12	139	53
13	489	424
14	-146	8
15	236	291
16	219	94
17	1130	1111
-40	0	L
6	372	407
8	-189	13
10	346	335
12	282	336
14	1016	911
16	617	603
18	166	68
20	536	553
-40	2	L
6	369	284
7	948	920
8	84	80
9	-227	164
10	110	50
11	486	443
12	40	153
13	440	354
14	161	65
15	428	390
16	1168	1179
17	264	141
18	342	364
19	526	512
-40	4	L
10	501	497
11	232	307
12	60	101
13	353	250
14	188	225
15	-184	32
16	639	628
-39	1	L
4	394	323
5	1099	1074
6	945	897
7	676	652
8	546	526
9	188	156
10	408	353
11	81	42
12	-193	103
13	571	542
14	645	636
15	491	480
16	504	517
17	415	488
18	263	248
19	204	205
20	114	112
21	361	304
-39	3	L
5	276	363
6	213	190
7	831	783
8	197	200
9	131	230
10	753	788
11	329	300
12	74	33
13	207	149
14	718	758
15	252	352
16	-43	42
17	758	692
18	-204	184
19	403	371
-38	0	L
2	33	109
4	943	842
6	1298	1412
8	357	364
10	920	917
12	366	395
14	1995	1973
16	852	762
18	860	815
20	-151	53
22	273	208
-38	2	L
3	478	534
4	477	556
5	271	64
6	626	637
7	290	268
8	460	485
9	102	128
10	685	710
11	521	490
12	543	474
13	551	590
14	1015	1025
15	887	882
16	336	209
17	755	713
18	255	138
19	382	346
20	621	553
21	335	280
-38	4	L
6	581	549
7	-166	131
8	324	384
9	289	272
10	82	83
11	545	557
12	328	342
13	344	229
14	151	130
15	39	75
16	410	372
17	84	140
18	-84	29
-37	1	L
1	-108	51
2	268	259
3	883	864
4	529	576
5	807	756
6	-24	39
7	33	82
8	121	248
9	660	603
10	88	149
11	40	152
12	417	384
13	922	914
14	177	314
15	847	899
16	352	330
17	-140	10
18	997	1084
19	478	545
20	414	287
21	-149	195
22	241	181
-37	3	L
3	209	62
4	612	650
5	-283	9
6	-88	56
7	275	244
8	705	729
9	294	399
10	219	121
11	300	283
12	266	170
13	333	340
14	879	803
15	409	370
16	250	248
17	974	977
19	277	213
20	342	296
21	173	1
-37	5	L
7	140	177
8	212	336
9	576	490
10	251	98
11	646	588
12	155	301
13	1072	1016
14	380	323
15	-64	42
16	257	358
17	590	575
-36	0	L
2	-82	157
4	733	749
6	525	499
8	612	541
10	603	561
12	299	247
14	134	38
16	593	654
18	206	218
20	305	243
22	427	337
-36	2	L
1	216	173
2	318	310
3	1032	1048
4	286	245
5	612	572
6	108	119
7	350	389
8	332	305
9	-51	3
10	241	229
11	255	271
12	-83	167
13	83	137
14	-90	177
15	247	120
16	1038	1035
17	532	502
18	352	398
19	429	546
20	283	271
21	184	212
22	79	42
-36	4	L
3	324	362
4	504	558
5	212	239
6	426	442
7	-30	78
8	484	505
9	584	554
10	-94	74
11	280	356
12	341	325
13	556	574
14	722	673
15	277	221
16	523	463
17	371	290
18	904	979
19	196	171
20	-79	124
-36	6	L
9	111	127
11	235	197
12	250	78
13	142	36
14	1149	1105
-35	1	L
1	255	357
2	162	217
3	-147	39
4	118	68
5	545	522
6	502	529
7	394	369
8	-105	15
9	146	114
10	288	156
11	140	41
12	-161	108
13	250	258
14	-59	42
15	672	678
16	-171	37
17	1975	1960
18	596	579
19	-169	37
20	809	775
21	702	652
22	-81	92
23	222	189
-35	3	L
1	723	718
2	903	865
3	474	549
4	588	631
5	90	159
6	683	654
7	528	569
8	506	515
9	-155	52
10	861	829
11	248	210
12	700	674
13	415	424
14	-107	127
15	-115	37
16	-71	1
17	717	770
18	183	239
19	807	809
20	268	192
21	298	255
-35	5	L
4	-145	47
5	27	148
6	198	153
7	536	553
8	269	271
9	315	326
10	417	444
11	766	782
12	161	158
13	159	25
14	248	275
15	59	4
16	-100	216
17	619	632
18	376	264
-34	0	L
2	679	664
4	853	795
6	1180	1166
8	257	50
10	641	674
12	-30	42
14	558	535
16	865	895
18	637	691
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 2  935  970
 3  509  605
 4  973  997
 5 1014 1027
 6  813  850
 7  652  641
 8  618  627
 9  224  235
10  120  115
11 2954 3032
12  997 1028
13  617  727
14  583  570
15 1049 1117
16  556  638
17   97  115
18 1135 1101
19 1441 1478
20  380  421
21 -201    7
22  375  316

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 1  930  888
 2  511  501
 3 1985 2057
 4 -110   58
 5  135  126
 6  756  769
 7 -109   68
 8  244  390
 9  156  178
10  497  537
11 1806 1819
12  383  429
13  629  622
14  517  473
15 1271 1288
16  438  421
17  150  116
18 -144   95
19 1460 1447
20  462  493

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 4 1419 1442
 5  211  265
 6 -142   77
 7  489  526
 8  265  152
 9  286  269
10  413  430
11 1407 1449
12  682  642
13  482  416
14  269  220
15 1025  996
16  628  656
17 -160  179
18  137  141

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 2  523  479
 3   72   85
 4 1144 1149
 5  181   21
 6  228  238
 7  513  462
 8  115  131
 9  332  312
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11  752  735
12  165  213
13  401  437

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 2  183  773
 4 1873 2015
 6 4190 3508
 8  978  965
10  183  194
12  450  437
14 1677 1624
16 -145  129
18 1673 1556
20   56   39
22 1652 1556

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 1  994 1101
 2 3518 3086
 3  736  563
 4 2070 2100
 5 3438 3544
 6  728  632
 7 1900 1902
 8 1519 1485
 9  548  492
10 1820 1764
11  672  611
12  423  438
13  133  183
14 1247 1318
15  925  927
16  249  206
17  143  181
18 1133 1171
19 1213 1190
20 1100 1086
21  853  725
22  694  773

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 1 1191 1236
 2  695  631
 3 3026 3105
 4 2141 2198
 5  440  448
 6  432  506
 7 1438 1530
 8 2194 2222
 9  352  366
10 1070 1008
11  157   49
12  771  745
13 -133   62
14  408  418
15  376  381

16 -129   83
17  328  287
18 -169  163
19  -95  173
20 1191 1158
21  234  113

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 2  691  670
 3  746  736
 4 3504 3545
 5 1957 2019
 6  279  229
 7  460  476
 8 1445 1399
 9  927  924
10  241  113
11   99  125
12  272  278
13  543  556
14  344  337
15  241  136
16  126  181
17  221  232
18  149  132
19  121   41

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 6  518  452
 7  126   50
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 9  233  198
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11  210  194
12  196  182
13  703  710
14  246  234
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16  342  371

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10 -226   34

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 1  156  241
 2 1415 1600
 3 3824 3716
 4 1848 1862
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 7 8225 8029
 8 3439 3351
 9 1038  961
10 1019  977
11  612  617
12  648  589
13  159  228
14  585  668
15  669  648
16  747  757
17 -110  136
18  653  727
19  557  543
20  152  148
21  164   29
22  386  286

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 1 2750 2790
 2 1506 1570
 3 1123 1274
 4 2358 2318
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 6  313  386
 7 1776 1656
 8   96  106
 9 1553 1521
10 1024 1105
11  769  763
12  767  807
13 1036  964
14  599  560
15  356  318
16  686  708
17  573  613
18  873  935
19  153  230
20  -73   38
21  746  798

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 8  216  260
 9 1829 1929
10  128  159
11  287  355
12  845  901
13  571  525
14 -144   56
15  132  234
16  555  554
17  134  118
18  337  285
19  255  351
20  334  303

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 7  348  364
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11  462  495
12  413  441
13  197   96
14  665  674
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 1  -81  160
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 3 1020  947
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 6  361  307
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10  -48   83
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12 -232   52
13  526  423

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 4 4239 4108
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10 2392 2380
12 4178 3996
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16 2029 1955
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22   48   48

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 2 1800 2071
 3 1524 1523
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 6  563  504
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 8  296  203
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10 2205 2161
11 1255 1210

12  359  393
13  743  702
14  216  122
15  -66   35
16 1263 1285
17  367  320
18  705  634
19  -51   67
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21  468  429
22  232  307

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 1 1564 1518
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 3 1085 1165
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 7 1657 1629
 8 1414 1358
 9 1042 1065
10 2191 2262
11  324  292
12  686  976
13  406  572
14  162  142
15  575  596
16  334  378
17  505  501
18   31    3
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20  134  199
21 -225   30

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 1 1240 1153
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 6 1380 1422
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11  285  299
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13  200  219
14  632  683
15  435  470
16   96  118
17  212  198
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19   91   48

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 1   66   56
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 3  370  252
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 7 1047 1045
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 9  303  273
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12  328  281
13  220  204
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 1 1310 1167
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 6 1833 1861
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 8 1017 1138
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10  737  694
11  900  902
12  577  498
13 1773 1830
14 1020 1041
15  178  313
16  508  476
17 1080  956
18  915  902
19  132  246
20  705  699
21 -151   98
22 -159   54

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 1 1778 1836
 2 2582 2515
 3 2082 2125
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11 2150 2097
12  593  598
13  150  210
14  129  175
15  608  485
16  598  508
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21  -23  112

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 7 3114 3241
 8 1117 1119
 9  435  478
10 -125   64
11 2985 2999
12  254  212
13  460  405
14  442  438
15 1426 1484
16  140   83
17  270  231
18 -247  101
19  596  585
20  302  138

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 1  396  442
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 4  253  253
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 6 1302 1358
 7 1477 1516
 8 1081 1064
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11 1226 1306
12  394  419
13  -52   37
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15  882  871
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17  332  253

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 1  587  555
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10 1190 1096
11 1039 1021
12 1479 1437
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14  836  850
15  -89   68
16  235  178
17  232  204
18  835  852
19  736  757
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 1  148  203
 2 1901 1934
 3  261  239
 4 1394 1397
 5  254  356
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 7 1770 1781
 8  791  816
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11  999 1018
12 1236 1248
13  809  812
14  613  619
15 1329 1316
16  842  804
17  796  789
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20  963  879

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 4 1603 1660
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10 -195   31
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12  944 1018
13  459  396
14  468  573
15  560  502
16 1603 1538
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18  343  265

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11  -87  124
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13  102  242
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15  499  507

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 4  227  151
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 6  213  213
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 3 3081 2937
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 8 1729 1799
 9  279  215
10  223  202
11 1064  958
12  142  204
13  607  575
14 1341 1345
15 1728 1819
16  581  618
17  329  328
18 -133  191
19 1473 1541
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 1 2649 2684
 2  696  938
 3 1751 1674
 4 4447 4293
 5 2390 2370
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 8 1894 1966
 9 1855 1858
10  551  598
11  199  125
12  554  550
13 1262 1280
14  734  743
15  413  420
16  342  306
17 -101   85
18  423  431
19  480  440
20  276  212
21  647  638

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 1 2232 2253
 2  666  628
 3 1425 1487
 4  156  177
 5 1068 1069
 6 1897 1861
 7 1224 1223
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10  532  479
11  384  269
12 1063 1107
13  651  634
14  292  354
15 -205   66
16   76  112
17  769  755
18  330  332
19  360  306

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 1 1270 1248
 2  470  463
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 7  894  876
 8  727  741
 9  323  344
10  258  178
11  427  296
12  162  195

13  -47  100
14  292  290
15  194   74
16  608  583
17  -91  128

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 1 -139   41
 2  210  190
 3  901  910
 4  485  494
 5  513  546
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 9 1055  341
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12 -105   74

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 4 3030 2304
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 8 5918 5394
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12 2107 2017
14  390  373
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18  370  317
20  652  617

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 1 1469 1414
 2  388   73
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 5 2867 2600
 6 1405 1417
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 8 3810 3762
 9  527  576
10  665  651
11  474  496
12 1191 1163
13  484  477
14  764  817
15  375  364
16  451  371
17  -59   66
18 -206    9
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21  222  204

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 3 2744 2737
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 5 1718 1814
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 9 1269 1285
10  812  748
11   18  225
12  213  144
13  203  171
14  487  566
15   95  153
16  166  159
17  143   83
18  239  172
19  435  413
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 1 1238 1223
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 4 1247 1253
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 6 1732 1761
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 9  211  273
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11  155  114
12  -14  127
13  188  213
14  314  367
15  229  191
16  390  278
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18  374  498

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 7  663  706
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11  -10   12
12  170   38
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 8 1011 1028
 9  176  228

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 1 1711 1471
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 6 1440 1362
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 8 1202 1104
 9 2299 2221
10  478  471
11  530  517
12  164  277
13  -69   24
14  321  346
15  260  140
16  512  551
17 1102  395
18  295  299
19  241  234
20 -115   98
21  -79    3

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 1 2885 2786
 2  565  483
 3 4525 4493
 4 4138 3984
 5 1192 1241
 6  443  476
 7 1912 1776
 8 2090 2147
 9  660  675
10  644  697
11 1540 1557
12 1745 1734
13  670  744
14  439  369
15  532  438
16  459  590
17   51  155
18  295  206
19  413  413
20 -157  114

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 1  645  602
 2 1507 1458
 3 1619 1545
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 6 1195 1219
 7 1820 1806
 8  512  480
 9  237  288
10  759  756
11 2326 2330
12  174  145
13  516  447
14   92  279
15 1034  967

16  135  156
17  246  305
18  216  205
19  276  275

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 2  167  156
 3 1236 1305
 4  224   54
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 6  555  560
 7 1484 1547
 8  945  966
 9 1028 1035
10  276  361
11 1031  993
12  920  921
13  314  391
14  456  309
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16  465  475

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 3  465  431
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 5  705  735
 6  650  613
 7  235  225
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12  399  347

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 8 1959 2075
10 3322 3253
12 1502 1531
14 1342 1450
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20  226  180

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 3 1088  939
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 6  671  606
 7 1190 1149
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 9 1011 1077
10 1557 1553
11 2730 2703
12 1830 1818
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14  911  880
15 1084 1070
16  427  404
17  144  235
18  471  428
19  247  254
20  430  364

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 3  579  472
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 5  952 1010
 6  -91   73
 7  -40  130
 8 1525 1621
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10  456  534
11 -206    0
12 2865 2955
13  318  314
14  373  377
15  844  850
16  905  910
17   99  216
18  220  124
19 -127   36

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 1   84   27
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 3  312  409
 4  575  606
 5  626  666
 6   53   69
 7  222  108
 8 1314 1320
 9  435  492
10 1165 1142
11  188  174
12 1169 1173
13  287  400
14  269  197
15  350  365
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17  494  431

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 3  390  437
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 5  282  354
 6  231  241
 7 1035 1081
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 9  159  149
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11  191  108
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14   68  139

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 8  289  242

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 9  445  419
10 1110 1110
11 3401 3363
12 1295 1272
13  594  537
14  388  320
15 2367 2326
16  275  335
17  131   20
18  350  337
19 1004  946
20  328  414

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 1 1827 1537
 2 2079 1801
 3  576  235
 4 1523 1535
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 6 1402 1294
 7 1612 1534
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 9  605  561
10 1160 1170
11 1159 1150
12  971  976
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 1 3244 3314
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 3 1484 1539
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10  144  149
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12  433  406
13  622  738
14  243  234
15  353  274
16  149  127
17  322  349
18  178   41

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10  423  415
11  -64  118
12  -78  103
13  311  477
14  116   69
15  232   40

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18  457  471
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 2 2656 2566
 3 1788 2052
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 6  718  772
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10  809  780
11  769  797
12  901  823
13 -143   39
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15 1053 1052
16 1126 1164
17  417  390
18  127  246
19  153   33
20  424  528

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 3 1046  995
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10  208  156
11  577  624
12  619  570
13  820  900
14 1302 1303
15 1351 1317
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18  395  386

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 9  205  202
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11  130   65
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13  268  222
14  784  699
15   86   29
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17  324  338

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12  202  172
13  304  288

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 2  157   56
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 6  124  147
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 8  215  261

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 1 4043 4071
 2 1927 1674
 3  386  593
 4  993  890
 5  951  861
 6 3643 3582
 7  652  787
 8 1256 1184
 9 3044 3086
10 1969 1915
11  502  494
12  402  345
13  273  370
14  521  574
15  359  333
16  136  208
17  179  134
18  -99    1
19  207   88

  1   3  L

 0 4049 3936
 1 2200 1972
 2 2559 2379
 3 1587 1670
 4 1339 1375
 5  577  627
 6  369  299
 7  937 1057
 8  772  766
 9  120  185
10 [illegible]
11 1094 1015
12  171   60
13 [illegible]
14  617  555
15  843  929

16  314  390
17   79   59
18  440  411
19 -167  146

  1   5  L

 0 1400 1362
 1 1157 1156
 2 1334 1312
 3 3695 3713
 4 1229 1174
 5 -156  219
 6  360  392
 7 1010 1057
 8  574  534
 9  946 1016
10  301  406
11  263  186
12  245  317
13  -54  165
14   40  168
15  665  678
16   70  166
17  232  222

  1   7  L

 0  989  959
 1 1066  995
 2  574  581
 3 1042 1039
 4 1044  985
 5   17   61
 6  342  386
 7  655  635
 8  668  727
 9  622  696
10  555  513
11  150  115
12  219  169
13  142   37
14  229  141
15  475  495

  1   9  L

 0  470  465
 1  792  748
 2  414  403
 3  383  363
 4  266  259
 5 1040 1067
 6  298  282
 7  -91    4
 8  708  735
 9  301  341
10  -59   26

  2   0  L

 2 3809 3391
 4 1430 1402
 6  994  852
 8  935 1003
10 2635 2560
12  731  781
14  560  422
16  609  573
18  259   70

  2   2  L

 0  683  672
 1  683  258
 2  761  868
 3 -109    7
 4   80    4
 5 2339 2480
 6  327  186
 7   51   53
 8  718  751
 9  171  176
10  687  632
11  702  674
12 1853 1912
13  480  429
14  304  270
15  354  352
16  193  237
17  -49   44
18  336  361
19  164   37

  2   4  L

 0 1811 1876
 1  196  302
 2 1762 1773
 3 1580 1675
 4 2546 2538
 5  802  826
 6  227  367
 7 2376 2409
 8 1938 1909
 9   97  239
10  524  589
11  221  276
12 1502 1457
13  313  360
14   98   10
15   70  114
16  106   85
17  180  214
18  296  315

  2   6  L

 0 2013 2013
 1 -116   31
 2  228  178
 3 1909 1903
 4 2904 2950
 5  746  704
 6 2041 2033
 7  848  850
 8 2344 2414
 9 1223 1200
10  138  210
11  208  108
12 1315 1353
13  341  370
14  298  276
15  103  170
16  679  603

  2   8  L

 0  403  345
 1  194  188
 2  621  549
 3  798  706
 4  323  309
 5 -133   56
 6  889  859
 7  839  815
 8  128  193
 9  615  541
10  662  615
11 -149   20
12  559  550
13  155  108

  2  10  L

 0  190  101
 1  188   64
 2  464  398
 3  805  786
 4 -235    7
 5  623  607
 6  700  698
 7  192  178

  3   1  L

 0  580  758
 1  355  157
 2 1336 1344
 3 3280 3284
 4 2405 2430
 5 1061 1035
 6 1774 1774
 7 2443 2333
 8  366  304
 9  334  303
10  248  241
11 3127 3071
12  928  974
13  520  554
14 -125  108
15  360  398
16  -73   77
17   97  134
18   84   58
19  443  463

  3   3  L

 0 1953 1994
 1 1960 1867
 2 1090 1078
 3  229  178
 4  119  157
 5   86  167
 6  361  435
 7  764  699
 8  305  301
 9  171   19
10 1297 1332
11 1045 1083
12 1256 1217
13  714  766
14  604  548
15  724  699
16  355  347
17  158    2
18  461  453

  3   5  L

 0 1654 1667
 1 1372 1387
 2 -112   47
 3  293  192
 4  980  906
 5  128   63
 6  899  885
 7  815  614
 8  554  578
 9 1719 1725
10 -222    4
11  264  191
12  -63  161
13 1623 1555
14  391  331
15  432  411
16  544  454
17  690  678

  3   7  L

 0  362  188
 1  898  899
 2  615  563
 3  503  587
 4  677  691
 5 1098 1082
 6  485  442
 7   86  284
 8  771  756
 9  267  161
10  828  785
11  498  476
12  463  425
13  318  294
14  369  398

  3   9  L

 0   74   28
 1  -96   75
 2  243  150
 3  192   69
 4  656  688
 5  185   68
 6  478  522
 7  759  655
 8 -146  211
 9  418  273
10  239   39

  4   0  L

 0 4394 4614
 2  376  775
 4  945  874
 6 1055 1030
 8 1544 1490
10 1912 1920
12 3851 3827
14  621  651
16 1096 1122
18  -97  242

  4   2  L

 0 3868 3458
 1 1811 1592
 2  452  353
 3 1569 1657
 4 2057 1981
 5 2270 2280
 6  290  317
 7 1481 1584
 8  175  233
 9 -154   50
10  143  103
11 1208 1226
12  835  893
13 1114 1062
14  914  930
15  461  495
16  799  813
17  117   57
18  205  157

  4   4  L

 0  636  671
 1 1484 1528
 2 1248 1235
 3  330  326
 4  374  355
 5 1789 1741
 6  262  225
 7 1562 1634
 8  386  343
 9  271  175
10  883  871
11  -85   79
12  249  335
13  540  510
14 1060 1110
15  709  704
16  187  192
17  438  394

  4   6  L

 0 1746 1700
 1  242  180
 2 1009 1027
 3 -110   22
 4  619  623
 5 1122 1139
 6  366  349
 7  321  323
 8  733  788
 9  666  670
10  626  679
11  139  207
12  337  325
13  367  430
14  527  545
15 -106  208

  4   8  L

 0  615  631
 1  155   59
 2  215  246
 3 -129   64
 4  128  139
 5 -163    7
 6  215  158
 7  160   33
 8  275  346
 9  355  299
10 -259   62
12  537  474

  4  10  L

 0  996  991
 1  203  133
 2  164   20
 3  164   91
 4  267  281
 5  425  380
 6  117  179

  5   1  L

 0  891  218
 1 5465 5246
 2 -146  106
 3 1226 1397
 4 2466 2347
 5 2495 2374
 6 2179 2261
 7  329  354
 8  628  554
 9 1952 1924
10   96  293
11   62    3
12  769  867
13  844  801
14  632  594
15  186  125
16  692  670
17  290  281
18  441  368

  5   3  L

 0 2899 2855
 1 4660 4643
 2 1958 1980
 3  412  487
 4 2401 2361
 5 1897 1949
 6  198  202
 7  -42   33
 8 1347 1407
 9  330  311
10  327  325
11  200   33
12  -92  124
13  203  183
14   88   34
15  902  902
16  423  326
17 -166   94

  5   5  L

 0  871  892
 1  446  417
 2  251  148
 3 1665 1687
 4 1096 1101
 5  843  816
 6  186   81
 7 -159  147
 8  854  838
 9  831  823
10  241  303
11  858  931
12  283  186
13  -98   78
14  -63  206
15  954  995
16  185  200

  5   7  L

 0  567  551
 1 1290 1391
 2  452  426
 3  577  628
 4  967  970
 5  105  187
 6  251  265
 7  213  124
 8  131  233
 9  233  184
10  713  685
11  371  383
12  290  247
13  203  186

  5   9  L

 0  412  439
 1 1146 1140
 2  261  245
 3  263  248
 4  246  157
 5  971  891
 6  410  325
 7  386  293
 8  437  373
 9 -229    7

  6   0  L

 0 1426 1177
 2 6227 5862
 4 2597 2492
 6  245  228
 8  693  703
10  -62  146
12  614  627
14 1186 1166
16  -91  127
18  455  536

  6   2  L

 0 2667 2798
 1 2069 2401
 2 1214 1129
 3  880  912
 4 2584 2518
 5 1845 1924
 6  -55   61
 7  114   54
 8  166    2
 9   19   11
10  795  794
11  424  394
12  217  115
13  443  321
14  145   29
15  238  284
16  298  309
17 -168   88

  6   4  L

 0 4024 3923
 1 1728 1789
 2  719  768
 3  157  106
 4 2558 2538
 5 1170 1173
 6  595  587
 7  896  844
 8 1998 2047
 9   43   45
10 -198   96
11  428  515
12  682  757
13  153   82
14  260  216
15 -156   58
16  463  487

  6   6  L

 0 2146 2100
 1  165  171
 2 2026 2009
 3  536  481
 4 2182 2148
 5  895  879
 6  467  550
 7  180  258
 8 1634 1506
 9  637  684
10  828  841
11  106  101
12  318  178
13  175  220
14  154  138

  6   8  L

 0 1597 1659
 1   99  136
 2  326  380
 3  155  217
 4 1014 1062
 5  710  707
 6  523  561
 7  260  260
 8  418  451
 9  374  428
10  427  386

  6  10  L

 0 -172   56
 1  310  280
 2  985  969
 3  332  381
 4  137   53
 5  189   51

  7   1  L

 0  394  495
 1 -163   48
 2  -33  207
 3 4720 4560
 4 2805 2847
 5  454  534
 6  283  215
 7  976  955
 8 1984 1990
 9  375  322
10  503  533
11 2232 2253
12  824  845
13  594  539
14  406  510
15 -154   38
16  209  247
17  139  195

  7   3  L

 0  384  290
 1 1544 1466
 2 2081 2028
 3  511  474
 4 2070 2068
 5 1770 1767
 6  280  310
 7  154  214
 8 1809 1780
 9 1976 1998
10 -146    5
11  417  364
12  514  515
13 1019 1050
14  247  208
15  217  199
16  254  311
17   93   16

  7   5  L

 0 -107  118
 1  463  465
 2  638  562
 3  539  555
 4  565  549
 5 1559 1575
 6   83  172
 7  290  270
 8 -156   94
 9  877  908
10  901  942
11  502  391
12  469  438
13  505  577
14  271  335
15 -175   84

  7   7  L

 0  319  401
 1  436  405
 2  157   26
 3  650  659
 4  -85  147
 5  785  783
 6  137  366
 7  -98  155
 8  283  273
 9  489  465
10 -150   13
11  251  344
12  226  257
13  459  489

  7   9  L

 0  495  512
 1  -74   66
 2   44  170
 3  558  626
 4 1158 1091
 5  325  324
 6 -115   12
 7  547  472
 8  764  689

  8   0  L

 0 1521 1495
 2 1638 1662
 4 1291 1345
 6  -83   65
 8 1554 1612
10  487  367
12 2094 2156
14  328  320
16  611  594

  8   2  L

 0 1875 1734
 1 1170 1185
 2 1193 1119
 3  653  550
 4 2705 2695
 5  149   13
 6  406  498
 7 -138   51
 8 2714 2677
 9  139  264
10  564  432
11 1251 1213
12 1581 1537
13  459  420
14  411  383
15  163  108
16  640  725
17  166  221

  8   4  L

 0 1147 1102
 1  943  894
 2  733  746
 3  148  130
 4  172  214
 5  683  680
 6  392  361
 7 1873 1827
 8  461  501
 9  339  294
10  689  643
11  649  681
12  -56  179
13  499  468
14  776  790
15  241  245
16  191  200

  8   6  L

 0  238   92
 1  147  193
 2  537  563
 3   58   11
 4  372  362
 5  787  754
 6  516  582
 7  312  248
 8 1204 1196
 9  426  384
10  268  275
11  104  226
12  545  547
13 -209  114
14  275  346

  8   8  L

 0  402  372
 1  195  149
 2  140   66
 3  190  157
 4  261  293
 5  690  690
 6  376  344
 7  330  306
 8  566  537
 9  510  532
10  -68  147

  8  10  L

 0   23   71
 1 -155  189
 2  205  179
 3  132   18
 4  509  457
 5  241   30

  9   1  L

 0  819 1438
 1 7091 6662
 2 1520 1563
 3  435  518
 4  191  139
 5 1036  988
 6 -173   20
 7  -48   52
 8  256  196
 9  170  230
10  289  222
11  314  342
12  261  198
13  331  394
14  222   32
15  184    2
16 -170  110
17  613  658

  9   3  L

 0 1334 1364
 1  216  289
 2  283  311
 3  150  176
 4  902  842
 5 1174 1168
 6  247  134
 7  572  536
 8 1799 1781
 9  324  357
10 -128  145
11  419  498
12  707  726
13  576  567
14  625  570
15  564  623
16  530  556

  9   5  L

 0 1049 1010
 1 1336 1277
 2  286  277
 3  871  962
 4  810  841
 5  182  269
 6 1272 1223
 7  934  870
 8  484  575
 9  800  871
10 -167   47
11 1276 1166
12 -218   45
13  231  259
14 -173  103

  9   7  L

 0  -30  175
 1  577  536
 2  421  360
 3  344  243
 4  462  506
 5  243  211
 6  459  439
 7  560  508
 8  315  273
 9 -111   40
11  695  666
12  384  371

  9   9  L

 0  494  412
 1  356  348
 2   98  154
 3  296  230
 4  202  183
 5 -214   65
 6  616  637
 7 -133   20

  9  10  L

 5  440  158

 10   0  L

 0 1774 1698
 2 4634 4585
 4  884  940
 6 1238 1273
 8 -112   34
10 1188 1153
12  456  428
14 1025 1049
16   86   27

 10   2  L

 0  981  801
 1 1512 1437
 2  859  700
 3 1105 1172
 4 1398 1429
 5  133   90
 6  360  358
 7  302  198
 8  897  899
 9  593  645
10  449  393
11  578  528
12 -110  134
13 -147   81
14  605  612
15 1013 1044
16  325  343

 10   4  L

 0 3205 3238
 1  509  527
 2 1324 1338
 3  170    2
 4 1160 1228
 5  657  587
 6  652  610
 7 -110    6
 8  308  313
 9  471  465
10  343  367
11  447  429
12  693  732
13  347  295
14  476  455
15  305  278

 10   6  L

 0 2786 2710
 1  712  681
 2  998 1065
 3  168  185
 4 1475 1590
 5   57   98
 6  381  341
 7  -46   37
 8  245  136
 9  -21   65
10  452  430
11  119   81
12 -134  243
13  224  250

 10   8  L

 0  973  956
 1  273  260
 2  855  828
 3  154   66
 4  457  460
 5  336  371
 6  251  319
 7  417  427
 8 -191   16
 9  267  287

 10  10  L

 0  288  338
 1  690  644
 2  643  625
 3  257  130
 5  241   98

 11   1  L

 0 2598 2298
 1 2167 2156
 2  811  939
 3 3408 3355
 4 1251 1150
 5 1409 1443
 6  446  453
 7  548  583
 8   82   29
 9 -169  119
10  491  442
11  239  257
12 -130   98
13   74   64
14  391  381
15  997  957
16  241  279

 11   3  L

 0 2571 2644
 1 1417 1452
 2  891  890
 3 1803 1887
 4 1066 1039
 5  124  118
 6  397  337
 7  573  476
 8 -207  121
 9  964  964
10  456  536
11  303  274
12   37   87
13  305  254
14  667  705
15  -87   39

 11   5  L

 0  765  739
 1 3116 3195
 2  282  338
 3  141  176
 4 1001 1024
 5 2903 2937
 6  749  741
 7 1196 1140
 8  218  255
 9 1104 1031
10  611  603
11  688  646
12  167  165
13  448  381

 11   7  L

 0  554  528
 1  618  640
 2 1080  991
 3  475  526
 4  924  925
 5  871  942
 6 1001 1034
 7 -108   35
 8  321  304
 9  572  554
```

$K_6[(CN)_5CoSSO_2Co(CN)_5]\cdot 6H_2O$

```
11  456  412

 11    9  L

 0  526  537
 1  441  506
 2   83   97
 3  759  728
 4  327  440
 5  147  154
 6  269  265

 11   10  L

 5  462   56

 12    0  L

 0 6449 6357
 2 1034 1007
 4 5804 5644
 6  690  782
 8 1068 1043
10  235  336
12 1256 1303
14  673  662

 12    2  L

 0 1427 1330
 1  680  692
 2  812  752
 3 2810 2854
 4 2552 2528
 5 1105 1101
 6  422  392
 7  449  467
 8  915  895
 9  122  127
10  660  710
11  248  232
12  900  902
13  426  504
14  418  471
15  417  391

 12    4  L

 0  455  392
 1   50   70
 2 1538 1495
 3  498  494
 4  729  716
 5  293  326
 6 1031 1010
 7 1677 1695
 8  196  206
 9  410  376
10  469  426
11 -150   25
12  513  502
13  756  659
14 -114  114

 12    6  L

 0 1166 1127
 1  -87   70
 2  -81  116
 3  162  179
 4  219  315
 5  624  640
 6  705  667
 7  457  475
 8  635  655
 9  352  434
11  476  466
12 -109   87

 12    8  L

 0  158  342
 1  -73   50
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 2  234  255
 3   24   72
 4  626  572
 5  535  543
 6 -136  187
 7  107   92
 8  782  688

 12   10  L

 0  449  436
 1 -159    9
 2  138   34
 5  250  152

 13    1  L

 0 1986 2024
 1 1350 1410
 2  700  692
 3  962 1010
 4 2166 2182
 5 1420 1355
 6 1204 1183
 7  346  304
 8  985  989
 9  502  522
10  720  691
11  228  315
12  864  891
13 1600 1589
14  190  238
15  165  245

 13    3  L

 0  822  798
 1  142   40
 2  220  186
 3  881  933
 4  593  591
 5  493  512
 6  -10  162
 7  415  467
 8  593  602
 9  188   18
10  145   49
11  728  747
12  107   60
13  392  431
14   44   92

 13    5  L

 0 1817 1844
 1  157  232
 2  198  149
 3 1543 1500
 4  129  174
 5  774  708
 6  389  429
 7 1156 1194
 8  491  467
 9  259  212
10  147   76
11  586  666
12  284  199

 13    7  L

 0  235  306
 1   93   99
 2  460  449
 3  225  263
 4  166  232
 5  460  505
 6  805  772
 7  321  337
 8  262  273
 9  295  277

 13    9  L
```

```
 0 -127  128
 1 -173   12
 2   96   65
 3  310  384
 4   37  249
 5  397  326

 14    0  L

 0 2240 2240
 2  717  598
 4  545  588
 6 1160 1136
 8  442  414
10  172  104
12  730  711
14 1393 1392

 14    2  L

 0  477  609
 1 1255 1246
 2 2901 2893
 3  837  851
 4  304  302
 5  262  247
 6  386  411
 7  477  406
 8  175  154
 9  194  161
10  444  451
11  518  471
12  677  651
13  807  706
14  274  258

 14    4  L

 0 1794 1779
 1  633  692
 2  615  582
 3   86  138
 4  423  460
 5  876  912
 6  209  255
 7  389  362
 8  476  486
 9  630  582
10   67   85
11  222  305
12  844  761
13  145    9

 14    6  L

 0  481  458
 1  448  466
 2  601  605
 3 -137  178
 4  149  147
 5  170   13
 6  424  397
 7  488  526
 8  861  882
 9   62   93
11  215  264

 14    8  L

 0  332  365
 1  696  636
 2  500  477
 3   28   13
 4  331  331
 5  178  240
 6  152   38
 7  833  795

 14   10  L

 0  145   73

 15    1  L
```

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 0 1605 1631
 1  728  740
 2  102  203
 3 1690 1629
 4  290  230
 5  176  129
 6 1194 1219
 7  527  537
 8  -37   33
 9   64  228
10  450  435
11  253  297
12  440  429
13  181  226
14  589  620

 15    3  L

 0  782  754
 1 3908 3847
 2  649  642
 3  123  160
 4  708  786
 5  915  953
 6   96  318
 7  149  188
 8  364  324
 9  483  452
10  318  264
11  129  145
12  460  455
13  202  246

 15    5  L

 0  650  660
 1 2354 2296
 2 1273 1222
 3  986  982
 4  332  396
 5 1214 1199
 6  386  292
 7  129   15
 8  254  225
 9  132   80
10  429  443
11  456  567

 15    7  L

 0  593  477
 1 1715 1684
 2 -140    3
 3  289  309
 4  256  161
 5  985  940
 6  185  276
 7  119  150
 8  450  504
 9  477  486

 15    9  L

 0  467  443
 1  432  442
 2  205  191
 3  440  477
 4  148  160

 16    0  L

 0  942  892
 2  654  681
 4 4213 4296
 6  434  373
 8  478  451
10  344  443
12 -151   61

 16    2  L

 0 2357 2397
```

```
 1 2430 2417
 2 1998 2012
 3 1207 1251
 4 2611 2540
 5 1710 1719
 6  894  852
 7  229   26
 8  574  667
 9  831  863
10  664  613
11  102  180
12  293  283
13 -183   13

 16    4  L

 0  322  351
 1  761  727
 2 2132 2146
 3  323  317
 4 -190   14
 5 -178   74
 6  747  782
 7  121   38
 8  167  101
 9  224  190
10  398  419
11  565  602
12 -194   16

 16    6  L

 0   70  104
 1 -160  101
 2  368  380
 3  152   57
 4  429  415
 5  124   78
 6  246  336
 7  -78   97
 8 -138   35
 9  627  667

 16    8  L

 0  405  370
 1  543  521
 2  573  615
 3  122   44
 4  392  442
 5  466  480
 6  360  339

 17    1  L

 0  154  209
 1 2002 2010
 2  642  569
 3  249   28
 4  475  487
 5 2210 2229
 6 1131 1091
 7  -40   73
 8  271  254
 9  779  777
10  211   83
11 -131   83
12  277  134
13  773  749

 17    3  L

 0 1494 1435
 1  859  817
 2 1197 1202
 3  860  882
 4 2090 2099
 5 1426 1490
 6 -218  186
 7 -237  119
 8  843  825
 9  737  733
10  192  190
```

```
11  721  678
12  212  264

 17    5  L

 0  941  911
 1 1048  986
 2  310  375
 3 1047 1085
 4  468  420
 5   98   56
 6  461  380
 7  822  831
 8  348  354
 9  159  183
10 -138   71

 17    7  L

 0  536  556
 1  -69  201
 2  256  246
 3  628  608
 4  236  161
 5  513  532
 6  390  424
 7  670  633
 8  409  314

 17    9  L

 0  190  157
 1  383  398
 2   88  125
 3 -167   94

 18    0  L

 0  474  404
 2 1032 1016
 4  913  939
 6  813  830
 8   59   18
10   77    7
12  181  133

 18    2  L

 0  723  688
 1  386  385
 2  280  334
 3  926  894
 4  740  740
 5  857  824
 6  628  655
 7  388  410
 8  402  313
 9  118   48
10  749  718
11  491  492
12  -59  228

 18    4  L

 0  201  182
 1  977  933
 2  807  799
 3 -111   68
 4 1529 1501
 5  318  277
 6  -45  106
 7  302  212
 8 1098 1094
 9  543  597
10  341  363
11  478  352

 18    6  L

 0  587  600
 1  158  171
 2  337  209
 3  133  120
```

```
 4  698  693
 5  213  212
 6  405  397
 7  451  432
 8 1085  979
 9  272  307

 18    8  L

 0  260  180
 1   96   10
 2   85  141
 3  283  338
 4  738  700
 5   53   56

 19    1  L

 0  739  788
 1  522  530
 2  440  466
 3  346  276
 4  497  548
 5  242  240
 6   98   20
 7  684  660
 8  390  391
 9  199  126
10  200  107
11  715  699
12  127  216

 19    3  L

 0  796  769
 1 1696 1742
 2  429  433
 3  372  298
 4  765  790
 5  419  461
 6  219  216
 7  128  131
 8  916  862
 9  431  442
10  452  503
11  104   14

 19    5  L

 0  -62  132
 1  749  803
 2  329  363
 3  490  533
 4  181  138
 5  272  176
 6  463  417
 7  413  380
 8  262  166
 9  299  319

 19    7  L

 0  -70  104
 1  565  545
 2  113  156
 3  289  379
 4  209   81
 5  147  176
 6  293  265

 19    9  L

 0  -60  190
 1  436  381

 20    0  L

 0 1587 1604
 2 1197 1243
 4  405  344
 6  646  615
 8  413  476
10  147   72
```

```
 20    2  L

 0 1235 1243
 1  860  812
 2 1461 1435
 3   44  105
 4  691  681
 5  328  159
 6  136  103
 7  810  804
 8  339  344
 9  170   36
10  316  382
11  506  544

 20    4  L

 0  125  131
 1  380  373
 2 1366 1306
 3 -142   10
 4  492  428
 5  745  768
 6  355  321
 7   57  173
 8  470  459
 9  285  270
10  119    1

 20    6  L

 0  949  955
 1  250  274
 2  927  866
 3  616  547
 4 -101   87
 5  165  177
 6  977  969
 7   37   23

 20    8  L

 0  732  660
 1  143   59
 2  234  242
 3  309  262
 4  715  683

 21    1  L

 0 1918 1896
 1 2445 2388
 2 1071 1067
 3  254  195
 4  793  827
 5 1719 1754
 6  -71  111
 7  301  310
 8   96  153
 9  766  799
10  181  149
11  413  391

 21    3  L

 0 1356 1304
 1  195  210
 2  556  554
 3 1398 1393
 4  -64  136
 5 1337 1282
 6  777  750
 7 -146   40
 8 -123  125
 9  515  472
10 -199   24

 21    5  L

 0  460  471
 1  -73   56
 2  346  428
```

```
 3  865  884
 4  126  109
 5  301  299
 6  581  560
 7  442  388
 8  405  342

 21    7  L

 0  355  311
 1  382  369
 2  195   69
 3  344  375
 4  254  212
 5  330  386

 22    0  L

 0 1090 1044
 2  789  811
 4 1097 1120
 6 1950 1931
 8  226  231
10  690  629

 22    2  L

 0  275  328
 1  671  658
 2  565  595
 3 1122 1145
 4  958  975
 5  790  804
 6  699  703
 7  606  615
 8  394  441
 9  708  630
10  188   83

 22    4  L

 0  720  707
 1  805  854
 2   47  223
 3 -161  165
 4 1245 1234
 5   61   39
 6   85  287
 7 -148  190
 8  412  411
 9  151  241

 22    6  L

 0 1204 1193
 1  257  172
 2  146  109
 3  197  199
 4  787  842
 5  -54  179
 6  127  222

 22    8  L

 0  151  147
 1  207  234
 2  379  391

 23    1  L

 0  235  261
 1  368  331
 2  318  357
 3  535  520
 4  931  935
 5  305  154
 6  750  799
 7 1065 1075
 8  228  204
 9 -114   57

 23    3  L
```

```
 0  698  711
 1  674  592
 2  217  237
 3  359  287
 4  271  367
 5  771  831
 6  317  238
 7  346  339
 8  249  327
 9  392  467

 23    5  L

 0  439  497
 1  469  431
 2  385  361
 3  642  577
 4  126  211
 5  895  895
 6  201   31
 7  416  473

 23    7  L

 0  829  861
 1  238   91
 2   71   73
 3  206   78
 4  523  506

 24    0  L

 0  197  232
 2 -117  234
 4  847  882
 6  823  789
 8  956  935

 24    2  L

 0  360  303
 1 1127 1128
 2  839  873
 3  642  711
 4  226  206
 5  477  494
 6  133   83
 7  724  760
 8  453  455
 9 -215   67

 24    4  L

 0  556  568
 1  310  408
 2  920  905
 3  806  755
 4   76  108
 5  204   30
 6  166  231
 7  463  461

 24    6  L

 0  689  672
 1  469  452
 2  443  507
 3   28   96
 4  137  214
 5  310  290

 24    8  L

 0  223  228

 25    1  L

 0  138   13
 1 1346 1347
 2  540  452
 3  476  491
 4  105  273
 5  988  995
```

```
 6  280  280
 7  375  467
 8  341  376

 25    3  L

 0  319  354
 1  145   33
 2  495  526
 3 1249 1264
 4 -153   22
 5  397  456
 6  275   41
 7  147  197

 25    5  L

 0  260  302
 1  194  228
 2   87   51
 3 -125   60
 4  394  410
 5  193  179

 25    7  L

 0  174  221
 1  155  211
 2  512  416

 26    0  L

 0  389  410
 2  285  309
 4  115  125
 6  296  413
 8  153  294

 26    2  L

 0  593  562
 1  364  389
 2 1020 1019
 3  460  512
 4  215  195
 5  525  528
 6 1141 1176
 7  318  289

 26    4  L

 0  557  570
 1 1043  981
 2  244   11
 3  175  115
 4  968  951
 5  590  472
 6  355  329

 26    6  L

 0  714  661
 1  287  294
 2  244  192
 3 -145    8

 27    1  L

 0  257  188
 1  537  507
 2   87  169
 3  578  610
 4  611  605
 5 -124   88
 6  113   62
 7  259  389

 27    3  L

 0  614  592
 1  600  553
 2  287  354
 3  152  102
```

```
 4 1100 1043
 5 1159 1131
 6  314  358

 27    5  L

 0  229  201
 1  861  857
 2  424  415
 3  413  407
 4 -103   62

 27    7  L

 0  870  838

 28    0  L

 0  409  395
 2  187  220
 4 1343 1322
 6 -118   57

 28    2  L

 0  751  742
 1  381  405
 2  252  265
 3  687  742
 4  696  687
 5  850  893
 6  415  463

 28    4  L

 0  380  393
 1  104   72
 2 -155   43
 3  288  272
 4  545  500

 28    6  L

 0  305  323
 1  396  369
 2  218  118

 29    1  L

 0 -192   73
 1  101  191
 2  265  228
 3  750  772
 4  334  248
 5  365  476

 29    3  L

 0  497  473
 1  422  370
 2  207  126
 3  317  296
 4  865  857
 5  234  104

 29    5  L

 0 -140   13
 1  169  108
 2  269  267

 30    0  L

 0  656  605
 2 1604 1576
 4  357  384

 30    2  L

 0  122   56
 1  481  458
 2  566  563
 3  123  124
```

```
 4  559  552

 30    4  L

 0  281  247
 1  263  184
 2 -188  189
 3  266  287

 30    6  L

 0  312  317

 31    1  L

 0  426  453
 1  192  194
 2  866  837
 3  618  557
 4  232  348

 31    3  L

 0  676  637
 1  665  660
 2  214  118
 3  258  195

 31    5  L

 0  341  252
 1  437  504

 32    0  L

 0  862  889
 2  -95  163

 32    2  L

 0  574  549
 1  151  289
 2  172  211
 3  381  393

 32    4  L

 0  204  211
 1  550  533

 33    1  L

 0  358  337
 1  323  286
 2 -175   51

 33    3  L

 0  765  728
 1  322  322

 34    0  L

 0  329  367
 2  426  412

 34    2  L

 0  255  242
 1  340  126

 35    1  L

 0  543  519
 1 -124   81

 36    0  L

 0 -221   30
```

spatially appropriate for partial occupancy of water molecules, were located with electron density of 1.5 eÅ^{-3} or greater on difference maps. Occupancies of these sites were assigned to yield reasonable temperature factors, and ranged from 0.15 to 1.0, with the integrated occupancy very close to six water molecules. These population factors were normalized to a total of six, and these populations were held constant in further refinement. Only two water molecules were treated as completely ordered. Due to the severe disorder of the solvent, hydrogen atoms were not located. Residual density was present in the vicinity of the ordered water molecules; however, hydrogen positions were ambiguous, and thus not included.

Refinement was terminated when all shifts were less than half their standard deviations. All shifts in parameters of the potassium ions and the binuclear anion were less than 20% of their standard deviations. The final R index is 0.088 based upon all measured reflections and 0.053 based upon all data for which $F_{obs} > 3\sigma(F_{obs})$. Approximately 2/3 of the 5084 data met this criterion. The goodness of fit is 1.98 for 5084 data and 373 parameters. A three-dimensional difference synthesis indicates residual density of up to 0.9 eÅ^{-3} in the disordered region, probably as a result of solvent disorder which is even more complex than the twelve-site model indicates; however, previous experimentation with various disorder models led us to the conclusion that slight perturbations in the solvent disorder cause no significant changes in the apparent geometry of the dicobalt species. Upon these grounds, further work on improvement of the solvent model was deemed unnecessary.

D. $\{Co_2O_2(NH_3)_{10}\}(SCN)_4$

All but the finest details (such as accurate bond distances) of this structure were known prior to this determination due to Vannerberg's original determination[29] based on film data and to the determination of the structure of an impure form (chloride ion partially substituted for thiocyanate) from diffractometer data in 1967 by Mr. Fred J. Hollander, then an undergraduate at Caltech. It is certain that refined parameters from either of these determinations could have served as an excellent starting point for refinement using the new data; however, the structure was completely rederived, mainly as an exercise in structure solution for the beginning crystallographer.

A three-dimensional Patterson map was calculated, from which the cobalt atom, the oxygen atom, and all three coordinated nitrogen atoms in the asymmetric unit were located. A sulfur atom was also located in a fourfold position. A Fourier map phased on these atoms yielded the positions of the carbon and nitrogen atoms in the ordered thiocyanate group, and also the positions of two twofold thiocyanate groups disordered across twofold axes. A structure factor calculation of all the nonhydrogen atoms yielded an R index of 0.30 at this point.

Two of the three crystallographically distinct thiocyanate groups in the asymmetric unit lie in positions in the (001) mirror plane and are disordered across twofold axes normal to that plane. The alternate thiocyanate orientations in each disordered region are almost colinear, such that the sulfur atom of one orientation has very nearly the same coordinates within the unit cell as the nitrogen atom of the orientation related to it by the twofold axis. The carbon atoms of the two alternate arrangements are in significantly different positions due to the unequal S-C and C-N bond lengths in a thiocyanate group. Due to the close proximity of S and N atoms resulting from the disorder, least squares refinement on all atoms was not feasible, since the sulfur and nitrogen atoms in nearly the same position cause near-singularities in the least squares matrices. We decided to refine the ordered atoms by full matrix least squares, holding the disordered atoms constant, and to refine the disordered thiocyanate ions by difference Fourier methods. After several cycles of least squares and difference map refinement, with R=0.09, the hydrogen atoms were located from difference maps calculated in the expected planes. The hydrogen atoms were assigned isotropic temperature factors with B=7.00. Their positions were refined, but their temperature factors were not. After several more cycles of least squares refinement of the ordered atoms and difference refinement of the disordered atoms, convergence was reached with R=0.042, and the difference maps showed no excursions greater than 0.4 e Å^{-3}; however the distances and angles in the disordered thiocyanate ions were not chemically reasonable. To facilitate least squares refinement, the sulfur atom and the alternate nitrogen atom in close proximity to it in the disordered region were combined and treated as a single atom, designated by SN, with averaged S and N form factors. Thus the disordered thiocyanate anion, for least squares purposes, was represented as an ordered group SN-C-C-SN, with the carbon atom positions half populated. Initially the R index jumped to 0.20, but a few cycles of least squares reduced it to a final value of 0.042. In the final cycle, no parameter shifted more than 25% of its standard deviation. Difference maps of the disordered thiocyanate groups calculated at the end of the refinement showed no excursions greater than 0.3 eÅ^{-3}. The final GOF is 1.97, as opposed to 2.89 for refinement by both ΔF and least squares.

Table III-7

Observed and calculated structure factors for Decaammine-μ-peroxodicobalt Tetrathiocyanate. Columns are h, $10F_{obs}$, $10F_{calc}$, and standard deviation of F_{obs}. A double dash in the esd column indicates reflections assigned zero weight in the refinement.

```
    H   0   0

 2   371    357  4
 4    42    -36  6
 6   455   -448  5
 8   562    544  7
10     0      6 --
12    78     67  7
14   367   -361  5

    H   1   0

 1   534    554  5
 2   864   -852  9
 3    86      1  4
 4   406   -396  4
 5   343    324  4
 6   368    346  5
 7   381    398  5
 8   313    305  5
 9   117    118  6
10   132   -137  6
11    39     44 13
12   116   -133  6
13    81    -69  6
14    69     75  5

    H   2   0

 0   279   -280  3
 1   709   -751  7
 2   510    525  5
 3   355   -364  4
 4   724   -652  7
 5   681    664  9
 6   892    860  9
 7   661    626  7
 8   235   -255  5
 9   227    234  5
10   187    191  5
11   153   -158  6
12   111    106  6
13   141   -146  5
14   182    196  4

    H   3   0

 1   605   -623  6
 2   321    314  4
 3   192    183  3
 4   704    695  7
 5   993    997 10
 6   446    455  5
 7    16     22 18
 8   131    132  5
 9   506   -518  6
10   146    144  6
11    72    -67  9
12    28     44 14
13   275    284  4

    H   4   0

 0   647    659  7
 1   219   -216  3
 2   434   -443  5
 3   306    317  4
 4   588    578  6
 5    65     49  6
 6   345   -348  5
 7   405   -420  6
 8   105     91  6
 9    39     16 13
10   354   -342  6
11   414    403  6
12   231    226  4
13    99    101  4

    H   5   0

 1   425   -446  5
 2   344    355  5
 3   367   -382  5
 4   332    340  5
 5   156   -135  5
 6   578   -587  7
 7   114    109  6
 8   476   -462  6
 9   136    128  6
10   302    305  5
11   150    147  5
12   278    280  4
13    52    -49  4

    H   6   0

 0    76    -77  6
 1    89    -83  6
 2   291    302  5
 3    95    -73  6
 4   552   -555 10
 5   167    166  5
 6   144   -140  5
 7    66    -64  9
 8    85     90  8
 9     5     -7 28
10   467    469  6
11    93     98  5
12   172   -185  4

    H   7   0

 1   131    139  5
 2   333   -343  5
 3    59    -46  9
 4   121     80  6
 5   322   -309  5
 6   159    157  6
 7   134   -137  6
 8    66     46  9
 9   164    153  5
10    54    -42  7
11   134   -131  3

    H   8   0

 0   240    237  5
 1   464   -485  6
 2   197   -211  5
 3   507   -507  7
 4   336    335  6
 5    41    -11 12
 6   290   -287  5
 7   229    218  5
 8    22      1 15
 9    42    -29  8
10   201   -213  4

    H   9   0

 1   471   -471  6
 2     1    -23 33
 3   228    219  5
 4    38    -29 12
 5   171    171  5
 6    25     14 14
 7    43    -33  9
 8    31    -40 10

    H  10   0

 0   485   -476  6
 1   113    111  6
 2   164    179  5
 3   175    178  5
 4    32     32 11
 5    94     95  5
 6   140    142  4
 7    94   -110  4

    H  11   0

 1    82     83  5
 2   346    325  5
 3    57     46  5
 4    97     89  3

    H   0   1

 1   775    711  8
 3  1003   -926 10
 5   155   -161  3
 7   274    276  4
 9   513    512  6
11    64     56  9
13   119   -109  5

    H   1   1

 0   563    583  6
 1   277   -309  3
 2   194    203  3
 3  1163  -1055 12
 4   471   -454  5
 5    51     36  6
 6   231   -234  4
 7   171    155  4
 8   262    247  5
 9   112    107  6
10   332    346  5
11   372   -384  6
12   130    121  5
13     3     23 26
14    61    -77  5

    H   2   1

 1   561   -601  6
 2   927   -928  9
 3   139   -152  3
 4   137   -130  3
 5   421    413  5
 6   344    342  5
 7   398    412  5
 8   114    110  5
 9   261   -262  5
10   163   -169  5
11     4     27 30
12   247   -242  5
13    79     89  6
14    74     82  4

    H   3   1

 0    43     34  5
 1   311   -312  4
 2    88     52  4
 3   112    111  4
 4   703    704  7
 5   247   -245  4
 6   243    234  4
 7   222    205  4
 8   481   -492  6
 9   130   -124  6
10   303   -299  5
11   121    116  6
12   155    149  5
13    88    -69  5

    H   4   1

 1   191   -159  3
 2   320    340  4
 3   256    259  4
 4   332    323  5
 5   445    448  5
 6   388   -386  5
 7    70    -73  8
 8   365   -367  6
 9   282   -280  5
10   171    174  5
11   319   -313  5
12   273    277  5
13   108    114  4

    H   5   1

 0   345    373  5
 1   413    439  5
 2   118    133  4
 3   243    250  4
 4   314   -306  5
 5    65     78  6
 6   186   -185  5
 7   547   -586  7
 8    50    -59 11
 9   241    234  5
10    90     85  7
11   260    243  5
12    26    -39 11

    H   6   1

 1   133    152  5
 2   202    200  4
 3   330   -328  5
 4   250    263  5
 5   536   -534  7
 6   167    162  5
 7    60     62 10
 8     0    -26 --
 9   225    211  5
10    67     58  7
11    23     28 13
12    66     79  4

    H   7   1

 0   250    266  5
 1   459   -465  6
 2    22     -4 17
 3    61    -46  9
 4   331   -330  5
 5    59     52 10
 6   367   -366  6
 7   427    426  6
 8    96     94  7
 9    24     39 15
10    84     81  6
11    29    -35  8

    H   8   1

 1   274   -286  5
 2   379   -399  6
 3   120   -120  6
 4    53    -63 11
 5    87     75  7
 6   261    252  5
 7    96   -110  6
 8   137    128  5
 9    74    -73  5
10   153   -163  4

    H   9   1

 0   587   -590  7
 1    87     92  7
 2   116   -120  6
 3   279   -281  5
 4   176    160  5
 5    71     80  8
 6    62     46  8
 7    64    -62  7
 8   142   -140  4

    H  10   1

 1   288   -276  5
 2   179    171  5
 3    91     88  6
 4   129    124  5
 5   122    116  4
 6   143   -145  3

    H  11   1

 0   136    129  4
 1    54     46  6
 2    43     27  7
 3   248    249  4

    H   0   2

 0  1559   1580 16
 2    28     34  8
 4    62     70  5
 6   701   -685  8
 8   778    758  9
10   365    305  5
12     0     12 --
14   268   -309  4

    H   1   2

 1   230    239  3
 2   148   -156  3
 3   779    720  8
 4    53     65  6
 5    35     36  9
 6   717    672  8
 7    96    109  6
 8   516    505  6
 9   293    294  5
10   174   -169  5
11     0    -17 --
12   169   -199  5
13   161   -154  4

    H   2   2

 0   148   -151  3
 1   395   -399  4
 2  1142   1135 11
 3   493   -498  5
 4   123   -117  4
 5   398    382  5
 6   402    373  5
 7   656    649  7
 8   340   -338  5
 9   231    221  5
10   121    123  6
11   226   -229  5
12    61    -85  7
13    73    -71  5

    H   3   2

 1   942   -976 10
 2   351    344  4
 3   386    374  5
 4   114   -108  4
 5   848    818  9
 6   107    117  5
 7    22     -3 16
 8   200    198  5
 9   295   -297  5
10    13     18 23
11    45    -35 11
12    56     65  8
13   229    242  4

    H   4   2

 0   125   -125  4
 1   354    364  4
 2   625   -626  7
 3   494    498  6
 4   481    472  6
 5    69    -65  7
 6   319   -314  5
 7    96   -101  6
 8   220    217  5
 9    73     68  8
10   194   -178  5
11   232    231  5
12   249    238  4
13   119    131  3

    H   5   2

 1   143   -136  4
 2   776    788  8
 3   238   -222  4
 4   252    255  5
 5   155   -147  5
 6   373   -380  6
 7    37     23 13
 8   175   -176  6
 9     4     30 30
10   175    178  5
11    80     77  6
12   193    196  4

    H   6   2

 0   262    274  5
 1   105    100  6
 2   398    407  5
 3   222   -226  5
 4   851   -846  9
 5   219   -213  5
 6    90    -93  7
 7     0    -14 34
 8    24     -7 17
 9    36    -15 12
10   344    334  5
11     1     10 25

    H   7   2

 1    37     17 13
 2   254   -255  5
 3   277   -272  5
 4   194   -195  5
 5   246   -235  5
 6    46     43 11
 7    12     10 22
 8    96     99  6
 9   170    158  5
10   126   -113  4

    H   8   2

 0   257    253  5
 1   280   -287  5
 2   342   -345  6
 3   347   -338  6
 4   202    198  5
 5    47     56 11
 6   131   -128  6
 7   361    355  5
 8     0      9 --
 9    27      8 10

    H   9   2

 1   228   -212  5
 2    56     46 10
 3   150    155  5
 4     5    -16 27
 5   209    210  5
 6    64     64  7
 7    26    -29 11
 8     5     17 17

    H  10   2

 0   278   -284  5
 1    76     64  6
 2   147    137  5
 3    81     64  6
 4     0    -17 --
 5    33    -26  9
 6   211    226  4

    H  11   2

 1     3     17 19
 2   267    271  4

    H   0   3

 1   265   -258  4
 3   564   -547  6
 5   414   -391  5
 7   194    186  5
 9   756    751  9
11   134  - 131  5
13   123   -116  4

    H   1   3

 0     0      4 --
 1    67     92  4
 2   458    444  5
 3   629   -597  7
 4   145   -134  4
 5   368    359  5
 6   482   -474  6
 7   400    390  5
 8   276    263  5
 9   171    167  6
10   354    353  6
11   401   -405  6
12     7    -26 24
13     1    -15 23

    H   2   3

 1   211   -219  4
 2   652   -658  7
 3   551    551  6
 4   436   -431  5
 5   239    231  4
 6   197    190  5
 7    71     76  8
 8   183    169  5
 9   223   -224  5
10   220   -221  5
11   106   -110  6
12   216   -212  4
13    27    -16  8

    H   3   3

 0   592   -593  6
 1   116   -126  4
 2    43     16  8
 3   144   -139  4
 4   642    633  7
 5   663   -656  7
 6   107     95  6
 7   182    176  5
 8   316   -310  5
 9   159   -160  6
10   169   -159  5
11    42     30 11
12   100     93  5
13    25     31  8

    H   4   3

 1   502   -510  6
 2   645    664  7
 3   190    196  4
 4   183    166  5
 5   311    312  5
 6   216   -216  5
 7    27    -30 17
 8   108   -107  7
 9    98    -95  7
10    55     55  9
11   197   -197  4
12   188    195  4

    H   5   3

 0   453    458  6
 1   675    699  8
 2   264    254  5
 3   318    336  5
 4   170   -181  5
 5    79     52  8
 6   200   -192  5
 7   286   -268  5
 8   116   -115  7
 9   247    244  5
10     0     -1 --
11   101     89  4

    H   6   3

 1   309    335  5
 2   257    261  5
 3   234   -226  5
 4   108   -101  7
 5   424   -424  6
 6    46     10 11
 7     0     24 --
 8    55     47 10
 9    87     65  6
10    42    -35  9
11    17    -14 11

    H   7   3

 0   162    162  6
 1   296   -301  5
 2   149   -166  6
 3   121   -117  6
 4   381   -377  6
 5   174   -161  5
 6   185   -184  5
 7   414    405  6
 8   134    129  5
 9    10     13 19
10   109    106  4

    H   8   3

 1   255   -250  5
 2   176   -177  5
 3   262   -262  5
 4    40    -17 12
 5   120    107  6
 6   337    323  5
 7    10    -12 20
 8   234    226  4
 9    85   -104  4

    H   9   3

 0   250   -252  5
 1   145    138  5
 2    67    -61  8
 3   218   -213  5
 4   140    125  5
 5    77     84  6
 6   116    112  4
 7    24     -2  9

    H  10   3.

 1   171   -158  4
 2    95     84  5
 3     0    -13 --
 4    21      4 10
 5   132    145  4

    H   0   4

 0  1395   1463 14
 2   123    123  5
 4    57    -58  8
 6   477   -463  6
 8   565    554  7
10   198    204  5
12    13      6 16

    H   1   4

 1   277    261  4
 2   282   -280  4
 3   381    357  5
 4    56    -38  8
 5    18    -17 18
 6   511    499  6
 7   118    114  6
 8   378    369  6
 9   212    217  5
10   137   -123  5
11     3    -22 27
12   149   -155  4

    H   2   4

 0   219   -225  4
 1   333   -336  5
 2   650    636  7
 3   350   -355  5
 4    59    -58  8
 5   316    314  5
 6   331    320  5
 7   494    489  6
 8   252   -238  5
 9   166    152  5
10    75     71  8
11   175   -178  4
12    51    -57  6

    H   3   4

 1   655   -658  7
 2   201    199  5
 3   237    244  5
 4    30     23 14
 5   586    586  7
 6   151    139  6
 7    25      3 17
 8   146    141  6
 9   247   -247  5
10     0      5 --
11    53    -27  7
12    48     60  5

    H   4   4

 0    80    -84  7
 1   248    247  5
 2   377   -382  5
 3   358    349  5
 4   393    377  6
 5    26    -26 17
 6   222   -211  5
 7   124   -113  6
 8   140    140  6
 9    37     40 13
10   171   -159  4
11   209    205  4

    H   5   4

 1    95    -94  7
 2   513    520  6
 3   167   -167  5
 4   178    166  5
 5   127   -114  6
 6   311   -303  5
 7     2     26 32
 8   164   -175  5
 9    44     40 10
10   147    149  4
11    64     68  4

    H   6   4

 0   146    161  6
 1    70     70  8
 2   271    267  5
 3   132   -129  6
 4   672   -646  8
 5   155   -144  6
 6    77    -75  8
 7    15    -21 21
 8    19     16 17
 9    32    -31 10
10   281    283  4

    H   7   4

 1    28     48 17
 2   229   -222  5
 3   205   -189  5
 4   132   -126  6
 5   209   -199  5
 6    78     68  7
 7    32     -4 11
 8    89     84  5
 9   133    131  3

    H   8   4

 0   210    201  5
 1   225   -226  5
 2   234   -239  5
 3   293   -284  5
 4   189    179  5
 5    55     46  8
 6   100    -98  5
 7   269    274  4

    H   9   4

 1   196   -184  4
 2    28     11 12
 3   143    133  4
 4    31    -28 10
 5   183    179  3
 6    48     46  4

    H  10   4

 0   245   -251  4
 1    64     56  4
 2    98     95  3

    H   0   5

 1   414    420  6
 3   472   -457  6
 5   225   -205  5
 7   144    132  6
 9   285    290  5
11    62     53  5

    H   1   5

 0   303    311  5
 1   117   -116  6
 2    57     45  9
 3   685   -680  8
 4   289   -284  5
 5   110     96  6
 6    99   -106  7
 7    80     68  8
 8   169    165  5
 9    75     69  7
10   176    178  4
11   251   -253  4

    H   2   5

 1   290   -301  5
 2   542   -543  7
 3    56    -52 10
 4   107   -115  6
 5   222    217  5
 6   200    195  5
 7   190    200  5
 8    63     69  9
 9   149   -162  5
10   120   -114  5
11    37     27  7

    H   3   5

 0   128   -137  6
 1   226   -230  5
 2    23     -1 18
 3   118    114  6
 4   380    385  6
 5   137   -135  6
 6   193    191  5
 7   148    146  6
 8   307   -302  5
 9   125   -119  5
10   230   -225  4
11    83     81  4

    H   4   5

 1    96    -75  7
 2   209    215  5
 3   179    181  5
 4   165    169  6
 5   261    256  5
 6   243   -235  5
 7    60    -64  9
 8   253   -247  5
 9   214   -205  4
10   131    124  4

    H   5   5

 0   222    227  5
 1   283    284  5
 2    57     53 10
 3   112    107  7
 4   163   -162  6
 5    80     78  8
 6    89    -94  7
 7   438   -415  6
 8     7    -19 23
 9   128    124  4

    H   6   5

 1   128    113  6
 2   112    108  6
 3   206   -198  5
 4   167    158  5
 5   346   -336  5
 6    96    100  6
 7    46     34  8
 8    10    -16 18
 9   152    165  3

    H   7   5

 0   172    157  5
 1   317   -319  5
 2     5     20 28
 3     0     -5 --
 4   203   -203  5
 5    55     64  8
 6   226   -219  4
 7   287    268  4

    H   8   5

 1   162   -157  5
 2   279   -273  5
 3    48    -50  8
 4    62    -57  6
 5    49     49  6
 6   166    168  3

    H   9   5

 0   405   -399  5
 1    56     56  5
 2    81    -90  4
 3   184   -196  3

    H   0   6

 0  1196   1225 13
 2   119    117  6
 4    54    -78 11
 6   169   -180  5
 8   233    238  5
10    28     10  8

    H   1   6

 1   269    284  5
 2   334   -333  6
 3    40    -12 13
 4   145   -135  6
 5    14     17 23
 6   227    225  5
 7   151    142  5
 8   163    151  5
 9    61     74  5
10    72    -67  4

    H   2   6

 0   171   -172  6
 1   278   -290  5
 2   163    162  6
 3   170   -184  6
 4   128   -119  6
 5   315    318  5
 6   362    352  6
 7   306    305  5
 8   149   -137  5
 9   120    113  4
10    57     66  4

    H   3   6

 1   267   -281  5
 2    32     61 17
 3   100     93  7
 4   229    225  5
 5   424    423  6
 6   197    189  5
 7    20     15 17
 8    81     82  6
 9   269   -264  4

    H   4   6

 0    77     66  8
 1    43     36 13
 2   202   -195  5
 3   197    193  5
 4   284    275  5
 5     0     16 --
 6    99   -101  6
 7   243   -232  4
 8    18     22 13
 9    17      4  9

    H   5   6

 1   113   -106  6
 2   171    175  5
 3   190   -175  5
 4   152    142  5
 5   102    -90  6
 6   272   -270  4
 7    52     46  6
 8   227   -244  4

    H   6   6

 0    28     15 14
 1    37    -25 12
 2   139    136  5
 3    10     -5 22
 4   449   -436  6
 5    50     52  7
 6    70    -64  5
 7    48    -44  5

    H   7   6

 1    94    102  5
 2   231   -221  4
 3    34    -16  9
 4     0     21 --
 5   164   -167  3

    H   8   6

 0    97     91  4
 1   223   -221  4
 2    96    -96  3

    H   0   7

 1   195    192  5
 3   272   -283  5
 5   174   -167  5
 7    68     56  6

    H   1   7

 0   155    142  6
 1    60    -47  5
 2    39     11 13
 3   409   -406  6
 4   174   -166  5
 5   102     95  6
 6    84    -84  6
 7    56     64  6
 8    98    102  3

    H   2   7

 1   158   -153  5
 2   333   -336  5
 3    51     19 10
 4    87    -88  7
 5   153    132  5
 6   109    113  5
 7    60     69  6
 8    58     62  4

    H   3   7

 0   133   -141  6
 1   151   -150  5
 2     0     -8 --
 3    54     53  5
 4   270    261  5
 5   143   -139  4
 6   125    124  4
 7    74     77  4

    H   4   7

 1    96    -92  6
 2   167    167  5
 3   121    115  5
 4    91     92  5
 5   158    152  4
 6   171   -170  3

    H   5   7

 0   146    146  5
 1   213    218  4
 2    56     38  7
 3   106    106  4
 4    89    -95  4
 5    56     61  5

    H   6   7

 1   133    121  4
 2    72     84  5
 3   108   -107  3

    H   0   8

 0   458    460  6
 2    45     32  8
 4    13    -13 16

    H   1   8

 1   129    133  4
 2   105   -103  5
 3   110    116  4
 4    15    -18 14
 5    47    -52  5

    H   2   8

 0   108   -126  5
 1   110   -119  5
 2   217    221  4
 3   119   -127  4
 4    53     42  5

    H   3   8

 1   234   -238  4
 2    56     55  5
 3    99    105  4

    H   4   8

 0   114   -120  3
 1   139    141  3
 2   152   -167  3
```

Table III-8 *Final positional and thermal parameters*

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0·10961 (6)	0·16208 (7)	0	0·00259 (5)	0·00402 (8)	0·0082 (2)	−0·0007 (1)	0·0	0·0
O*	0·0106 (3)	−0·0682 (3)	0	0·0024 (2)	0·0028 (3)	0·0146 (7)	0·0001 (5)	0·0	0·0
N(1)	0·1640 (3)	0·0495 (3)	0·1714 (5)	0·0038 (2)	0·0062 (3)	0·0097 (6)	−0·0003 (5)	−0·0030 (7)	−0·0012 (8)
N(2)	0·0493 (3)	0·2719 (4)	0·1723 (5)	0·0053 (3)	0·0053 (3)	0·0126 (7)	0·0000 (5)	0·0006 (7)	0·0035 (8)
N(3)	0·2334 (5)	0·2652 (7)	0	0·0048 (4)	0·0068 (6)	0·027 (2)	−0·0036 (9)	0·0	0·0
N(4)	0·3683 (5)	0·0292 (6)	$\frac{1}{2}$	0·0076 (5)	0·0088 (7)	0·028 (2)	−0·0003 (9)	0·0	0·0
S(1)	0·2536 (1)	0·2498 (2)	$\frac{1}{2}$	0·0061 (1)	0·0057 (2)	0·0140 (3)	−0·0013 (2)	0·0	0·0
SN(2)	0·5396 (3)	0·6136 (4)	0	0·0063 (2)	0·0126 (5)	0·0121 (5)	−0·0009 (6)	0·0	0·0
SN(3)	0·5914 (3)	0·9808 (4)	0	0·0070 (3)	0·0139 (4)	0·0285 (8)	0·0006 (6)	0·0	0·0
C(1)	0·3208 (5)	0·1211 (6)	$\frac{1}{2}$	0·0051 (4)	0·0062 (6)	0·012 (1)	−0·0042 (9)	0·0	0·0
C(2)	0·535 (1)	0·994 (2)	0	5·1 (4)					
C(3)	0·510 (4)	0·527 (2)	0	0·005 (3)	0·013 (5)	0·007 (2)	0·007 (6)	0·0	0·0
H(1)	0·212 (4)	0·030 (5)	0·164 (8)	7·0					
H(2)	0·158 (4)	0·083 (5)	0·272 (8)	7·0					
H(3)	0·130 (4)	−0·022 (5)	0·162 (7)	7·0					
H(4)	0·046 (4)	0·356 (5)	0·149 (7)	7·0					
H(5)	0·007 (4)	0·247 (6)	0·200 (8)	7·0					
H(6)	0·083 (4)	0·284 (6)	0·247 (7)	7·0					
H(7)	0·217 (6)	0·361 (7)	0	7·0					
H(8)	0·256 (4)	0·268 (6)	0·085 (7)	7·0					

* Coordinates of the oxygen atom bonded to Co are given, rather than those of the symmetrically equivalent oxygen atom chosen by Vannerberg.

E. $(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$

As mentioned in the experimental section, space group and cell parameters for this complex grown from sodium bicarbonate solution are virtually identical with those of its linkage isomer $(NH_3)_5CoNCCo(CN)_5$. The only significant difference in cell dimensions is the length of the a axis, which is 0.04 Å (8σ) longer in this structure. Weissenberg photographs for the first four reciprocal lattice nets normal to c for the two structures appeared indistinguishable to the casual observer, and thus the phase problem did not rear its ugly head. A reasonable scale factor for the isocyano data was deduced by comparison to the final structure factors of the cyano structure, and the R index calculated using the cyano structure factors and the isocyano data was 0.136. This structure was refined by full-matrix least squares without changing the bridging C and N atoms to their expected identities; hydrogen atoms were assigned B=5.0 and not refined. After three cycles of refinement, it became obvious that the orientation of the bridging group should be reversed to its expected linkage mode. The anisotropic thermal parameters of both atoms had refined to somewhat unreasonable values, and a difference map in the Co-C-N-Co plane (see Figure III-3) showed the carbon atom to be in a region of positive electron density and the nitrogen atom to be in a region of negative

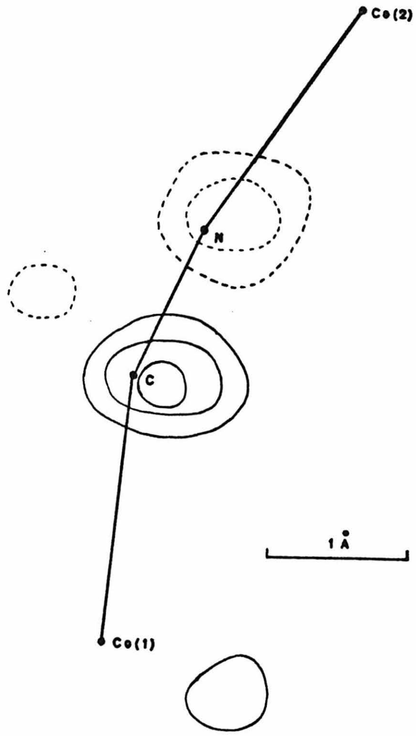

Figure III-3

Difference map in the bridging plane with cyanide in the incorrect orientation. Contours are 0.5 electrons per cubic Angstrom. Dotted contours are negative.

Table III-9

Observed and calculated structure factors for the isocyano molecule. Columns give h, $10F_{obs}$, $10F_{calc}$, and $10X(\Delta F_{obs}/\sigma F_{obs})$. A double dash indicates zero weight in the refinement.

```
    H   0   0

 2  158   122  27
 4 4119 -4305 -61
 6  121   134  -5
 8 2284  2365 -39
10  429   378  25
12 1118 -1123  -2
14  163  -149   2
16  257   228   8
18  137   190 -14

    H   1   0

 2  320   319   1
 4 1204 -1143  48
 6  776  -803 -22
 8  556   550   4
10    0   -58  --
12  547  -472  32
14    0  -100  --
16  195   109  16
18   99   136  -6

    H   2   0

 0 1103 -1109  -5
 2   63    62   0
 4  156   117  16
 6 3458 -3251  73
 8  691  -682   6
10 1467  1420  24
12  208   213  -1
14  155  -164   6
16  131   -32  11
18  312   333  -9

    H   3   0

 2 1476 -1444  22
 4    0   -84  --
 6  134   193 -26
 8  755   741   8
10  220  -241  -7
12    0   -59  --
14  538   555  -9
16   69   -31   2
18  214  -245 -12

    H   4   0

 0  594  -633 -33
 2  816   775  31
 4 1118  1055  16
 6  433   376  34
 8 1162 -1196 -20
10  408  -412  -1
12  814   834  -9
14  214   186   6
16  808  -800   4
18  231  -281 -19

    H   5   0

 2 1043 -1039   2
 4  443   461 -11
 6  337  -317   9
 8  233  -205   9
10  221  -204   6
12  816   817   0
14  250   248   0
16  478  -479   0

    H   6   0

 0   57    81   3
 2  131   -83  10
 4  654  -712 -36
 6  545   543   1
 8  563   566  -1
10  193  -140  11
12   49   -73  -1
14  276   181  29
16  311   327  -8

    H   7   0

 2 1917  1949 -15
 4    0    -3  --
 6 1694 -1692   0
 8   31   -63  -2
10 1109  1096   6
12  363   371  -3
14 1060 -1038  23
16  100  -114  -4

    H   8   0

 0    0     0  --
 2  150   164   8
 4  270  -290  -6
 6  268  -262   1
 8  270   290  -6
10   99    29   5
12  115   -85   4
14  415  -410   2

    H   9   0

 2  261  -279  -5
 4   58  -201 -17
 6  395   361  14
 8   88   101  -1
10  261  -237  18
12   75   -65   1

    H  10   0

 0   76   111  -4
 2   96    89   0
 4  104  -119  -2
 6  193  -191   0
 8    0   127  --
10  357   340   8
12    0     1  --

    H  11   0

 2  973  -964   4
 4  140   -77  11
 6  944   929   8
 8  167   182  -4
10  442  -422  14

    H  12   0

 0  286   263   8
 2   88    63   2
 4  247  -259  -5
 6  147   181 -12

    H  13   0

 2  109    92   4

    H   1   1

 1  616  -632 -20
 2 1353  1330  15
 3  448   477 -30
 4   67   -29   7
 5 1289  1293  -2
 6  657  -669 -13
 7  930  -920   7
 8  678  -641  24
 9  756  -798  -1
10  976   979  -1
11  315   275  15
12  417   405   4
13  309   263  14
14  244  -256  -3
15  206   149  10
16  299  -276   6
17  127  -150  -4
18  227   179  15

    H   2   1

 0 2216  2154  34
 1 1869 -1821  30
 2  102    56  14
 3 1114 -1115   0
 4 1102 -1081  16
 5  103   -19  15
 6  488   460  20
 7 1386  1388   0
 8 1401  1407  -3
 9  563  -618 -21
10  264   241  20
11  768  -748 -15
12  555  -545   4
13  683   654  13
14  290  -336 -14
15  180   183   0
16  152   156   0
17  372  -381  -3
18  405   438 -16

    H   3   1

 1  761   783 -20
 2 1089 -1074  12
 3  353  -418 -52
 4    0    54  --
 5  411  -460 -38
 6  875   866   6
 7  681   709 -19
 8  178  -204  -9
 9  426   404  11
10  638  -653  -8
11 1052 -1049   2
12  504  -485   8
13  149   -29  12
14  269   329 -17
15  571   585  -6
16  201   192   2
17  162   131   6
18  237  -306 -29

    H   4   1

 0  278  -279   0
 1  701  -613  67
 2  820  -760  46
 3  310   367 -38
 4  129  -147  -5
 5  579  -613 -24
 6  440  -416  15
 7  410  -414  -2
 8  155   190 -10
 9 1142  1167 -13
10  214   227  -3
11  421   397   9
12  523  -544  -8
13  542  -535   3
14  194  -158   8
15  192  -179   3
16  232   262  -9
17  449   451  -1

    H   5   1

 1  760  -764  -2
 2  475  -466   6
 3  400   403  -1
 4  300  -289   5
 5  469   449  12
 6 1277  1246  18
 7  329  -294  15
 8  544   557  -6
 9  389  -418 -13
10  815  -824  -4
11  253   277  -6
12  328  -365 -13
13  332   354  -7
14  533   481  23
15  301  -292   3
16  417   412   2
17   36    40   0

    H   6   1

 0  557  -643 -30
 1  108   105   0
 2  178  -205  -9
 3  566  -583  -9
 4 1231  1217   6
 5  248  -185  21
 6  260   242   6
 7    0    90  --
 8  670  -628  20
 9   98    15   6
10  389  -403  -5
11  212  -197   3
12  452   453   0
13  105     0   7
14  561   549   6
15   91   -45   5
16  341  -340   0

    H   7   1

 1  267  -307 -15
 2  229   217   3
 3  548   535   6
 4  378   415 -16
 5  134    63  11
 6  304  -263  16
 7  126  -108   2
 8  216  -212   1
 9   68  -102  -3
10  203   166   9
11  217   262 -11
12    0    28  --
13  116  -161  -9
14  250  -239   4
15  232  -222   4

    H   8   1

 0  171  -136   7
 1  296  -316  -7
 2   48    46   0
 3  430  -455 -10
 4  541   562  -9
 5  591   614 -11
 6    0   -88  --
 7  417   382  14
 8  513  -534  -9
 9  437  -356  32
10    0   -59  --
11  169    87  15
12  316   332  -6
13  413   365  25
14  212   209   1
15    0    77  --

    H   9   1

 1  524   526   0
 2  510   540 -12
 3  783  -768   6
 4  229   202   6
 5  504  -532 -12
 6  706  -696   5
 7  796   786   5
 8  214  -158  13
 9  282   238  13
10  264   300  -5
11  442  -405  19
12  259   221  15
13  220  -191  12

    H  10   1

 0  710   731 -10
 1  424   406   7
 2    0     6  --
 3  373   413 -12
 4  707  -720  -6
 5  582  -567   7
 6  192  -266 -22
 7  338  -335   1
 8  290   239  19
 9  292   218  28
10   95   112  -3
11  158   134   8
12  249  -259  -5

    H  11   1

 1  317  -306   3
 2    0    16  --
 3  355   367  -4
 4  171   -66  19
 5  312   331  -7
 6  117   -65   5
 7  355  -352   1
 8  223   208   5
 9  133   -31  22
10   65    34   5

    H  12   1

 0  187   275 -32
 1   74   -57   1
 2  205   158   3
 3    0    49  --
 4  189  -199  -3
 5   88    90   0
 6    0   -76  --
 7    0    33  --

    H  13   1

 1  136  -144  -3
 2  362  -424 -40
 3   70   -25   7

    H   0   2

 0  379  -390 -13
 1   76   -89  -5
 2  435  -427   8
 3  107   -92   5
 4  517   425  75
 5  284   312 -20
 6  668   733 -55
 7  146   -52  16
 8    0    72  --
 9  334  -382 -25
10  941  -973 -16
11  274   296  -7
12  470  -479  -3
13  157    27  14
14  380   368   3
15  149  -275 -24
16  155    37  13
17   64     6   4
18  625  -603  12

    H   1   2

 1  504   515 -12
 2 3154  3120  17
 3  463  -472  -8
 4  116   105   3
 5  971  -923  37
 6 2076 -2078  -1
 7  587   608 -15
 8  147    50  22
 9  464   465 -12
10 1550  1566  -8
11  571  -571   0
12   87   -25   4
13  120    28   9
14  532  -536  -1
15  256   166  20
16   96   -17   5
17    0   -69  --
18  540   563 -12

    H   2   2

 0 1924 -1846  47
 1  287   312 -22
 2  412  -375  33
 3  457   416  34
 4  635   660 -21
 5  185   174   5
 6  376   306  43
 7  218  -270 -27
 8  540  -523  10
 9  237   283 -19
10  216   211   1
11    0    79  --
12  573   564   4
13  226  -181  10
14    0    31  --
15    0    43  --
16  100   -31   5
17  136    35  12
18  136   108   6

    H   3   2

 1  223   214   5
 2 1139  1114  19
 3  158  -167  -4
 4  924   901  17
 5    0     0  --
 6  799  -831 -23
 7  227  -221   3
 8  869  -847  13
 9  191   171   5
10  746   731   7
11  160   240 -19
12  249   262  -3
13  117   -49   7
14  351  -372  -7
15  284  -316 -10
16  455  -479 -10
17  157   161   0
18  296   302  -3

    H   4   2

 0  863   849  11
 1 1086  1017  49
 2 1191  1133  40
 3  344   331   7
 4  666  -649  11
 5  161  -199 -16
 6   51    57   0
 7   21    81  -6
 8  351   385 -15
 9    0   -34  --
10  278   266   3
11  375  -374   0
12  273  -257   4
13   72   -60   0
14  593  -606  -5
15  250   218   9
16   90    89   0
17   88     4   6

    H   5   2

 1   65    63   0
 2 1020 -1034  -9
 3   81    65   2
 4  284  -253  14
 5  156   120  10
 6 1046  1055  -5
 7  356  -349   3
 8    0   -63  --
 9    0   -66  --
10 1009 -1037 -14
11  192   167   5
12   93  -128  -5
13  231   209   5
14  583   568   7
15   45     8   1
16    0   -40  --
17  192  -207  -6

    H   6   2

 0  660   708 -31
 1  257  -259   0
 2  207  -207   0
 3   69    42   2
 4 1632 -1672 -21
 5  819   815   2
 6  333  -344  -7
 7  127   -41  12
 8  987   957  15
 9  688  -678   4
10   94  -189 -13
11   88    82   0
12  708  -653  26
13  173   149   5
14  284   256   9
15    0   -55  --
16  608   602   4

    H   7   2

 1   90    85   0
 2   48   -60  -1
 3  277   240  12
 4  209  -227  -5
 5  168  -191  -6
 6  303   313  -3
 7  266  -303 -12
 8  476   436  16
 9    0     7  --
10  240   254  -4
11   12   -38   0
12  340  -265  25
13    0   151  --
14  169   -66  22
15  124   153  -8

    H   8   2

 0  775  -766   5
 1  270   301 -10
 2    0    13  --
 3  534   548  -6
 4 1503  1597 -47
 5  393  -373   7
 6  240   238   0
 7  208  -188   4
 8  958  -912  23
 9  228   241  -3
10  303  -266  12
11   96   -30   6
12  646   633   6
13    0   -70  --
14  178   177   0

    H   9   2

 1  310   300   3
 2  121   -52   6
 3  270  -234  14
 4  305  -302   1
 5   95    46   4
 6    0    -5  --
 7  124  -154  -5
 8  225  -205   5
 9  183  -153   7
10   95    29   6
11   90    37   6
12   87   -47   6
13  126   146  -6

    H  10   2

 0  578  -618 -16
 1  152  -165  -2
 2  281  -308  -7
 3    0    25  --
 4  614   651 -17
 5    0   -32  --
 6  103    57   5
 7  114   -22   7
 8  461  -445   7
 9    0    26  --
10   50  -102  -7
11  124   145  -6
12  211   210   0

    H  11   2

 1    0    57  --
 2    0    74  --
 3    0    59  --
 4   62   115  -6
 5   41   -87  -4
 6  102   -11   9
 7  144  -124   5
 8  194  -167   9
 9    0    14  --
10  148   174 -12

    H  12   2

 0  589   609 -11
 1   43   -89  -5
 2    0  -101  --
 3  234  -225   3
 4  557  -580  10
 5  143  -119   7
 6   93    48   9
 7  183   188  -2

    H  13   2

 1    0    38  --
 2  249   266  -9

    H   1   3

 1  544  -564 -18
 2  997  -977  16
 3  695   715 -17
 4  230   215   8
 5   87   150 -22
 6  712   725  -9
 7  223  -213   4
 8  564   594 -19
 9  111     3  11
10  930  -915   8
11  710   740 -16
12  577  -636 -29
13  126   -86   5
14  329   309   6
15  373  -401  -9
16  316   329  -4
17  254  -305 -17
18   81    14   6

    H   2   3

 0 2698 -2616  37
 1 1496 -1504  -5
 2  245   247  -1
 3  493   449  33
 4  966  1008 -32
 5 1391  1362  19
 6  150   154  -1
 7  500  -480  12
 8 1473 -1475  -1
 9  930  -976 -27
10  701  -684   8
11    0   -57  --
12  908   931 -11
13  332   317   4
14  352   349   0
15  132    -6  10
16  389  -429 -14
17  252  -247   1
18  223  -234  -4

    H   3   3

 1 1518  1557 -26
 2  183  -154  12
 3 1620 -1602  11
 4  752   715  27
 5 1159 -1154   3
 6    0   -36  --
 7 1075  1107 -20
 8   19    -3   0
 9  693   688   2
10   55    85  -2
11  529  -483  20
12  295   288   1
13  499  -464   6
14   86   -27   4
15  201   208  -1
16    0   -27  --
17  147   173  -5
18    0    98  --

    H   4   3

 0  386   406 -14
 1 2016  2011   2
 2  784   749  24
 3 1467  1463   2
 4    0     0  --
 5  768  -819 -35
 6  236   242  -2
 7  223  -275 -22
 8    0    57  --
 9  569   520  24
10   62   -85  -2
11  135   109   3
12   90    89   0
13  320  -250  21
14   20    69  -2
15   99    34   6
16  219   237  -6
17  274   278  -1

    H   5   3

 1   67    17   4
 2 1238  1220  11
 3  272   265   3
 4  256  -290   2
 5  458  -435  13
 6 1004  -958  26
 7  339  -421 -39
 8  235  -164  21
 9   66    99  -3
10  569   552   7
11  405   389   6
12  270   222  13
13  139   174  -6
14  711  -681  15
15  431  -408  11
16  217  -245 -11
17  157   123  12

    H   6   3

 0 1067  1041  15
 1   20    -2   0
 2  113    93   3
 3  434  -387  22
 4 1108 -1137 -17
 5  437   423   7
 6  452  -464  -1
 7  177  -103  15
 8  651   641   5
 9  352  -322  10
10  200   176   5
11  334  -352  -6
12  406  -380  10
13  142  -104   7
14  245  -229   5
15  194   191   1
16  281   285  -2

    H   7   3

 1    0    67  --
 2  247  -258  -3
 3  458   503  -2
 4  310  -322  -4
 5  111   -65   5
 6  226   226   0
 7  375  -374   0
 8  164   156   1
 9    0  -103  --
10    0   130  --
11  224   206   4
12  241  -232   2
13   83    94  -1
14  156   -55  19
15  122  -101   6

    H   8   3

 0  239   244  -1
 1  481  -437  20
 2  174    61  17
 3  575  -613 -16
 4  154  -194  -8
 5  738   724   7
 6  284  -272   3
 7  452   395  20
 8    0     7  --
 9  398  -347  19
10  242   245  -1
11   65   -37   4
12  114   -13  12
13  283   257   2
14  207  -214  -3

    H   9   3

 1  343   355  -5
 2 1053  -999  26
 3  495  -457   0
 4  172  -166   1
 5  207  -257 -13
 6  853   885   4
 7  159   116   7
 8  151   158  -9
 9   68   170 -16
10  388  -375   5
11  177  -112  16
12  167  -185  -6
13  113   -76  10

    H  10   3

 0  144   -74  10
 1  439   481 -17
 2  154    54  11
 3  396   327  22
 4  253   226   7
 5  611  -636 -12
 6  230   213   5
 7  261  -255   2
 8  150  -194 -11
 9  262   265  -1
10  153  -105  12
11  155   161   6

    H  11   3

 1   15    64  -2
 2  148   112   6
 3  107    50   6
 4   75   -59  -3
 5  109   133  -4
 6  138  -177 -10
 7  207  -197   3
 8    0   -27  --
 9    0     4  --

    H  12   3

 0  384  -395  -5
 1  144  -138   1
 2   81   -68   1
 3  121    83   7
 4  247   265  -8
 5   91    86   1
 6   83    41   7
 7   83    -4  13

    H   0   4

 0 1325  1357 -24
 1 1006 -1006   0
 2  738   693  37
 3  836   739  73
 4  451   316  83
 5  402   406  -2
 6   39   -54  -1
 7  658   683 -16
 8 2151  2150 -18
 9  778  -756  12
10  313   354 -15
11  675  -561 -13
12 1798 -1753   2
13  784   795  -5
14  218  -238  -4
15  237   257  -4
16  703   708  -2
17  284  -287  -1
18    0    19  --

    H   1   4

 1  104   176 -25
 2  140  -103  12
 3  360   327  22
 4  146  -163  -6
 5  141  -158  -5
 6  538  -582 -31
 7   85   126  -9
 8  268   301 -16
 9   53   -20   7
10  172   154   3
11  242  -254  -3
12  790  -831 -20
13   31   128  -9
14  192  -143   9
15  262   257   1
16  317   356 -12
17  121    15  11
18   77   127 -10

    H   2   4

 0 1089 -1080   8
 1   95   121  -7
 2 2009 -1911  53
 3 1281  1255  30
 4   90   -51   6
 5  170  -203 -13
 6  755   746   4
 7  566  -577  -6
 8  471  -491 -12
 9  132   113   3
10  322  -315   2
11   51   110  -6
12  262   292  -5
13    0   -61  --
14  207   179   6
15  161  -125   6
16  188  -112  15
17  188   210  -5
18  166   197 -12

    H   3   4

 1  215  -165  20
 2 1458 -1422  22
 3  555   634 -28
 4  186   144  14
 5    0    21  --
 6 1257  1228  17
 7  180  -128  16
 8  537   546  -4
 9  719  -738  -9
10  716  -747 -16
11   86    85   0
12  460  -469  -3
13  488   494  -2
14  455   447   3
15   38   -24   0
16  297   269   9
17    0   -85  --

    H   4   4

 0 2187 -2157  15
 1  648   647   0
 2  287   317 -15
 3  336   375 -20
 4 2087  2112 -12
 5  314  -316  -1
 6  537   559 -13
 7  649  -673 -13
 8 1294 -1291   1
 9  147   130   3
10  329  -298  10
11  468   448   8
12  563   585  -9
13   42     6   1
14  106    15   7
15  320  -288  12
16  466  -468  -1
17    0   -21  --

    H   5   4

 1  325  -343  -9
 2  204  -232 -10
 3  620   639 -11
 4  247   228   7
 5   81  -136 -10
 6  346   301  16
 7  280  -248  11
 8  187   -94  18
 9  329  -348  -7
10  512  -482  12
11  348   343   1
12  263   263   4
13    0   -15  --
14  150   141   1
15    0   -48  --
16  156   -66  21

    H   6   4

 0  182   132  13
 1    0   -35  --
 2   76    67   1
 3  500  -468  15
 4  550  -626 -19
 5  181   162   5
 6  155   204  -1
 7   39   165 -17
 8  680   685   0
 9  244  -174  19
10  254  -211  -5
11   91   101  -1
12  179  -170   1
13  168   156  -6
14  421   427  -3
15  148   137   3
16  210   208   1

    H   7   4

 1  593   609  -8
 2 1540  1542  -1
 3  657  -728 -15
 4  241   331   4
 5  303  -318  -5
 6 1334 -1291  21
 7  705   704   2
 8  162  -158   0
 9  113    94   2
10  729   678  24
11  251  -215  10
12   84    44   3
13  280  -247  13
14  643  -599  28
15  153   208  -7

    H   8   4

 0  345   346   0
 1   60   -13   2
 2    6    21   0
 3  176  -219  -9
 4  273  -202  20
 5  136  -121   2
 6  372  -325  16
 7  176   174   0
 8   59   -10   6
 9  161   -61  22
10  308   231  28
11  152   -57  17
12    0   -72  --
13   62   -82   0
14  404  -427 -16

    H   9   4

 1  386  -358  10
 2   86    31   4
 3  307   290   5
 4  113    43   7
 5  166   104  15
 6  183   147   8
 7  181  -164   0
 8  171  -150   4
 9  160   173  -3
10  155  -135   4
11   79    12   7
12   38     6   1

    H  10   4

 0  207   202   1
 1    0   -46  --
 2    0    58  --
 3  119   -25   8
 4  221  -165  14
 5   57   111  -2
 6  151  -110   8
 7  128    19  14
 8  105   151 -10
 9    0     3  --
10  121   148  -8
11   88   -58   6

    H  11   4

 1  191  -150   9
 2  628  -614   6
 3   51     4   1
 4  138    71  11
 5  301   314  -5
 6  740   735   3
 7   79   -71   1
 8   52   -22  10
 9  186  -193  -2

    H  12   4

 0   66    10   5
 1   12    44  -1
 2   74    42   3
 3    0    -4  --
 4    0   -26  --
 5  218   181  19
 6  156   167  -5

    H   1   5

 1  228   222   3
 2  956  1010 -40
 3  317  -300   5
 4  151   160  -2
 5  136  -158  -7
 6 1033 -1087 -35
 7  456  -475 -11
 8    0    64  --
 9  477   460   8
10  850   896 -24
11    0   167  --
12   77    22   3
13  112  -219 -20
14  352  -331   7
15  191  -181   2
16  208  -189   4
17  134   100   6

    H   2   5

 0  351   339   7
 1 1579 -1527  31
 2 1035  1019  11
 3  665  -706 -30
 4  516  -520  -2
 5  636   656 -42
 6  673  -686  -8
 7  645   669 -12
 8  377   414 -16
 9  618  -615   1
10  854   900  -3
11  553  -534   8
12  227  -227   0
13  561   554   3
14  680  -634  22
15  259   242   4
16   67   215 -28
17  256  -265  -3

    H   3   5

 1  629   665 -18
 2 1396 -1440 -27
 3  746  -772 -17
 4  475  -458 -13
 5    0   106  --
 6 1052  1094  -1
 7  635   612  13
 8    0    28  --
 9  300   338 -14
10 1030  -959  15
11  550  -608  -8
12    0   -31  --
13  187   -63  20
14  316   334  -6
15  309   271  13
16    0   -12  --
17    0   -10  --

    H   4   5

 0 1265  1262   1
 1  488   519 -19
 2  141   -27  20
 3  831   864 -20
 4 1662 -1646   8
 5  793  -808  -8
 6  109  -105   0
 7  261  -254 -12
 8  829   851 -11
 9  566   610 -11
10  256  -270  -4
11  163   168   0
12  379  -357   7
13  219  -156  14
14  166   -40  19
15  182  -151   5
16  151    82  16

    H   5   5

 1 1351 -1326  14
 2  584  -554  16
 3  757   826 -41
 4  121   -28  11
 5  745   748  -1
 6  349   337   5
 7  424  -422   0
 8  222   166  14
 9  273  -362 -28
10   76    46   2
11  197   201   0
12  140   -74   9
13  320   271  17
14   45    79  -3
15  174  -204 -11
16  368   391 -15

    H   6   5

 0  573  -575  -1
 1  104   128  -4
 2  225  -184   9
 3  422   458 -15
 4  954   965  -6
 5  147   -52  15
 6   40   103  -6
 7  562  -550   5
 8  475  -465   4
 9   98  -125  -3
10   82   -16   4
11  259   185  22
12  315   329  -4
13    0    26  --
14  108    77   5
15  332  -332   0

    H   7   5

 1  147  -162  -2
 2  758   793 -17
 3  165    76  17
 4  151  -191  -8
 5  169   227 -14
 6  504  -476  11
 7  240   275 -10
 8  130  -159  -5
 9  343  -289  17
10  350   326   8
11    0     7  --
12    0   119  --
13    0    43  --
14  138  -107   8

    H   8   5

 0  602  -562  18
 1   49   -56   0
 2  246  -205  10
 3  137   113   3
 4  751   762  -5
 5  341   289  17
 6  238   224   3
 7  277   256   6
 8  438  -415   9
 9  210  -133  18
10   13   -11   0
11  143  -142   0
12  262   237  10
13  264   224  10

    H   9   5

 1  346   317   9
 2  334   389 -18
 3  380  -317  20
 4  180   156   5
 5  478  -505 -13
 6  231  -244  -3
 7  405   399   2
 8  377  -375   0
 9  336   305  13
10  109    66   7
11  207  -183   8
12  288   290  -1

    H  10   5

 0  251   253  12
 1   53    27   1
 2    0   -63  --
 3   87    33   4
 4  616  -601   7
 5  192  -115  17
 6  113   -57   8
 7    0     1  --
 8  509   480  16
 9    0   -33  --
10  120    72  12

    H  11   5

 1  100   -55   5
 2   62   115  -6
 3  238   190  14
 4  269   281  -4
 5   70    77   0
 6  226  -229  -1
 7  207  -156  23
 8    0    -1  --

    H  12   5

 0  240   248  -3
 1  101  -117  -3
 2   64    47   2
 3  204  -159  16
 4  101  -137 -11
 5   76   138 -14

    H   0   6

 0 1110  1131 -14
 1  545  -580 -24
 2  194  -141  18
 3  366  -330  19
 4   75    41   3
 5  355  -372  -9
 6  468   447  11
 7  239  -222   5
 8  479  -439  19
 9  129  -107   3
10  731  -699  15
11  143   177  -6
12   36    94  -4
13  256   299 -13
14  436   414   8
15  221  -168  13
16  150  -210 -15
17  549  -576 -17

    H   1   6

 1  419   457 -24
 2  802   850 -33
 3  917  -960 -29
 4  261   256   2
 5  479  -485  -3
 6  873  -895 -13
 7  514   547 -19
 8  223  -210   3
 9  550   572 -11
10 1024   955  14
11  446  -484 -15
12  410   396   5
13  405  -427  -9
14  537  -530   3
15  138   192 -10
16  148   -55  16
17  330   372 -22

    H   2   6

 0  960 -1004 -30
 1  275   305 -15
 2    0   -44  --
 3  185  -130  15
 4  468   500 -18
 5  343  -372 -15
 6  379  -361   9
 7  156  -125   8
 8  444  -463 -18
 9  514   544 -14
10  285   243  13
11  489   515 -11
12  530   518   4
13  203  -240  -8
14  139   120   3
15  181  -173   1
16  132  -141  -2
17  133   111   6

    H   3   6

 1  103   -25  10
 2 1102  1096   3
 3  306  -291   6
 4  379  -343  16
 5   95     6   8
 6  829  -824   2
 7  515   546 -16
 8  274   270   1
 9  341   328   4
10  438   404  13
11  465  -459   2
12    0    14  --
13  117   -64   4
14  183   -86  19
15   45   -64  -3
16  228  -248  -7

    H   4   6

 0  745   763 -11
 1    0    -5  --
 2  595   574   8
 3 1005 -1034 -16
 4  344  -329   6
 5  150    53  13
 6  264  -313 -19
 7  440   434   2
 8  537   535   0
 9  132   140  -1
10  488   456  12
11  327  -310   5
12  462  -455   2
13  297  -271   9
14  443  -469 -12
15  180   219 -12
16    0    32  --

    H   5   6

 1 1141 -1114  15
 2 1632 -1641  -4
 3  890   877   6
 4  187   154  -1
 5  800   841 -21
 6  847   851  -2
 7  457  -440   7
 8  315  -272  14
 9  230  -251  -5
10  609  -601   3
11  264   237   7
12   67    56   0
13  117   158  -7
14  267   226  15
15  212  -192   8

    H   6   6

 0  786   799  -7
 1  731  -727   2
 2  408  -426  -7
 3  899  -892   3
 4 1259 -1293 -17
 5  620   645 -12
 6  119    66   6
 7  695   661  15
 8  677   669   3
 9  283  -268   4
10  109    31   6
11  442  -429   5
12  298  -299   0
13   38    63  -2
14  102  -124  -5
15  209   235 -15

    H   7   6

 1  168   102  11
 2  203   115  16
 3  563  -532  13
 4  203  -151  10
 5  334   344  -3
 6  148   224 -17
 7  175   260 -21
 8  533   513   9
 9  235  -184  12
10  107   -55   1
11  237  -242  -1
12  263  -266  -1
13   60    53   4
14   56   116 -15

    H   8   6

 0  501  -523  -9
 1  148   184  -7
 2  248   215   8
 3  356   318  12
 4  772   766   2
 5  387  -414 -10
 6   76    49   2
 7  127   -43   9
 8  322  -265  13
 9  223   224   0
10  131   -16  10
11  135   183 -13
12  311   269  22
13  205  -207  -1

    H   9   6

 1   78     3   3
 2  100    91   0
 3    0    30  --
 4   85    55   3
 5   38    -7   1
 6   86   -66   2
 7  122  -151  -6
 8  193  -205  -3
 9  216   259 -15
10    0  -123  --
11   11    -5   0

    H  10   6

 0  340  -313  10
 1   90    -9   6
 2    0   -67  --
 3  230   257  -7
 4  240   236   1
 5  241  -241   0
 6  106   -81   4
 7  124   -63  12
 8  299  -318  -9
 9  213   227  -6

    H  11   6

 1   65    94  -4
 2  326   297  13
 3   48     0   2
 4  165   179  -4
 5   51  -127 -15
 6   72   -89  -3
 7   43   -81  -8

    H  12   6

 0  523   553 -21
 1  386  -389  -2
 2  118    49  18

    H   1   7

 1  644  -657  -8
 2  561  -534  15
 3  693   687   3
 4  346  -384 -17
 5  564   585 -12
 6    0   -70  --
 7  207  -235  -9
 8  237   215   6
 9  739  -730   4
10   86   141  -7
11  318   333  -4
12  289  -289   0
13  286   302  -5
14  127   172  -9
15  117   -22  11
16    0    40  --

    H   2   7

 0 2183 -2190  -3
 1  477   468   4
 2  141  -133   1
 3    0    33  --
 4 1091  1125 -19
 5  267  -262   1
 6  323   370  -3
 7  181  -107  16
 8 1107 -1127 -10
 9  288  -252  11
10  162  -132   5
11  164   191  -6
12  797   771  12
13  194   158   8
14    0   -58  --
15  256  -279  -8
16  522  -514   4

    H   3   7

 1  665   686 -12
 2  160  -215 -16
 3  466  -455 -14
 4  147   213 -16
 5  844  -855  -6
 6  311   350 -16
 7  604   600   1
 8  370  -328  16
 9  370   314  21
10  230  -204   7
11  460  -471  -4
12  628   653 -12
13  203  -256 -15
14  237   261  -9
15  256   232  10
16  270  -261   5

    H   4   7

 0  342   326  16
 1  374   355   8
 2  108   128  -3
 3  372   402 -11
 4  365  -404 -16
 5  207  -188   5
 6  364   356  11
 7  492  -446  19
 8  798   798   0
 9  601   600   0
10  101  -109  -1
11  550   566  -7
12  417  -357  24
13  297  -325 -10
14    0    82  --
15  121   -77  10

    H   5   7

 1  181   131  11
 2 1584  1595  -7
 3    0    13  --
 4   23   137 -11
 5  196  -204  -2
 6 1071 -1082  -5
 7  150  -159  -1
 8  278  -305  -9
 9  273   267   1
10  488   457  -3
11   64   160 -12
12  129   165  -7
13  167  -203 -11
14  423  -404  10
15   97    24  13

    H   6   7

 0  433   426   2
 1  256  -235   5
 2  258  -279  -5
 3  623  -658 -15
 4  323  -352  -9
 5  201   161   9
 6  277  -287  -2
 7  226   245  -5
 8  401   416  -6
 9  272  -243   8
10  254   253   0
11  332  -236  25
12  278  -303 -10
13    0   -49  --
14  300  -285   9

    H   7   7

 1  188  -151   7
 2  194   215  -4
 3  244   217   6
 4  286   273   4
 5  417   420  -1
 6    0     5  --
 7  266  -202  20
 8  285  -344 -19
 9  294  -312  -6
10  108    24   8
11  117   121   0
12   51    66  -1
13  237   189  26

    H   8   7

 0    0    90  --
 1  208  -146  12
 2  176  -123   8
 3  363  -359   1
 4  171   165   1
 5  246   239   2
 6   98   -52   5
 7  377   374   1
 8  175  -135   9
 9   80  -108  -3
10  154   140   3
11  147  -118   8
12   77    20   9

    H   9   7

 1  185  -243 -14
 2  573  -551   9
 3  124   -66   7
 4    0    60  --
 5    0   159  --
 6  688   661  14
 7   28    64  -2
 8   64    30   3
 9   86  -115  -6
10  564  -537  19

    H  10   7

 0    0    -1  --
 1  224   201   6
 2  151    34  15
 3  348   309  14
 4   39     4   1
 5  222  -223   0
 6  231   221   4
 7  487  -468  12
 8    0    23  --

    H  11   7

 1  177  -130  14
 2  209   208   0
 3  167   149   6
 4    0    52  --
 5  276   320 -29

    H   0   8

 0 1873  1838  17
 1 1846 -1900 -27
 2  652   636   8
 3  897  -983 -38
 4  979 -1019 -22
 5  801   803  -1
 6  110   116   0
 7  911   954 -22
 8  583   589  -3
 9  632  -593  19
10   69   137  -8
11  661  -668  -3
12  639  -595  20
13  502   451  24
14  251  -273  -7
15  362   359   1
16  313   317  -2

    H   1   8

 1  251   269  -6
 2    0     3  --
 3  209  -230  -6
 4  146  -233 -19
 5  129  -102   5
 6   26    83  -4
 7  576   599  -6
 8  143   -17  14
 9    0    15  --
10  177  -115  11
11  401  -422  -7
12  228  -249  -5
13  203   207  -1
14  134   -57   7
15  254   212  16

    H   2   8

 0  626  -632  -3
 1   57   -48   0
 2  207  -188   5
 3  269   216  16
 4  236  -213   6
 5  310  -333  -9
 6  320  -331  -4
 7  150    10  16
 8  198  -239 -10
 9  357   336   7
10  100    67   3
11  112   -51   6
12  322   301   7
13    0   -42  --
14   58    -3   3
15  145  -114   8

    H   3   8

 1  576  -606 -16
 2  372  -415 -19
 3  427   420   2
 4   69   -54   1
 5  358   356   0
 6  649   659  -5
 7    0   -67  --
 8  103   105   0
 9  455  -441   5
10  344  -372 -10
11   15   132 -10
12  164  -194  -2
13  339   365  13
14  306   273  15
15  187  -160   3

    H   4   8

 0  444  -452 -21
 1 1015   979  18
 2  323   317   2
 3  608   598   4
 4  866   866   0
 5  693  -671  11
 6    0    58  --
 7  696  -650  21
 8  613  -617  -1
 9  442   453  -4
10  307  -264   7
11  366   351  14
12  317   288  11
13  292  -285   3
14  193   210  -6

    H   5   8

 1  251  -264  -3
 2   95  -166 -10
 3  240   225   3
 4    0    28  --
 5    0   -62  --
 6  124   146  -4
 7   68   -60   0
 8  120  -150  -5
 9  160  -140   3
10    0    69  --
11  318   344  -9
12  121    57   4
13  139   -50  12
14  157   129  10

    H   6   8

 0  373   346   9
 1  311  -278  10
 2  143  -144   0
 3  339  -367   5
 4  121  -148  -4
 5  463   439  11
 6  177   167   2
 7  218   187   7
 8   97   -46   4
 9  487  -486   0
10   79   -53  -1
11  131   141  -2
12    0    13  --
13  329   319   6

    H   7   8

 1  613   617  -1
 2  627   605   9
 3  380  -340  13
 4  212  -248  -8
 5  745  -715  14
 6  612  -580  15
 7  512   490   9
 8    0     1  --
 9  627   615   6
10  501   523 -12
11  297  -248  25
12    0    75  --

    H   8   8

 0   79   120  -5
 1  125    18   9
 2    0    77  --
 3   67     7   2
 4  150  -142   1
 5  145  -171  -5
 6  181  -241 -16
 7  150    74  15
 8  146   148   0
 9    0    63  --
10  117    84   7
11  121  -126  -1

    H   9   8

 1   67    19   3
 2  388  -403  -6
 3  279  -244  11
 4  179  -140   9
 5  166   158  -9
 6  103    56   7
 7   58    12   3
 8    0    82  --
 9  241  -233   4

    H  10   8

 0  162   179  -5
 1   74    -4   5
 2   88   -82   0
 3    0   -54  --
 4  100  -127  -6
 5    0     2  --
 6   46    73  -4
 7   83   112  -8

    H  11   8

 1  419  -426  -5
 2  409  -403   4
 3  419   460 -34

    H   1   9

 1  265   236   9
 2  989   978   5
 3  220  -262 -11
 4  303   303   0
 5  339  -344  -1
 6  755  -770  12
 7  102   -15   6
 8   67    56   0
 9  414   383  11
10  431   423   3
11   91   -61   3
12    0    12  --
13  207  -202   1
14  284  -273   5
15   37   -56  -2

    H   2   9

 0  346  -388 -16
 1  726  -716   5
 2  503   482   9
 3  707  -756 -24
 4   66    44   1
 5  625   646 -10
 6   58  -105  -5
 7  563   580  -7
 8  176  -201  -5
 9  348  -347   0
10   56   126  -4
11  472  -445  12
12  278   300  -8
13    0    57  --
14  145  -267 -20

    H   3   9

 1   92   138  -6
 2 1389 -1404  -7
 3  139   108   4
 4    0   166  --
 5  157   187  -6
 6  824   825   0
 7  178     4  25
 8    0   -15  --
 9  170   -56  11
10  833  -804  15
11  131   -53  10
12  115   -48   8
13  136   138   0
14  301   268  19

    H   4   9

 0  507   452   6
 1   61   121  -4
 2    0    65  --
 3   75    63   1
 4  750  -761  13
 5  165  -140   5
 6    0   -18  --
 7    0    56  --
 8  375   364   4
 9  166   128   7
10  169  -212 -10
11    0   -35  --
12  348  -323  11
13   43   -29   1
14  104   100   1

    H   5   9

 1  341  -362  -7
 2  139  -126   1
 3  106   124  -2
 4  433  -439  -2
 5  333   350  -6
 6  226   252  -6
 7  381  -375   2
 8  526   554 -11
 9  535  -506  13
10    0    -7  --
11  208   173  10
12  228  -202  10
13  423   429  -4

    H   6   9

 0  441  -439   0
 1  273   245   7
 2   87   -22   4
 3  433   423   3
 4  530   520   4
 5  434  -460 -11
 6   27   104  -7
 7  419  -425  -2
 8  335  -353  -7
 9  199   185   4
10  263  -268  -2
11  298   248  24
12  350   386 -24

    H   7   9

 1  148   132   2
 2  190    17  21
 3   81   192 -16
 4  292  -296  -1
 5  104  -116   0
 6    0   -42  --
 7  228  -150  12
 8   83   111  -4
 9  173   136  10
10  292   261  15
11  135    92  14

    H   8   9

 0  516  -551 -16
 1   19  -123  -9
 2    0    70  --
 3   87    60   2
 4  614   611   1
 5   86    72   1
 6    0   -66  --
 7  161   -45  23
 8  410  -421  -6
 9    0     8  --
10   34    87 -11

    H   9   9

 1  374   359   7
 2  393  -394   0
 3  356  -342   6
 4   88    21   7
 5  440  -421  11
 6  316   262  30
 7  314   313   0
 8  176  -170   3

    H  10   9

 0  633   612  14
 1   93   -79   2
 2  138   -75  15
 3  150  -170  -7
 4  664  -695 -26
 5   72  -137 -22

    H   0  10

 0  364  -406 -16
 1  231  -223   2
 2  206   284 -20
 3  279   267   3
 4  451   488 -14
 5  460   412  20
 6  131  -132   3
 7   60  -217 -24
 8   83  -233 -25
 9  747  -761  -6
10  161  -167  -1
11  110   -15   8
12    0   -55  --
13  265   253  14
14  175   185  -5

    H   1  10

 1  893   934 -20
 2  632   664 -15
 3  913  -912   0
 4    0   -38  --
 5  967  -991 -12
 6  566  -552   6
 7  576   573   1
 8  201   215  -3
 9  538   563 -11
10  385   358  -4
11  531  -506  13
12    0     8  --
13  269  -235  13
14   69   -60  -2

    H   2  10

 0    0   -14  --
 1  580   562   0
 2  203  -271 -16
 3  711   668  15
 4  145   -16  11
 5  155  -201 -10
 6    0    24  --
 7  152  -165  -2
 8  180  -159   4
 9  303   276   8
10    0    35  --
11  122     8  13
12  186   210  -8
13  136  -121   4

    H   3  10

 1  651   701 -23
 2   97    25   4
 3  148  -145   0
 4  171   146   4
 5  765  -753   5
 6  276  -204  22
 7   79  -121  -5
 8  250  -218  10
 9  598   575   4
10  106   157 -10
11   36    15   1
12  303   301   0
13  284  -268   9

    H   4  10

 0  601   645 -20
 1  131   -80   6
 2   62    74   0
 3  274  -241   5
 4  244   -63  32
 5  272   301  -9
 6   23   -75  -3
 7   90   -45   4
 8  240   158  12
 9  114  -144  -5
10  151   138   3
11  115  -131  -8
12  197  -168  11

    H   5  10

 1  101  -125  -3
 2  259  -182  18
 3  321   324   0
 4  137  -161  -4
 5  336   292  15
 6  110    59   6
 7  484  -442  10
 8  143   172  -6
 9  433  -402  15
10  256  -246   4
11  505   483  14
12    0   -55  --

    H   6  10

 0    0    92  --
 1  200  -146  11
 2  154  -157   0
 3  377  -348   9
 4  405  -357   3
 5  318   343 -10
 6  179  -189  -2
 7  334   319   6
 8  267   258  12
 9  517  -493  14
10   32    78  -1
11  201  -165   7

    H   7  10

 1    0    20  --
 2  221  -223   0
 3  130   -73   8
 4  136    89   8
 5  107   -82   4
 6  119   155  -8
 7    0    69  --
 8  217   204   5
 9   65   -73  -1
10   78   -57  -5

    H   8  10

 0  276  -195  29
 1  453   420  16
 2   34   153 -16
 3  725   702  18
 4  307   305   0
 5  412  -420  -4
 6   83   148 -15
 7  631  -643  -8
 8  247  -248   0

    H   9  10

 1   58   -13  10
 2  165     6  11
 3   58     7  10
 4   74    44   5
 5  119   130  -3
 6  127  -144  -8

    H   1  11

 1  368  -312  -1
 2  340   325   4
 3  326   367 -12
 4    0   -16  --
 5  330   292  13
 6    0   -64  --
 7  127  -144  -3
 8  123  -110   2
 9  354  -358   0
10   62   121  -8
11   39    62  -2
12  155  -206 -19

    H   2  11

 0 1277 -1271   2
 1  446   443   1
 2   26    41   0
 3  254   307  -3
 4  853   856  -1
 5  252  -258  -1
 6  133   -61  10
 7  633  -622   5
 8  826  -809   9
 9  165    56   1
10    0   -46  --
11  396   373  13
12  446   434   8

    H   3  11

 1  150   191  -7
 2  259  -282  -5
 3  258  -254   1
 4  116   112   0
 5  232  -257  -7
 6  466   445   5
 7  190   123  13
 8  159  -124  16
 9  227   228   0
10  350  -313  17
11    0   -65  --
12  161   157   1

    H   4  11

 0  560   563  -1
 1  287   261   7
 2    0     3  --
 3    0   105  --
 4  217  -206   2
 5    0   -45  --
 6  265   228  12
 7  107   -23   5
 8  261   254   2
 9    0    43  --
10  217  -230  -5
11  271   270   0

    H   5  11

 1  215   202   3
 2  335   325   3
 3  224  -308   3
 4    0   116  --
 5  233  -210  20
 6  379  -370   3
 7  341   342   0
 8  152  -150   0
 9  319   308   5
10  351   341   6

    H   6  11

 0  272   257  -6
 1  352  -337   5
 2  152  -161   2
 3  302  -264   6
 4  163   -83  15
 5  113    59   2
 6  112  -122  -2
 7  306   275  14
 8   54    -1  10
 9  180  -183  -1

    H   7  11

 1  157  -195 -10
 2  181   167   2
 3  143   127   3
 4  265  -278   4
 5  281   288  -3
 6    0   -71  --
 7    0   -26  --
 8  308   305   2

    H   8  11

 0  156  -156  13
 1  251  -252   0
 2   84    46   5
 3  121   -58   5
 4  348   318  17
 5  255   266  18
 6  172  -221 -29

    H   9  11

 1  282  -296 -10
 2  735  -766 -18

    H   0  12

 0  244   260  -3
 1 1203 -1211  -3
 2  328   366 -12
 3 1070 -1095 -12
 4  265  -241   6
 5  769   765   2
 6  385   370   8
 7  665   663   3
 8  237   254  -5
 9  555  -539   9
10  118  -154  -5
11  601  -561  15

    H   1  12

 1  153   222 -13
 2  263  -233  17
 3  304  -301   0
 4   67   -74   0
 5  130   154  -4
 6  173   169   1
 7  369   370   0
 8    0    18  --
 9   55   -86   1
10  144  -151  -2
11  229  -218   5

    H   2  12

 0  468  -513 -11
 1  173   216  -9
 2  127   -83   5
 3    0    26  --
 4  157  -129   4
 5  276  -306 -10
 6   47   -82  -3
 7  185   120  18
 8  128    67  11
 9  340   356  -8
10    0    29  --
11   45   -64  -3

    H   3  12

 1  456  -438   7
 2   72   -97  -2
 3  355   315  13
 4  152  -176  -4
 5  109   286   8
 6  204   222  -5
 7  262  -178   7
 8  122    59  11
 9  109  -164 -15
10   60   -57   0

    H   4  12

 0    0     3  --
 1  447   387  25
 2  145   -53  11
 3  386   352  12
 4  300   286   5
 5  280  -239  15
 6  148   176  -7
 7  525  -536  -6
 8    0  -100  --
 9  181   161   0
10   36  -119 -16

    H   5  12

 1   57  -137 -10
 2  145   142   0
 3  190   146  10
 4   34   -43   0
 5   26   -22   0
 6  119    84   7
 7  244  -224   9
 8  155  -135   8
 9   84    35  11

    H   6  12

 0  177  -154   6
 1  103  -108   0
 2  128   -87   7
 3  171   -89  18
 4   79   127  -9
 5  270   241  13
 6   70   -39   4
 7  186   156  -4

    H   7  12

 1  763   747  10
 2  192   206  -5
 3  606  -571  22
 4  113   140  -8
 5  517  -505   9

    H   8  12

 0  267   239 -18
 1   85  -118 -11

    H   1  13

 1  204   235  -8
 2  366   311  22
 3  266  -277  -3
 4  102    50   5
 5  431  -411  10
 6  477  -460   9
 7  231   225   2
 8   24    32   0
 9  346   330  10

    H   2  13

 0  278  -318 -13
 1  137   -44  11
 2   29    71  -2
 3  405  -407   0
 4  238   215   6
 5  222   260 -14
 6   71    38   4
 7  401   367   8
 8  249  -200  25
 9  167  -144  11

    H   3  13

 1  222  -149  20
 2  460  -437  10
 3  283   284  -7
 4    0    -8  --
 5  259   258   0
 6  388   333  32
 7   29   -44  -1
 8   72   -76   0

    H   4  13

 0  282   228  21
 1  168   -73  29
 2    0    30  --
 3   49  -112  -8
 4  445  -482 -21
 5  279   281   0
 6   86    37   8
 7   81    85  -1

    H   5  13

 1  304  -319  -7
 2  214   230  -5
 3  138   118   4
 4  143   136   1
 5  234   165  25
 6  155  -149   2

    H   6  13

 0  212  -197   7
 1  232   220   6
 2   83   -29   7
 3  339   320  11
 4  136   121   5

    H   0  14

 0  182  -171   3
 1   40  -100  -6
 2   91    19   6
 3   57   129 -11
 4  163   169  -1
 5   97   -46   9
 6  181   209 -13
 7  303  -304   0

    H   1  14

 1  449   416  17
 2   93   -54   5
 3  500  -455   0
 4   58    99  -6
 5  470  -454  10
 6  163   164   0
 7  349   341  30

    H   2  14

 0  121  -141  -5
 1  207   150  19
 2  124  -106   4
 3  238   220   7
 4   90   -64   4
 5  129  -152  -8
 6   36   -22   1

    H   3  14

 1  183   175   1
 2  174   242 -27
 3  188  -179   3
 4  135   103   9
 5  161  -160   0

    H   4  14

 0  346   339   4
 1  123   -90   5
 2   21   -30   0
 3  283  -281   1
 4    0    26  --

    H   5  14

 1  451  -446   2

    H   1  15

 1  223  -253 -16
 2   71    41   2
```

TABLE III-10

Positional and Thermal Parameters for Heavy Atoms[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	12970 (7)	66957 (10)	2137 (8)	211 (5)	489 (9)	280 (6)	−16 (12)	21 (10)	53 (14)
Co(2)	11692 (6)	38569 (9)	26567 (8)	184 (4)	444 (9)	274 (6)	2 (12)	0 (9)	−53 (14)
N(1)	10051 (34)	57081 (51)	12591 (39)	257 (27)	544 (56)	287 (37)	−94 (63)	−94 (50)	52 (73)
C(1)	9738 (40)	50553 (66)	18213 (48)	202 (30)	623 (72)	234 (41)	−97 (71)	−41 (56)	91 (91)
C(2)	16196 (43)	76372 (62)	−7724 (54)	217 (31)	418 (65)	376 (47)	29 (74)	58 (60)	−193 (92)
N(2)	18295 (38)	81867 (58)	−13762 (47)	333 (30)	609 (66)	566 (49)	42 (73)	175 (63)	458 (96)
C(3)	11116 (41)	55812 (60)	−7208 (49)	195 (30)	491 (61)	302 (42)	21 (75)	−48 (62)	263 (88)
N(3)	10117 (38)	49570 (57)	−12966 (45)	363 (33)	621 (66)	519 (46)	14 (74)	−142 (63)	−305 (93)
C(4)	14878 (44)	78527 (70)	10999 (53)	203 (31)	646 (74)	371 (49)	27 (81)	54 (61)	101 (102)
N(4)	16129 (39)	85417 (58)	16255 (51)	345 (32)	825 (78)	621 (53)	−25 (77)	−161 (65)	−579 (102)
C(5)	23346 (40)	61882 (65)	3292 (50)	202 (31)	561 (66)	324 (42)	−71 (72)	20 (56)	0 (98)
N(5)	29476 (35)	58933 (54)	3644 (46)	237 (27)	706 (67)	535 (47)	84 (69)	−22 (58)	74 (91)
C(6)	2758 (45)	72269 (62)	527 (49)	286 (32)	547 (68)	242 (46)	99 (75)	11 (59)	−2 (85)
N(6)	−3190 (37)	75481 (59)	−603 (47)	275 (28)	932 (71)	487 (49)	424 (79)	−13 (60)	−33 (93)
N(7)	14546 (35)	25910 (49)	34676 (43)	265 (27)	491 (55)	446 (41)	31 (63)	−150 (54)	60 (78)
N(8)	7394 (33)	46378 (48)	37773 (39)	211 (25)	436 (53)	367 (39)	−178 (59)	44 (48)	821 (73)
N(9)	15977 (33)	31032 (53)	15246 (44)	239 (27)	804 (71)	443 (43)	−153 (68)	−261 (54)	−425 (90)
N(10)	1580 (33)	31791 (45)	23989 (41)	223 (25)	491 (52)	369 (37)	28 (56)	40 (48)	−21 (79)
N(11)	21765 (32)	45182 (48)	29426 (40)	221 (24)	512 (55)	362 (39)	139 (39)	17 (48)	−113 (75)
O(1)	7322 (30)	8057 (42)	18097 (36)	336 (25)	668 (53)	489 (36)	95 (58)	39 (47)	180 (68)

Positional Parameters Assigned to Hydrogen Atoms[b]

	x	y	z		x	y	z
H(1)	1946	2311	3227	H(10)	−103	3650	1927
H(2)	1494	2862	4135	H(11)	−103	3108	3026
H(3)	1062	2032	3377	H(12)	260	2447	2124
H(4)	1147	4891	4136	H(13)	2531	4288	2441
H(5)	410	4103	4110	H(14)	2328	4283	3573
H(6)	439	5256	3512	H(15)	2118	5322	2887
H(7)	1327	2407	1467	H(16)	1171	509	1465
H(8)	2147	2982	1669	H(17)	767	582	2492
H(9)	1522	3565	998				

[a] Temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. All values have been multiplied by 10^5. [b] All values have been multiplied by 10^4.

electron density of somewhat greater than 1 e Å^{-3}. Therefore the identities of the two atoms were interchanged to the isocyano configuration, and refinement was continued. Hydrogen positions were occasionally adjusted by means of difference maps, but were not refined by least squares. A secondary extinction factor was judged to be appropriate, and was placed into the list of refinable parameters. Convergence was reached after a few further cycles, with no parameter shifting by more than 30% of its estimated standard deviation. The final matrix contained 182 parameters, corresponding to a data-to-parameter ratio of 10.0. The final R value is 0.085, and the final goodness of fit is 1.76. The value of the secondary extinction parameter is 0.34(4) x 10^{-5}. A three-dimensional difference Fourier calculated at the conclusion of the refinement indicated no discrepancies greater than 0.4 eÅ^{-3}.

F. $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$

A three-dimensional Patterson map was calculated, from which two cobalt atoms were located in general positions. Successive structure factor-Fourier work led to the positions of all ligand atoms and the oxygen atom of the water molecule. A structure factor calculation based upon this unrefined model yielded an R index of 0.38. Refinement by full-matrix least squares was initiated, allowing the thermal parameters to refine anisotropically after a few cycles. Ammine hydrogen atoms were located by difference syntheses in the expected planes, and were assigned isotropic temperature factors with B=5.0. Their positions were periodically adjusted during the refinement on the basis of difference maps. Near the end of the refinement, a number of reflections distributed widely in intensity but closely in reciprocal space were noted to systematically calculate considerably larger than their observed F values. Examination of the raw data indicated that these reflections were all collected close together in real time. Standard reflections for this phase of the data collection procedure appeared mostly normal; however, several strings of "bad" reflections were noted occurring between measurements of standards, consecutively in the order of data collection. We believe that this problem is due to fluctuations of some portion of the apparatus on a time scale which was short with respect to the remeasurement of the standards, which occurred about every six hours. A consecutive string of data consisting of 249 reflections was given zero weight in further refinement, indiscriminately with regard to individual agreements with calculated F values.

Convergence was fairly rapid. Refinement was discontinued when all shifts were smaller than ½ of their standard deviations. Final values of R and goodness of fit are 0.050 and

2.33, respectively. In the expression for GOF, m is 2453 observations and s is 190 parameters. A three-dimensional difference Fourier synthesis calculated at the conclusion of the refinement indicated no discrepancies greater than ±0.8 $e\text{Å}^{-3}$. One of the most outstanding features of this map is a toroid of electron density of about 0.3-0.7 $e\text{Å}^{-3}$ around the position of the water molecule, for which discrete hydrogen positions were never assigned.

Table III-11

Observed and calculated structure factors for $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$. Columns give h, $10F_{obs}$, $10F_{calc}$. An asterisk (*) indicates zero weight in the refinement.

$(CN)_5CoSCNCo(NH_3)_5\cdot H_2O$

```
H  0  0

0      016539*
2  327  371
4 2345 2504
6  214  272
8  344  346
10 1593 1664
12  628  625
14  711  688
16  710  659

H  1  0

2  626  620
4 1047 1067
6  717  784
8  966 1024
10  302  320
12  733  738
14  304  311
16  756  719

H  2  0

0  450  552
2 4135 4068
4 1357 1245
6  917  925
8 1635 1657
10  190  219
12  388  390
14  277  251
16  248  232

H  3  0

2   54   26
4   86   59
6  183  198
8 1819 1862
10  459  461
12  556  560
14  519  507
16  500  492

H  4  0

0 2282 2056
2  943  872
4  289  310
6 1493 1443
8  203  214
10  908  953
12   30   10
14  369  355
16   82   10

H  5  0

2 1677 1620
4  664  647
6 2091 2072
8 1097 1118
10 1789 1787
12  330  314
14  509  512
16  790  730

H  6  0

0 1234 1140
2 2837 2741
4  247  260
6 1031 1011
8 1201 1183
10   86   28
12  655  648
14  376  368

H  7  0

2  -52    1
4 1472 1461
6   65   73
8 1372 1378
10  396  373
12  327  306
14  788  770

H  8  0

0 1909 1750
2 2355 2269
4 1359 1353
6  632  604
8  813  810
10  151  168
12  353  353
14   73   33

H  9  0

2  522  539
4   57    9
6 1286 1265
8  400  394
10  783  776
12  410  410
14  346  332

H  10  0

0 1666 1651
2  100  110
4 1527 1538
6  982  995
8  502  500
10  659  657
12  316  313

H  11  0

2  412  419
4 1415 1430
6  565  586
8 1230 1226
10  245  267
12  985  963

H  12  0

0  249  283
2  930  952
4  506  525
6  382  359
8  751  763
10  -97   21
12  588  575

H  13  0

2  449  465
4  280  265
6  447  476
8  404  406
10  513  510

H  14  0

0  571  985
2   40   45
4 1036 1093
6  534  573
8  104  107

H  15  0

2  115  140
4  123   87
6  724  755
8  115  146

H  16  0

0  191  208
2 1308 1371
4  150  166
6  649  661

H  17  0

2   61   26

H  1  1

1  224  292
2 1147 1185
3  289  220
4 1610 1652
5  630  646
6 1110 1190
7  138  143
8  532  603
9  524  535
10  509  522
11   79   56
12   92   68
13   62   46
14  249  237
15  -29   24
16  444  386

H  2  1

0 1873 1852
1  135  199
2 1588 1543
3  159  174
4 2142 2130
5  205  184
6  401  427
7  558  598
8   43    7
9   68   10
10  554  568
11  118   87
12  531  538
13   55   73
14  555  536
15   51   16
16  406  393

H  3  1

1   67   16
2  327  358
3  419  365
4 2133 2071
5  538  521
6 1742 1801
7   91   56
8 1410 1392
9  268  264
10  779  804
11  279  284
12  523  532
13  345  352
14   99   74
15  125  113
16  337  311

H  4  1

0  351  300
1   40   15
2  295  231
3  763  727
4 1044 1000
5  260  258
6  410  380
7  281  262
8  209  204
9  209  210
10  317  313
11  -20   13
12  400  381
13   76   50
14  216  221
15  158  167
16  106   87

H  5  1

1 1768 1627
2   31    4
3 1462 1337
4  816  795
5  690  634
6  697  681
7  270  292
8  124  109
9  -39   56
10  266  265
11  113  104
12   90   80
13   15   31
14  427  445
15   71  106
16  219  175

H  6  1

0  185  100
1  449  425
2 1626 1525
3  131  143
4  122  149
5  478  456
6  337  326
7  293  245
8  294  301
9  441  445
10  680  691
11  223  196
12  840  810
13  151  174
14  568  576
15  231  270

H  7  1

1  518  482
2  519  496
3  494  470
4  567  549
5  114   64
6  478  464
7  -52   61
8  137  151
9  104  108
10  190  180
11   61    4
12  324  339
13  -34    2
14  -19   48
15  242  235

H  8  1

0 1491 1454
1  201  188
2 1082 1087
3  785  785
4 1426 1383
5  258  247
6  299  301
7  230  213
8  292  315
9   98   41
10  627  630
11  170  156
12 1026 1027
13  -38   17
14  766  768

H  9  1

1   72   43
2  140  136
3  412  412
4  148  161
5  271  273
6  117  104
7  314  322
8  221  200
9  248  269
10  314  327
11  164  148
12  -35    7
13  108  101
14   69   89

H  10  1

0  468  491
1  156  142
2  478  479
3  174  195
4  280  286
5  299  327
6   85  106
7   74   30
8   19   24
9   27   47
10  355  323
11  133  142
12  417  423
13   86   67

H  11  1

1  -16   45
2  381  371
3  120   57
4  534  539
5  301  300
6  481  494
7  246  252
8  258  225
9  103   78
10  414  396
11  190  186
12  136  127

H  12  1

0  396  408
1  181  207
2   81   81
3  291  287
4  143  127
5  207  229
6   91   92
7   -4   96
8   29   67
9  219  244
10  204  182
11  169  199
12  107   70

H  13  1

1  320  323
2  499  532
3  202  214
4  745  751
5  136  163
6  943  978
7  158  167
8  858  887
9  156  185
10  510  510
11   49   35

H  14  1

0  292  288
1  235  238
2  408  419
3  120  131
4   72   60
5  435  473
6  363  382
7  104  130
8   96  127
9  288  303

H  15  1

1   64   39
2  170  191
3  -42   47
4  215  226
5  150  129
6  269  241
7  171  147
8  508  509

H  16  1

0  215  205
1  247  252
2  287  293
3  171  187
4   96   21
5  222  225
6   94   63

H  17  1

1 -100   36
2  194  205
3  175  193

H  0  2

0    8  530*
1  979 1166
2 4399 4534
3 1125 1198
4   61   41
5 1316 1309
6  447  495
11  486  448
12 1218 1261
13  404  417
14  646  608
15   23   35
16  739  768

H  1  2

1  585  574
2  106  127
3  143   61
4  558  575
5  853  810
6 1066 1129
11  652  673
12   94   35
13  -62   25
14  413  397
15  363  355
16  356  367

H  2  2

0 4314 4342
1 1669 1501
2  158  119
3  881  851
4  961  943
5  755  789
6  863  687
7  491  502
11  122   97
12  237  219
13   40    6
14  399  357
15  181  150
16  269  238

H  3  2

1 1064  985
2 1328 1254
3 1036  594
4  132  121
5  308  305
6 1607 1627
7  366  377
11  557  574
12  771  771
13  380  377
14  578  548
15  277  271
16  680  607

H  4  2

0 1001  893
1  987  963
2 2539 2432
3  119   63
4  192  235
5  936  909
6  553  554
7  931  931
11   79   13
12  540  549
13   59   60
14  -54   24
15  150   87
16  -61   96

H  5  2

1  862  812
2  994  936
3  730  730
4 2098 2072
5   71   73
6  553  548
7  179  202
11  -24   39
12  804  789
13  721  708
14  636  614
15  104   73
16  222  207

H  6  2

0 2283 2145
1 1196 1128
2  325  338
3  757  742
4 1958 1924
5  681  684
6 1110 1100
7  119  135
11   46   42
12  264  281
13   79  100
14  436  439
15   78  108

H  7  2

1  229  250
2  894  898
3  457  447
4  461  467
5   96   81
6 1437 1426
7  402  399
12  413  392
13   73   86
14   97   56
15  196  186

H  8  2

0 2130 2059
1  454  466
2 1041 1022
3  763  746
4  994  984
5  792  777
6  333  305
7  576  578
12   45   86
13  219  221
14  172  178

H  9  2

1  269  266
2   62   64
3  371  368
4 1229 1207
5  263  272
6  441  453
7   52    8
12  509  509
13  265  261
14  427  428

H  10  2

0  172  189
1  511  525
2 1488 1495
3  736  727
4  380  405
5  198  215
6  826  835
7  536  530
12  624  594
13  177  187

H  11  2

1  469  476
2  556  548
3   62   45
4  618  642
5  530  539
6 1163 1185
7  341  347
11  397  398
12  272  286

H  12  2

0  992 1016
1  232  212
2  261  292
3  348  373
4  952  976
5  221  219
6  761  780
7  352  334
10  555  547
11  203  223

H  13  2

1  145  161
2   97   63
3  142  138
4  381  388
5  376  419
6  288  290
7  402  405
9  358  357
10  478  486

H  14  2

0  151  129
1  368  374
2 1205 1246
3  412  409
4  299  313
5  153  136
6  592  609
7  292  274
8  530  534
9   65    3

H  15  2

1  -45   13
2   70   72
3  283  310
4  392  412
5  231  269
6  -43   25
7  166  186
8  365  378

H  16  2

0 1231 1284
1  278  306
2   62  108
3  162  200
4  892  934
5  492  523
6  289  277

H  17  2

1   29   32
2  173  182

H  1  3

1  658  614
2  631  588
3  342  340
4  449  397
5  399  368
6 1459 1538
7  456  458
8  823  877
9   97  136
10  425  438
11  142  165
12   50   36
13  -49   45
14   88   92
15  192  151
16  557  510

H  2  3

0 1371 1262
1  183  160
2  168  192
3   62   15
4  133  127
5 1250 1214
6   44   19
7  710  733
8  604  627
9  633  654
10  559  566
11  260  295
12  503  509
13  174  148
14  536  528
15  131  155
16  351  343

H  3  3

1 1590 1520
2  631  559
3  993  936
4 1414 1378
5  860  819
6  868  915
7  364  343
8 1464 1494
9  175  176
10  608  618
11  361  374
12  438  416
13  529  539
14  297  285
15  430  403
16  325  298

H  4  3

0  897  864
1  255  226
2 1161 1086
3  751  663
4   54    5
5   68   46
6  169  110
7  278  270
8  409  426
9  298  310
10  472  469
11  445  449
12  459  453
13  255  243
14  274  262
15  136  113
16   60   67

H  —5  3

1  432  391
2  325  264
3  172  165
4   48   62
5   66  108
6  320  320
7  204  176
8  735  756
9  273  273
10   74    5
11  124  144
12   80   77
13  184  158
14  -61   42
15   65   38

H  6  3

0 1325 1310
1  242  246
2 1049 1023
3  292  312
4 1414 1352
5   47   52
6   97   92
7  580  574
8  337  336
9  146  162
10  391  394
11  124  131
12  395  375
13  160  157
14  443  425
15  110  118

H  7  3

1  678  672
2  428  394
3  270  259
4  110  108
5  100   78
6   62   59
7  464  475
8  240  211
9  288  272
10  -40   53
11   69  114
12  107   88
13  145  136
14  -30   73
15  118  146

H  8  3

0 1305 1290
1  571  554
2 1667 1653
3  896  861
4  572  574
5  937  917
6  125  118
7  619  617
8  114  122
9  657  566
10  560  544
11  -82   70
12  893  871
13   41   16
14  608  590

H  9  3

1   78   63
2  428  409
3  272  265
4  696  661
5   10   10
6  341  320
7  587  598
8   73   17
9  235  249
10  150  135
11   42   30
12   98   99
13  103   27
14  360  345

H  10  3

0  851  839
1  123  102
2   69   70
3  228  248
4  464  449
5  549  568
6  154  140
7   90  113
8  271  286
9  245  269
10  454  456
11   45   20
12  305  287
13   97   93

H  11  3

1  240  226
2  113   71
3  171  162
4  359  358
5  197  205
6  967  963
7   59   71
8  284  273
9  338  338
10  511  495
11  144  143
12   -7   20

H  12  3

0  160  172
1  202  181
2  358  334
3  121  126
4  235  267
5   96   80
6  355  361
7  260  275
8   63    5
9  -91   17
10   76  135
11  148  154

H  13  3

1  427  433
2  274  261
3  452  446
4  689  700
5  177  200
6  598  621
7   85   33
8  578  571
9   27    0
10  498  518

H  14  3

0  430  442
1  113   12
2  122   91
3  519  542
4  353  368
5   72  124
6   30   96
7  438  456
8   53   20
9  -59    2

H  15  3

1  109  117
2  187  201
3  204  197
4  300  300
5  -36   55
6  406  407
7  -62    4

H  16  3

0  453  451
1  223  238
2  127  104
3  245  249
4  254  281
5  -35   42

H  17  3

1  110   41

H  0  4

0 2027 2146
1 1723 1693
2  303  250
3  487  446
4 1430 1498
5 2914 3065
6  -34   15
7  399  369
8   51   20
9 1614 1673
10 1161 1189
11  503  538
12  456  460
13  393  378
14  590  550
15  170  146
16  619  586

H  1  4

1  929  905
2  206  210
3 1332 1334
4  766  755
5  267  280
6  707  729
7  918  976
8  644  652
9  853  858
10  333  340
11  715  710
12  466  470
13  666  647
14  284  274
15  284  246
16  263  229

H  2  4

0  758  753
1 1243 1123
2 1597 1524
3 1361 1379
4  110  109
5  533  553
6  394  430
7 1195 1265
8  737  783
9  491  538
10  293  307
11  476  483
12  803  795
13  280  260
14  379  376
15  134  101
16  150  132

H  3  4

1  540  491
2 2280 2137
3  730  722
4  814  801
5  140  140
6  137  154
7  520  552
8 1026 1059
9 1283 1332
10  197  203
11  513  532
12   97  101
13  861  845
14  432  412
15  376  331
16   48   13

H  4  4

0  838  860
1  522  390
2  677  574
3  757  795
4  770  789
5 1084 1133
6  324  333
7 1253 1240
8  404  402
9  608  622
10  644  667
11  257  240
12  155  137
13  -46    2
14  149  129
15  271  269

H  5  4

1 1473 1435
2  762  760
3 1145 1088
4 1307 1286
5 1345 1320
6 1594 1598
7  452  479
8  414  389
9  501  521
10  618  621
11 1375 1354
12  218  213
13  -64   54
14  228  221
15  804  762

H  6  4

0  170  167
1 1541 1493
2 1527 1483
3 1192 1184
4   43   27
5  383  376
6  300  306
7 1313 1285
8  212  229
9  149  139
10  286  318
11  739  743
12  333  314
13  -23   71
14  221  218
15   85   59

H  7  4

1   59   43
2  287  297
3  869  836
4 1498 1480
5  337  309
6  443  430
7  443  435
8  788  798
9  731  730
10  -63   47
11  209  211
12  406  388
13  634  608
14  331  320

H  8  4

0  593  601
1 1415 1388
2  764  747
3 1660 1598
4  729  711
5  815  796
6  735  718
7  798  792
8   49   45
9  603  591
10   35   62
11  254  222
12  181  176
13  -13   54
14   95   31

H  9  4

1  327  318
2  729  715
3  -58   31
4  745  744
5  286  275
6 1187 1194
7  753  746
8  212  211
9  273  263
10  558  545
11  715  709
12  230  235
13  181  159

H  10  4

0 1240 1238
1 1332 1344
2  192  158
3  283  285
4  991  962
5 1452 1419
6  263  240
7   29   42
8   57   72
9  716  706
10  437  410
11   41   41
12  293  270
13  193  206

H  11  4

1  771  771
2  229  218
3  692  700
4  549  551
5  160  126
6  472  481
7  386  383
8  559  550
9  613  601
10   82   67
11  116  112
12  352  362

H  12  4

0  -71   65
1  514  527
2  739  746
3  665  681
4   20   45
5  410  425
6  356  357
7  422  433
8  401  393
9  277  267
10  103   74
11  191  185

H  13  4

1  232  268
2  196  227
3  193  169
4  -45   52
5  192  196
6  174  173
7  351  370
8  -33    5
9  256  228
10  -49  104

H  14  4

0  977 1006
1  820  863
2  137  154
3  529  546
4  587  601
5  549  542
6  271  283
7  100   53
8   95  152
9  391  392

H  15  4

1  242  211
2  241  270
3   72   46
4  143  160
5  416  439
6  -32  107
7  204  205

H  16  4

0  276  240
1  580  611
2  742  782
3  811  832
4  119  149
5  142  170

H  1  5

1 1372 1318
2  676  628
3  643  620
4  981 1031
5  114  135
6  673  748
7  460  454
8  746  752
9  563  586
10  470  492
11  233  246
12  105  100
13  160  161
14  199  210
15  204  219
16  379  341

H  2  5

0 1492 1375
1 1746 1593
2  164  130
3  295  313
4  455  428
5  493  534
6   15    4
7  868  904
8  339  322
9  832  853
10  247  235
11  265  273
12  193  210
13  -23    2
14  113   16
15   84   35
16  305  278

H  3  5

1 2102 1985
2  676  667
3 1095 1116
4  284  319
5  446  446
6 1116 1093
7  209  221
8  605  614
9  514  545
10  701  684
11  512  518
12   67   57
13  483  451
14  139  148
15  496  476

H  4  5

0  908  937
1  342  282
2  868  860
3   79   65
4  261  260
5   45   25
6  318  330
7  341  348
8  429  420
9   95   83
10  560  566
11  271  290
12  371  355
13  208  210
14  469  464
15  119  126

H  5  5

1  471  461
2  322  303
3  366  343
4  497  516
5  -22   18
6  -35    1
7   -4   43
8  282  279
9   60    5
10  403  406
11  -15   14
12  304  324
13  211  186
14   70  114
15  -71   35

H  6  5

0  263  226
1  271  212
2 1075 1051
3  801  785
4  298  303
5  199  195
6  176  155
7  611  602
8  557  560
9  426  433
10  160  178
11   63   14
12  649  622
13  104  134
14  418  418
15  139  149

H  7  5

1  778  759
2  176  172
3  380  371
4  -59   31
5  194  218
6  247  261
7   90   54
8  175  172
9   75   34
10  160  186
11  135  171
12  136   91
13  285  279
14   50   34

H  8  5

0 1224 1195
1  153  134
2  933  910
3  714  702
4  887  875
5 1481 1472
6   -9   15
7 1056 1039
8  167  164
9  647  638
10  431  427
11  409  399
12  400  370
13  175  178
14  418  418

H  9  5

1   36   27
2  591  602
3   93   64
4  301  312
5  347  332
6  645  631
7   42   50
8   58   66
9   65   66
10  209  185
11  101   91
12  124  127
13  249  264

H  10  5

0  662  663
1  751  752
2  676  676
3  335  323
4  336  336
5  278  294
6   96  104
7  132  147
8   93   67
9  -89   35
10  378  356
11   76   27
12  487  499

H  11  5

1  561  574
2   68    9
3  321  347
4  744  735
5  -97   52
6  326  327
7  188  189
8  531  530
9   30   52
10   57   81
11  133  139
12  184  207

H  12  5

0  423  422
1   85   65
2   43    0
3  209  219
4  277  294
5  186  182
6   23   72
7   71   70
8  -74   18
9  260  239
10  434  428
11  198  178

H  13  5

1  677  703
2  246  237
3  684  705
4  235  203
5  309  325
6  433  431
7  118  115
8  251  253
9  358  345
10  323  316

H  14  5

0  253  245
1  138  155
2  410  435
3  365  382
4  180  219
5  205  182
6  151  192
7  173  170
8  369  365

H  15  5

1  121  126
2  311  326
3  -45   60
4  350  348
5  -21   35
6  222  232

H  16  5

0   49  120
1  107   62
2  391  401
3  -36   42
4  128  156

H  0  6

0 1585 1572
1  990 1034
2  461  507
3 2465 2692
4  483  503
5  283  335
6  349  382
7 2110 2229
8  101   69
9  388  398
10  395  405
11  698  682
12  -51   51
13  117   95
14  450  422
15  310  310

H  1  6

1  193  193
2 1246 1202
3   88   82
4  351  334
5  877  907
6   10    8
7  562  592
8  205  240
9  615  621
10  295  288
11  565  571
12  -61   14
13  413  421
14  -22   26
15  605  584

H  2  6

0 1540 1444
1 1301 1270
2  635  654
3 1217 1252
4  410  420
5 1798 1869
6  367  374
7  347  325
8  452  462
9  814  844
10  590  609
11  251  254
12  468  471
13  120  112
14  107  101
15  287  261

H  3  6

1  316  337
2   40   27
3  255  263
4  998 1000
5  940  964
6  306  311
7  720  739
8  575  579
9  563  571
10   60   71
11 1186 1206
12   69    7
13  517  516
14  -42   11
15  796  737

H  4  6

0  886  854
1  766  750
2  479  472
3 1679 1671
4  180  159
5 1165 1182
6  237  255
7 1165 1201
8  319  329
9  364  370
10  243  263
11  466  473
12  271  265
13  297  280
14  558  600
15  127  155

H  5  6

1  807  770
2 1037 1013
3 1538 1499
4  252  233
5  110   98
6  575  564
7  637  626
8  320  335
9 1292 1291
10  213  206
11   94  124
12   57   45
13 1501 1467
14   74   49
15  -56   66

H  6  6

0  -34   37
1 1527 1448
2  -34    3
3  889  844
4   78   63
5 1642 1601
6  101  129
7   53    3
8   90   75
9 1105 1097
10  153  155
11  121   70
12   66   15
13  264  250
14 -100   22

H  7  6

1  465  470
2  376  367
3  324  345
4  719  708
5  808  776
6  860  872
7  793  774
8  453  444
9  273  256
10  231  226
11  793  761
12  123  113
13   84   70
14   36  103

H  8  6

0  256  233
1 1370 1323
2  353  355
3  767  734
4  141  146
5 1236 1199
6  131  110
7  395  391
8  182  179
9  472  472
10   84   98
11  111  118
12   91  150
13  138   97

H  9  6

1  436  434
2  354  346
3  657  652
4  892  888
5   77   53
6  719  729
7  608  612
8  531  534
9  415  410
10  205  190
11  155  158
12   45   20
13  598  589

H  10  6

0  365  357
1  924  914
2  250  249
3 1262 1248
4  311  309
5  -50   27
6  192  213
7 1043 1041
8  121   95
9  -33   32
10  184  165
11  693  688
12  152  157

H  11  6

1  909  940
2  285  310
3  260  263
4  217  218
5  606  615
6  306  311
7  373  363
8  270  257
9  154  211
10   56   38
11 1039 1005

H  12  6

0  266  258
1  735  749
2  533  539
3  518  502
4  326  326
5  976  973
6  180  183
7  362  360
8   59   78
9  429  428
10   70   96

H  13  6

1  200  184
2  -53   13
3 -133   23
4  259  317
5  384  409
6  259  267
7  426  453
8  157  160
9  644  652

H  14  6

0  532  524
1  718  730
2  379  383
3  861  870
4  255  277
5  132  146
6  144  134
7  733  726
8 -111   69

H  15  6

1  209  204
2  323  384
3  426  437
4  114   90
5  232  195
6   99  132

H  16  6

0  252  237
1  837  846
2  337  358
3  183  201

H  1  7

1 1091 1077
2  587  593
3  702  727
4  427  453
5  211  240
6  873  931
7  418  435
8  745  799
9  364  356
10  537  537
11  710  728
12  118  143
13   92   81
14   57   31
15  238  185

H  2  7

0  374  365
1  447  444
2  260  226
3 1011  994
4  -50   31
5  625  652
6  -35   25
7  615  607
8   47   93
9  669  721
10  157  125
11   43   39
12   46   11
13   90    0
14   87   48
15   93   53

H  3  7

1 1274 1248
2  347  323
3 1146 1125
4  274  287
5   59   25
6  151  169
7   37   54
8  211  182
9  613  599
10   91   20
11  448  454
12  -51   21
13  754  756
14  153  142
15  369  360

H  4  7

0  631  597
1  841  811
2  949  929
3  520  520
4  402  409
5  146  111
6  400  404
7  338  332
8  191  191
9  132  135
10  277  292
11   65   78
12  231  237
13  127  126
14  344  313
15   78   22

H  5  7

1  574  547
2   50   72
3  696  664
4  428  409
5  255  249
6  148  104
7  338  341
8  243  240
9  111  144
10  253  250
11  332  316
12  -49    4
13  115  146
14   99   15

H  6  7

0 1092 1073
1  136   89
2  594  591
3  744  793
4  561  540
5 1253 1247
6  232  217
7  584  588
8  127   93
9  318  306
10  350  310
11   85  105
12  499  502
13    8    8
14  333  312

H  7  7

1  327  292
2  -46   51
3  291  307
4   45   69
5  114  120
6  376  370
7  310  305
8  143  113
9  367  364
10  158  141
11  342  354
12  227  234
13  110  115

H  8  7

0  247  222
1  532  527
2  444  447
3  771  759
4   81   77
5  952  931
6  105   94
7  950  957
8  342  342
9  584  577
10  361  380
11  551  548
12  191  175
13   46   87

H  9  7

1  -48   41
2  225  214
3  221  226
4  497  496
5  -61   23
6  380  390
7  211  247
8  333  335
9  259  295
10   -5   38
11  149  164
12  110   90

H  10  7

0  817  810
1  228  228
2   77  111
3  261  256
4  407  420
5  566  571
6  129  134
7   36   24
8  165  140
9  224  197
10  276  266
11  -68    1
12  391  367

H  11  7

1  536  554
2  361  373
3  421  420
4  132  192
5  469  462
6  324  320
7  150  121
8  100  102
9   65   20
10  341  310
11  400  387

H  12  7

0  223  237
1   82   45
2  592  614
3  223  227
4  196  203
5  -80   17
6  310  328
7  268  240
8  341  323
9   68    3
10  174  220

H  13  7

1  788  837
2   84   97
3  586  600
4  114   91
5  243  277
6  138  162
7  229  210
8  172  130
9  425  414

H  14  7

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1   69   22
2  150  141
3   44  111
4  111  127
5  210  248
6  189  195
7  146   95

H  15  7

1  247  255
2  272  288
3  -19   83
4  153  189
5   57   66

H  0  8

0  888  882
1 1749 1923
2 1138 1194
3  998 1066
4  961 1014
5 2313 2472
6  398  389
7 1141 1212
8  312  317
9 1092 1116
10  -43   84
11  223  234
12  384  373
13   79   65
14  198  204
15  291  264

H  1  8

1  269  283
2   90   11
3  574  599
4  869  893
5  543  578
6  370  407
7  630  650
8  520  522
9  195  168
10   39   73
11  511  510
12  458  473
13  569  584
14  208  198
15  367  359

H  2  8

0 1274 1250
1 1118 1079
2  166  161
3 1591 1603
4 1353 1390
5  424  436
6  360  374
7 1257 1310
8  244  239
9  257  281
10  389  381
11  373  367
12  157  136
13  142  152
14  348  357

H  3  8

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2  620  634
3  465  470
4   29  106
5  258  253
6  782  799
7  256  270
8   80   30
9  490  505
10  530  542
11  189  213
12  115  178
13  812  801
14  416  420

H  4  8

0  237  237
1  895  870
2 1460 1449
3  580  607
4   99   79
5 1257 1257
6  278  291
7   52   17
8  283  280
9  568  578
10   -8    9
11  214  210
12  535  543
13  100   90
14  123  128

H  5  8

1 1237 1221
2   94  101
3  914  873
4  568  557
5  749  732
6  424  439
7  520  501
8  219  199
9   57    4
10  396  390
11  894  873
12  220  223
13  164  151
14  409  391

H  6  8

0  -45    3
1  641  606
2  867  841
3 1483 1452
4  356  357
5  227  227
6  818  830
7  896  873
8  184  138
9   59   41
10  177  148
11  403  416
12  117  128
13  -75   40

H  7  8

1  465  437
2  453  443
3 1008 1015
4  482  469
5  418  406
6  756  718
7  322  302
8  186  190
9  693  683
10  458  453
11   60   12
12  212  187
13  866  847

H  8  8

0  872  856
1 1173 1150
2  551  539
3  966  935
4  786  762
5  424  415
6  363  326
7  653  618
8  184  173
9   43   18
10  309  311
11  316  312
12  170  157

H  9  8

1  504  486
2   68   79
3  -49   25
4  556  560
5  759  734
6  329  308
7  449  427
8  554  537
9  332  348
10  -43   34
11  852  824
12  341  321

H  10  8

0  812  813
1  516  495
2  180  168
3  443  446
4  605  590
5 1069 1061
6  228  233
7  -49   49
8  442  422
9  757  754
10  217  190
11  144  116

H  11  8

1  498  498
2  -17   14
3  468  460
4  -70   34
5  166  171
6  408  428
7  555  577
8  357  374
9  761  726
10  188  183

H  12  8

0  804  812
1  403  418
2  -92   17
3  555  548
4  362  359
5   92   96
6  243  225
7  684  689
8  100   69
9  169  177

H  13  8

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4  214  220
5  380  399
6   63   94
7  108  120
8  446  447

H  14  8

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2  615  609
3   59   58
4  -50   58
5  692  695
6  311  331

H  15  8

1  298  326
2   85   67
3   83   49

H  1  9

1 1337 1323
2  452  467
3  386  404
4  298  301
5  362  372
6  480  513
7   98   95
8  680  704
9  760  791
10  330  339
11  602  604
12   85   59
13  296  294
14  -38   46

H  2  9

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1  820  801
2  -59   45
3  515  516
4  203  174
5  518  507
6  157  162
7  527  564
8   93  107
9  528  510
10  -57   16
11  135  113
12  276  248
13  149  152
14  166  161

H  3  9

1 1496 1429
2   42   39
3  863  853
4  425  413
5  286  296
6  175  187
7  -58   28
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9  436  440
10  209  234
11  527  517
12   42   89
13  344  311
14 -105   42

H  4  9

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2  511  500
3  646  655
4  428  408
5  613  613
6    7    8
7  306  312
8  127  156
9  301  278
10   83   67
11  136   95
12  252  253
13  -95   32
14  260  246

H  5  9

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3  342  346
4   92   90
5  113  128
6  625  608
7  565  552
8  201  207
9  289  288
10  159  170
11  110   52
12  131  156
13  251  231

H  6  9

0 1047 1017
1   98   76
2  332  345
3 1242 1220
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5  385  410
6  319  318
7  894  880
8  369  343
9  318  342
10  314  317
11   80   40
12  223  182
13   66   34

H  7  9

1  -61   21
2  352  348
3  140  104
4  319  307
5  530  519
6   58   66
7  232  241
8  302  299
9   64   25
10  329  327
11   72   32
12  102   41

H  8  9

0  134  110
1  425  397
2  309  313
3  440  449
4  123  111
5 1125 1104
6  267  285
7  446  434
8   60   47
9  497  470
10  -41   50
11  409  405
12   97   56

H  9  9

1   60    6
2   83   57
3   76   95
4  203  201
5    9   42
6  235  239
7  -48   50
8  257  242
9  -20    9
10  366  345
11  381  362

H  10  9

0  -93    3
1   16   43
2  448  441
3  223  214
4  143  100
5  365  369
6  254  270
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8  192  162
9  219  172
10  153  177

H  11  9

1  288  275
2  -47   93
3  501  494
4  127  112
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6   52   98
7  239  253
8  203  164
9  393  385

H  12  9

0  435  439
1  136  167
2  248  264
3  130   27
4  356  382
5  346  361
6  127   69
7   54  137
8   18   86

H  13  9

1  700  691
2  -82   29
3  471  471
4   95   96
5  100   83
6  149   94
7   56  157

H  14  9

0  153  202
1  209  257
2  224  215
3  243  219
4  209  201
5  175  191

H  0  10

0  947  954
1  235  240
2 1197 1281
3  850  891
4 1013 1053
5  780  840
6  745  781
7  922  950
8  302  321
9  887  906
10  273  274
11  377  398
12  299  302
13  160  164
14  159  181

H  1  10

1  191  175
2  224  200
3  647  681
4  171  175
5  392  405
6  765  832
7  247  243
8   31   59
9  235  243
10  519  512
11  164  129
12  364  352
13  276  283

H  2  10

0  697  696
1  451  425
2 1368 1335
3  196  175
4  912  898
5 1284 1317
6  767  794
7  587  607
8  345  356
9  647  666
10  184  168
11  113  132
12  421  385
13  105   74

H  3  10

1  885  847
2  167  185
3  280  259
4  517  530
5  563  568
6  355  355
7  251  261
8  419  442
9   63   15
10  379  395
11  523  513
12  620  612
13   36   30

H  4  10

0 1176 1121
1  659  646
2  552  551
3  882  883
4 1251 1254
5  299  288
6  658  665
7  723  720
8  126  147
9   73   76
10  537  527
11  310  316
12  -78   14
13  219  183

H  5  10

1  807  754
2   58  106
3  983  966
4  561  558
5  104   91
6  268  240
7  235  240
8  700  691
9  405  403
10  286  290
11  162  127
12  657  643
13  738  695

H  6  10

0  962  946
1  402  359
2  744  728
3  217  216
4 1069 1052
5  665  635
6  516  503
7  158  165
8  416  413
9  238  214
10  323  327
11  110  124
12   93   46

H  7  10

1  631  616
2  131  115
3  250  238
4  634  630
5  446  453
6   86   42
7  361  339
8  708  673
9   48   39
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$(CN)_5CoSCNCo(NH_3)_5\cdot H_2O$

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11  717  677
12  523  508

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 2  757  718
 3  301  297
 4  761  730
 5  308  292
 6  454  431
 7  241  236
 8  479  482
 9  110  105
10  307  287
11  107   37

 H    9   10

 1  424  412
 2  134   76
 3  668  666
 4  149  134
 5   98   68
 6  523  504
 7  -37   60
 8  215  190
 9  544  526
10  531  520

 H   10   10

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 1  249  257
 2  936  836
 3  440  437
 4  426  401
 5  217  197
 6  454  447
 7  556  548
 8  525  491
 9  -72    8
10  129   82

 H   11   10

 1  290  221
 2  217  239
 3  436  433
 4  145  124
 5  327  333
 6  521  522
 7   84    0
 8  276  268
 9  -65   55

 H   12   10

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 2  779  781
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 5  622  611
 6  460  459
 7  148   82

 H   13   10

 1  -36  106
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 4  237  246
 5   79  133
 6  361  369

 H   14   10

 0  596  620
 1   72   52
 2  300  316
 3  616  637

 H    1   11

 1 1562 1560
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 3  471  474
 4  360  377
 5  396  412
 6  181  189
 7   97   86
 8  144  111
 9  462  483
10  -81   28
11  604  600
12  103   72
13  273  267

 H    2   11

 0  441  406*
 1  237  259
 2  374  368
 3   86   81
 4  138  141
 5  169  161
 6   73   93
 7  210  199
 8  -32   26
 9  125  153
10   89  133
11 -110   35
12  142  137
13   59  110

 H    3   11

 1  712  713
 2  146  134
 3  712  675
 4   37   17
 5  -92   11
 6  319  304
 7  267  295
 8  382  417
 9  578  583
10  140  186
11  236  232
12  200  180
13  352  327

 H    4   11

 0  479  475*
 1  288  275
 2   50   73
 3  766  757
 4   58   60
 5  531  517
 6  210  221
 7  766  763
 8   42   43
 9  434  453
10  113  134
11   97   64
12  221  216

 H    5   11

 1  275  262
 2   69   33
 3  199  221
 4  316  316
 5   42   80
 6  303  323
 7  202  205
 8  -51   32
 9   88   62
10  260  296
11  163  123
12  170  164

 H    6   11

 0  476  468*
 1  427  429
 2  370  355
 3  552  576
 4   54   70
 5  757  722
 6   24   76
 7  525  524
 8  127   88
 9  599  567
10  182  182
11  308  301
12  -77   32

 H    7   11

 1  122  141
 2   91   30
 3  289  289
 4  394  387
 5   22   69
 6  153  173
 7  206  180
 8  326  310
10   85   37
11   26   31

 H    8   11

 0   76   24
 1  -63   65
 2  356  347
 3  592  592
 4  165  195
 5  618  605
 6  114  137
 7  669  622
 8  104  117
 9  214  228
10  233  207

 H    9   11

 1   79   90
 2  194  207
 3  495  502
 4   87  139
 5   33   29
 6   53   72
 7   26   82
 8  287  290
 9  366  357
10  164  180

 H   10   11

 0   63   65
 1  268  270
 2  272  257
 3  165  180
 4  312  307
 5  757  759
 6  -49    8
 7  328  303
 8  -34   57
 9  218  205

 H   11   11

 1  692  680
 2  -33   71
 3  309  316
 4   19   98
 5  200  169
 6   65   31
 7  234  247

 H   12   11

 0  290  287
 1  128  106
 2   39    0
 3  365  370
 4   59    3
 5  157  197
 6   26    5

 H   13   11

 1  335  351
 2  -68   23
 3  340  349
 4  218  190

 H    0   12

 0 1154 1200*
 1  246  271*
 2  381  399*
 3  486  519*
 4 1199 1284*
 5  100   80*
 6  328  362*
 7  620  694*
 8  568  623*
 9  235  239*
10  460  515*
11  254  225
12   42    4

 H    1   12

 1  390  555*
 2  171  216*
 3   66  113*
 4  442  497*
 5  333  401*
 6  305  365*
 7   74   79*
 8  635  774*
 9  -11   23*
10  319  357*
11  116  124
12  663  661

 H    2   12

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 1  293  377*
 2  464  630*
 3  277  374*
 4  651  821*
 5  672  835*
 6  560  764*
 7  591  786*
 8  264  362*
 9  542  646*
10  269  315*
11  114   43
12  213  208

 H    3   12

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 3  413  560*
 4  351  482*
 5  293  434*
 6  255  367*
 7  159  213*
 8  370  487*
 9  193  228*
10  585  581
11  346  357
12  556  530

 H    4   12

 0  107   65*
 1   53   30*
 2  684  639*
 3  385  491*
 4  433  559*
 5  365  518*
 6  551  839*
 7  427  595*
 8  320  425*
 9  308  345*
10  298  290
11  400  409

 H    5   12

 1  450  436*
 2  468  556*
 3  156  161*
 4   79  171*
 5   62   18*
 6  449  663*
 7   34   90*
 8  131  204*
 9  290  369*
10  634  644
11  345  333

 H    6   12

 0  610  572*
 1   71   36*
 2  877  992*
 3   99  162*
 4  455  541*
 5  -34   56*
 6  314  420*
 7   37   76*
 8  333  425*
 9   92  138
10  255  248
11  -87   45

 H    7   12

 1  583  561*
 2   80    9*
 3  662  737*
 4  330  389*
 5  204  210*
 6  374  502*
 7  106   45*
 8  248  229
 9  331  312
10  609  594

 H    8   12

 0  792  740*
 1   48   88*
 2  824  810*
 3   10   19*
 4  497  550*
 5  342  380*
 6  495  646*
 7   42   45
 8  500  452
 9  128  134

 H    9   12

 1  817  804*
 2  117  108*
 3  648  683*
 4  213  199*
 5  346  402*
 6  361  340
 7  155  126
 8  483  473
 9  262  268

 H   10   12

 0  870  846*
 1   41   66*
 2  561  562*
 3  292  261*
 4  703  690
 5  259  281
 6  351  335
 7  145  142

 H   11   12

 1  271  270
 2  -77   49
 3   80   48
 4  419  390
 5  277  254
 6   93   50

 H   12   12

 0  687  669
 1  119  125
 2  387  378
 3  307  265
 4  543  558

 H    1   13

 1  335  878*
 2   66  161*
 3  404  643*
 4  137  168*
 5   76  100*
 6   81   74*
 7   62   63*
 8  160  211*
 9  339  354*
10   74   51
11  569  558

 H    2   13

 0  658  733*
 1  -25   81*
 2   60  310*
 3   11  119*
 4  302  524*
 5  -41    8*
 6  -37    5*
 7   62   10*
 8   70  100*
 9   87   41*
10   69   67
11   94  129

 H    3   13

 1  280  397*
 2   60  150*
 3  129  230*
 4  136  140*
 5   70   89*
 6  192  310*
 7  143  229*
 8   82  214*
 9  132  150
10  371  379
11  222  219

 H    4   13

 0  181  179*
 1  198  321*
 2  -35   21*
 3  250  573*
 4  127  220*
 5  396  659*
 6  102  118*
 7  452  664*
 8  -29    3*
 9  452  461
10  -70   28
11  -63   30

 H    5   13

 1  198  212*
 2  110  187*
 3  331  607*
 4  -16  127*
 5   40   30*
 6  -67    5*
 7  -48   39*
 8  -89    6
 9   59   27
10  -53   46

 H    6   13

 0  149  153*
 1  143  184*
 2  297  408*
 3  371  655*
 4  -35   56*
 5  432  665*
 6  106  202*
 7  466  634*
 8  231  234
 9  407  387
10  109   99

 H    7   13

 1  227  307*
 2   40   95*
 3  146  205*
 4   78  172*
 5  166  292*
 6  152  206*
 7  126  141
 8  314  309
 9  118  111

 H    8   13

 0  475  478*
 1  133  141*
 2  168  226*
 3  203  297*
 4  101  135*
 6   63   40
 7  339  324
 8  -62  105

 H    9   13

 1  518  548*
 2  136  166*
 3   86  103
 4   31   63
 5  349  348
 6   62   37
 7  106  109

 H   10   13

 0  186  182
 1  -76   23
 2  178  132
 3  554  548
 4  197  207
 5  545  556
 6 -130    6

 H   11   13

 1  444  449
 2   48   55
 3  500  488
 4   65   97

 H   12   13

 0  149  119

 H    0   14

 0  254  300*
 1  449  528*
 2  686  766*
 3  300  334*
 4  245  268*
 5  564  574*
 6  601  666*
 7   65    4*
 8  449  453
 9  551  552
10  248  255

 H    1   14

 1  140  273*
 2   65   81*
 3  100  154*
 4  214  254*
 5  275  330*
 6  151  191*
 7  335  382*
 8  322  338
 9   87   37
10  590  577

 H    2   14

 0  676  743*
 1  188  264*
 2  319  471*
 3  500  687*
 4  352  452*
 5   89  173*
 6  314  381*
 7  716  825*
 8  233  259
 9  225  199
10  316  329

 H    3   14

 1  252  379*
 2  239  363*
 3  222  306*
 4   88   27*
 5  188  250*
 6  176  256*
 7  194  293*
 8  291  266
 9  599  611
10  450  454

 H    4   14

 0  374  440*
 1  340  445*
 2  461  635*
 3  -83   27*
 4  343  486*
 5  519  670*
 6  367  456*
 7  347  338
 8  592  599
 9  651  644

 H    5   14

 1  293  342*
 2  195  264*
 3   84  127*
 4  334  439*
 5  276  397*
 6  -95   15*
 7  396  376
 8  619  581
 9   76   19

 H    6   14

 0  844  869*
 1  385  428*
 2  220  252*
 3  266  283*
 4  441  558*
 5  258  345*
 6  390  393
 7  226  232
 8  282  262

 H    7   14

 1  696  763*
 2  323  365*
 3  574  704*
 4  -78   16
 5  215  205
 6  408  389
 7  140   86
 8  254  267

 H    8   14

 0  528  484*
 1  347  362*
 2  253  243
 3  515  514
 4  527  498
 5  332  307
 6  244  243
 7  328  309

 H    9   14

 1  633  616
 2  134   90
 3  432  425
 4  320  322
 5  249  256
 6  -70   48

 H   10   14

 0  346  357
 1  369  343
 2  605  566
 3  243  267
 4  168  140

 H    1   15

 1  508  702*
 2   91   91*
 3  284  328*
 4  215  262*
 5  197  216*
 7  -73   54
 8  150  190
 9  352  390

 H    2   15

 0  -92   41*
 1  270  320*
 2   69   49*
 3  -95   50*
 4  -76   17*
 5  -27   30*
 6   38   80
 7   88   92
 8   77   23
 9   82   44

 H    3   15

 1  206  225*
 2  -67    3*
 3  -53   76*
 4  158  221*
 5  -74   27*
 6   99  140
 7  -90    3
 8  268  295

 H    4   15

 0   62    1*
 1   65  128*
 2   65   76*
 3  384  502*
 4  -10   58*
 5  421  409
 6  132   44
 7  484  469
 8   78  112

 H    5   15

 1  335  367*
 2 -119   48*
 3  220  303*
 4  198  175
 5  205  177
 6  170  167
 7  -74    5
 8   72   61

 H    6   15

 0  440  390*
 1  139  122*
 2  303  311
 3  393  386
 4  287  263
 5  677  670
 6   31   84
 7  609  595

 H    7   15

 1  112  114
 2  101   31
 3  183  181
 4   43   39
 5   63   45
 6  168  128

 H    8   15

 0   94   57
 1 -107   85
 2  251  249
 3  448  426
 4  288  267
 5  257  272

 H    9   15

 1  336  362
 2  -62   51
 3  337  330

 H    0   16

 0  768  832*
 1  613  652*
 2   22    9*
 3  674  724*
 4  137  133
 5   83   73
 6  299  338
 7  521  501

 H    1   16

 1  269  336*
 2  195  214*
 4   87   23
 5  110   49
 6  142  155
 7  297  337

 H    2   16

 0  213  245*
 1  618  785*
 2  458  613*
 3  184  214
 4  101  109
 5  729  717
 6   93   72
 7  -97   31

 H    3   16

 1  322  357*
 2  145  192
 3  -72    6
 4  -62   14
 5  457  436
 6  212  207
 7  205  206

 H    4   16

 0  667  656
 1  615  603
 2  182  242
 3  748  751
 4  428  408
 5  -75   31
 6  266  265

 H    5   16

 1  -68    2
 2  149  137
 3  331  305
 4  140  162
 5  149  153
 6  183  152

 H    6   16

 0  178  226
 1  460  435
 2  297  293
 3  532  519
 4  120   59
 5  355  357

 H    7   16

 1  557  526
 2   23   31
 3  310  331

 H    8   16

 0  -15   64

 H    1   17

 1  661  643
 2  356  331
 3  444  433
 4  265  259
 5  142  147

 H    2   17

 0  -48   15
 1   43   95
 2   52   58
 3   85   93
 4  -13   45
 5   79   55

 H    3   17

 1   72   67
 2  -42   53
 3   99   22
 4  255  260

 H    4   17

 0  357  312
 1   70   55
 2  167  157
 3  161  121
 4  304  297

 H    5   17

 1  225  198
 2  206  183

 H    0   18

 0  557  616
 1  724  772
```

TABLE III-12. POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS FOR THE HEAVY ATOMS, $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	53962(4)	3468(4)	22776(4)	232(3)	183(3)	174(4)	8(6)	-16(6)	-57(5)
Co(2)	73390(4)	25384(4)	45684(4)	257(3)	141(3)	177(4)	4(6)	-70(6)	-16(6)
S	46781(9)	15849(9)	29897(10)	218(6)	288(7)	308(9)	90(11)	-92(12)	-258(11)
C(1)	55591(33)	19776(32)	35867(35)	263(27)	188(24)	242(29)	68(43)	78(44)	-88(43)
N(1)	61748(27)	22416(26)	40042(30)	248(22)	209(21)	277(26)	14(36)	-34(38)	-87(37)
C(2)	59662(35)	-6343(34)	17007(36)	359(30)	242(26)	201(29)	-35(46)	104(46)	-68(45)
N(2)	63734(35)	-12169(33)	13719(34)	543(32)	411(28)	389(32)	96(52)	135(50)	-330(51)
C(3)	65694(33)	9319(33)	22492(34)	265(26)	250(25)	165(27)	46(45)	-49(43)	-102(42)
N(3)	72816(31)	13064(32)	21934(31)	349(27)	332(25)	417(30)	-9(45)	44(46)	-233(45)
C(4)	42205(36)	-2714(35)	22304(33)	353(28)	288(26)	145(28)	-98(50)	5(45)	-125(44)
N(4)	35230(33)	-6408(34)	21882(34)	403(29)	491(30)	465(33)	-312(50)	117(48)	-433(52)
C(5)	51072(34)	9452(37)	12152(37)	229(27)	349(31)	275(33)	-41(47)	24(45)	50(48)
N(5)	49304(33)	13714(37)	5990(34)	366(27)	625(35)	309(31)	98(52)	8(45)	250(51)
C(6)	56449(38)	-2163(34)	33788(39)	458(34)	205(26)	296(35)	164(49)	-43(52)	-99(48)
N(6)	57668(42)	-5492(37)	40510(37)	980(44)	460(32)	291(33)	590(64)	-66(59)	117(51)
N(7)	85210(29)	28270(28)	51385(30)	315(24)	234(21)	314(28)	-59(39)	-254(39)	-2(38)
N(8)	69042(29)	38140(29)	47339(29)	362(26)	194(21)	302(27)	65(39)	-17(40)	-41(38)
N(9)	77419(29)	12496(28)	43927(28)	354(25)	192(20)	299(26)	43(39)	71(41)	-2(37)
N(10)	67879(31)	22124(30)	57210(29)	446(27)	273(23)	212(27)	20(41)	53(41)	1(38)
N(11)	78767(27)	28538(28)	34081(29)	314(23)	221(20)	238(25)	-48(38)	-31(37)	34(37)
O	33045(29)	-651(27)	42650(26)	534(25)	341(21)	381(25)	-93(38)	174(40)	16(37)

All values have been multiplied by 10^5. The anisotropic temperature factor is of the form $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+\beta_{12}hk+\beta_{13}h\ell+\beta_{23}k\ell)\}$. Estimated standard deviations are given in parentheses.

TABLE III-12. Part 2. COORDINATES (x 10^3) ASSIGNED TO THE HYDROGEN ATOMS

Atom	X	Y	Z
7H(1)	890	226	519
7H(2)	839	312	573
7H(3)	889	329	473
8H(1)	731	411	516
8H(2)	623	379	491
8H(3)	695	413	412
9H(1)	846	124	444
9H(2)	753	106	379
9H(3)	745	87	488
10H(1)	720	173	599
10H(2)	614	198	560
10H(3)	679	280	609
11H(1)	852	307	351
11H(2)	746	333	315
11H(3)	786	222	304

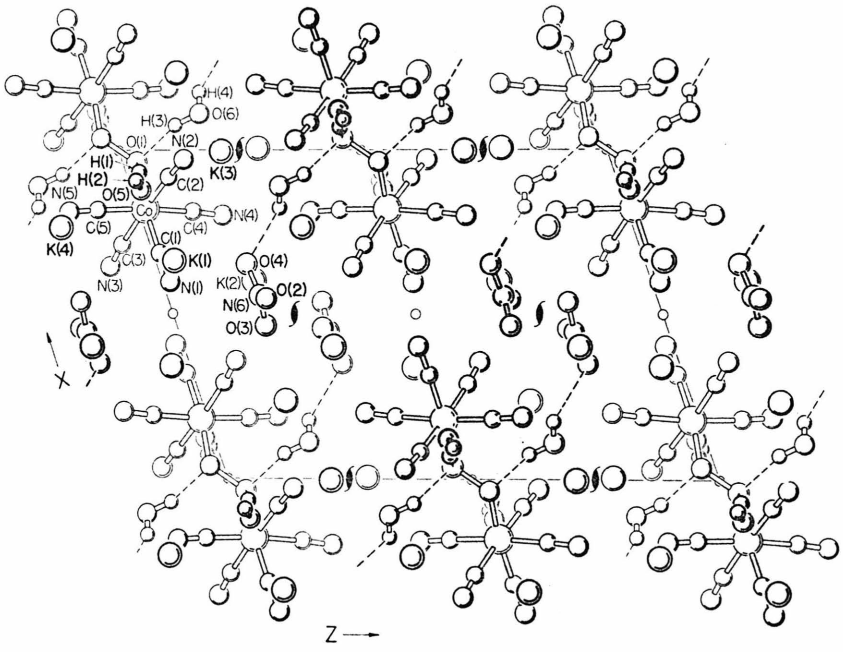
CHAPTER IV. STRUCTURE DESCRIPTIONS

A. $K_8\{(CN)_5CoO_2Co(CN)_5\}(NO_3)_2\cdot 4H_2O$

This structure is composed of four separate discrete ionic and molecular species efficiently packed in the solid state. Sixteen potassium ions, eight neutral water molecules, two peroxo-bridged binuclear anions of charge (6-), and four nitrate ions are contained in the unit cell. A diagram of the contents of the unit cell, viewed in projection down y, is shown in Figure IV-1. The centrosymmetric binuclear ions are seen to be surrounded by cations and water molecules hydrogen bonded to the bridging peroxo group. Voids in this packing are filled by nitrate ions which are oriented edge-on in this projection. These nitrate ions are seen to be hydrogen bonded to water molecules also.

The distribution of the water molecules about the binuclear ion is seen more clearly in Figure IV-2, a stereo-pair of that portion of the structure, and also in Figure IV-3, a projection of the same grouping down the long direction of the binuclear ion. These diagrams illustrate that the water molecules complete a tetrahedral coordination around each oxygen atom of the bridging group; i.e., they are located along the expected directions of the peroxo lone pairs. The hydrogen bonds are strong, and in fact, one is tempted to think of

Figure IV-1



The crystal packing, viewed in projection down the *b* axis.

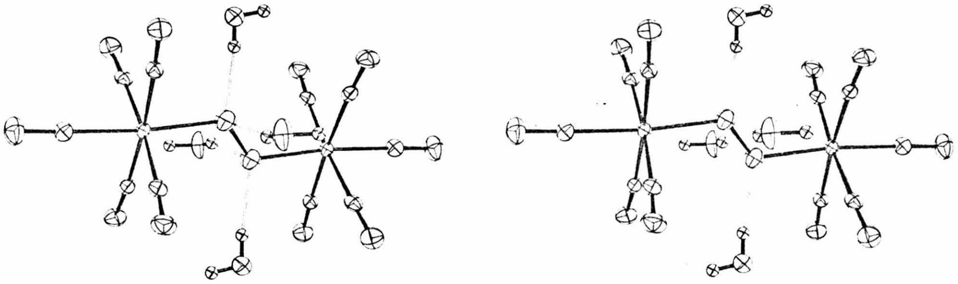
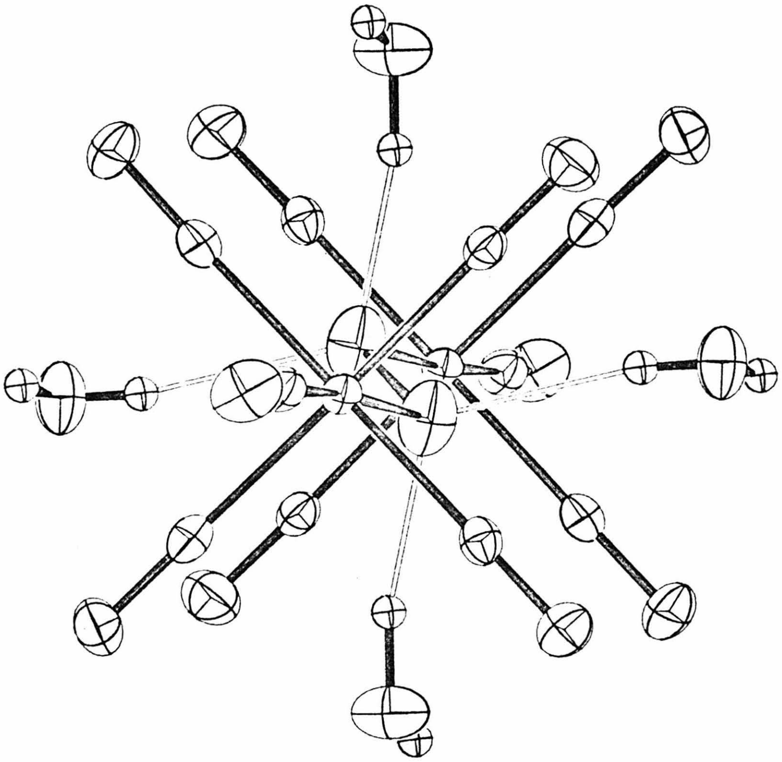


Figure IV-2
ORTEP stereopair illustrating the binuclear ion and the hydrogen bonding to it. Thermal ellipsoids are drawn at the 40% probability level.

Figure IV-3



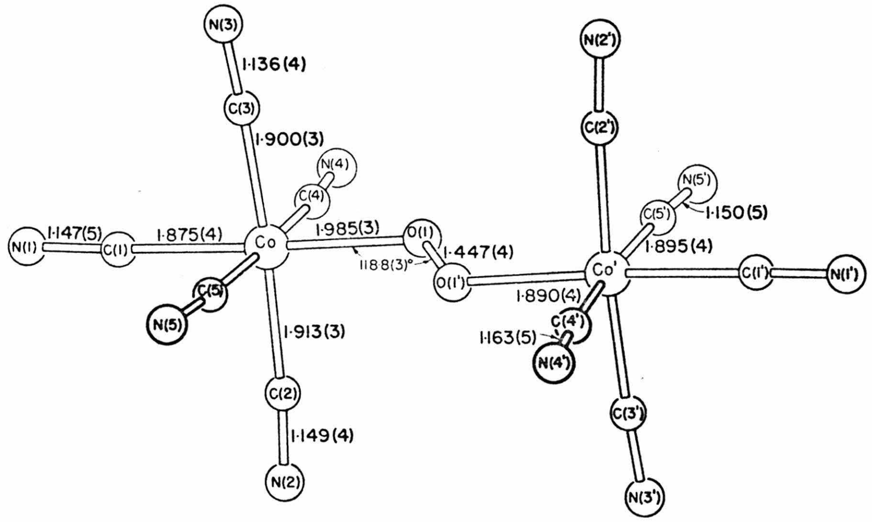
An ORTEP drawing of the binuclear anion illustrating the eclipsed conformation of the equatorial ligands and the staggering of the water molecules between them. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are represented by spheroids of arbitrary radius.

the bridging group of the binuclear ion as $H_8O_6^{2-}$ rather than simply O_2^{2-}. The hydrogen bond involving water molecule O(5) has an O···O distance of 2.69 Å, an H···O distance of 1.95 Å, and an O-H···O angle of 165°. The hydrogen bond involving O(6) has an O···O distance of 2.75 Å, an H···O distance of 1.83 Å, and an O-H···O angle of 165°. These, and their inversion-related equivalents, are the only four hydrogen bonds which exist to the binuclear anion. The $\{(CN)_5CoO_2Co(CN)_5\}^{6-}$ anion apparently distorts somewhat in order to allow this hydrogen bonding to take place. Figures IV-2 and IV-4 illustrate that the equatorial cyanide ligands of the complex ion all bend outward from the center of the molecule. The cobalt atom lies about 0.07 Å out of the best plane of the equatorial carbon atoms and about 0.20 Å out of the best plane of the equatorial nitrogen atoms. Deviations from these planes of the atoms comprising the planes are about 0.005 Å and 0.01 Å respectively. The average O(1)-Co-C(eq) angle is 92.2°, and the average C(1)-Co-C(eq) angle is 87.8°. Close contacts to the water molecules also apparently cause distinct nonlinearities in the Co-C-N angles. The average deviation from linear coordination in the equatorial cyanide ligands is almost 3.5°, and all are in such a direction as to increase the distance between the nitrogen atom and the water molecule. Such deviations are most often the case in cyano complexes situated in low symmetry environments, and are usually blindly attributed to the overused and poorly understood effects of the great catch-all "packing forces". Rarely do we see such clear indication of packing forces in action and the effects they cause upon bond angles. Not so obvious and probably far more important are the mysterious effects of packing upon bonding distances, which will be speculated upon with respect to Co-C distances shortly.

The binuclear anion $\{(CN)_5CoO_2Co(CN)_5\}^{6-}$ has rigorous crystallographic point symmetry C_i in this crystal, and deviations from ideal symmetry C_{2h} are not extreme. The ion contains identical cobalt(III) atoms in slightly distorted octahedral environments bridged together by a dioxygen ligand in the asymmetric, staggered orientation. The Co-O-O-Co grouping is, of course, rigorously planar. Interatomic distances and the angle at the bridging oxygen atoms are given in Figure IV-4; other important angles are tabulated in Table IV-2. The O-O distance of the dioxygen group, 1.447(4) Å, indicates the appropriateness of its characterization as a peroxide. The Co-O distance is a very long 1.985(3) Å, and is the subject of mild surprise. This bond length will be discussed comparatively in more detail in another section of this document; however, it is pertinent to the present discussion to point out that this long distance is probably due at least in part to distortions imposed upon the ion by

Figure IV-4

Structure of $K_8[Co_2O_2(CN)_{10}](NO_3)_2 \cdot 4H_2O$



Interatomic distances within the $[(CN)_5CoO_2Co(CN)_5]^{6-}$ anion. Esd's are given in parentheses.

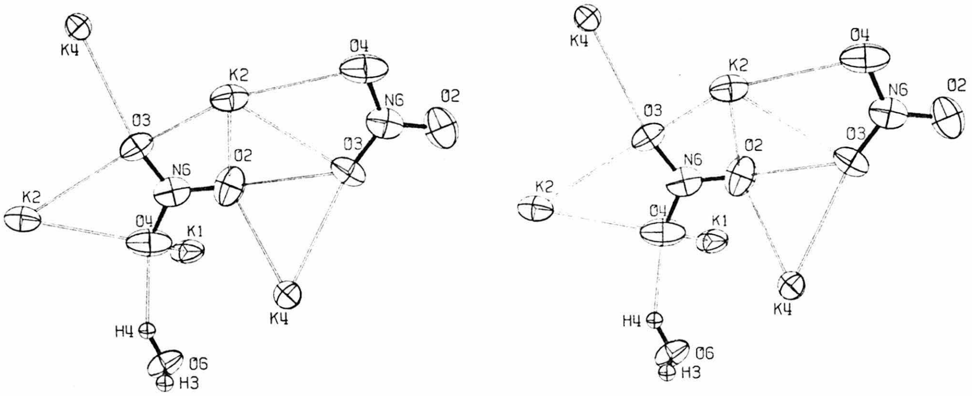


Figure IV-5

The nitrate ion and its surroundings. The two nitrate ions shown are related by a twofold screw axis, and the interionic contactOO(2)-O(3) is 2.97Å. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are represented by spheroids of arbitrary radius.

TABLE IV-2. ANGLES IN THE BINUCLEAR ANION $\{(CN)_5CoO_2Co(CN)_5\}^{6-}$

Atoms	Angle (Degrees)	Atoms	Angle (Degrees)
Co-C(1)-N(1)	177.4(4)	O(1)-Co-C(2)	93.0(1)
Co-C(2)-N(2)	175.9(3)	O(1)-Co-C(3)	91.8(1)
Co-C(3)-N(3)	176.5(4)	O(1)-Co-C(4)	84.5(2)
Co-C(4)-N(4)	177.5(4)	O(1)-Co-C(5)	99.6(2)
Co-C(5)-N(5)	176.3(3)		
C(1)-Co-O(1)	172.2(2)	C(2)-Co-C(3)	175.2(2)
C(1)-Co-C(2)	87.7(2)	C(2)-Co-C(4)	90.5(2)
C(1)-Co-C(3)	87.6(2)	C(2)-Co-C(5)	90.1(2)
C(1)-Co-C(4)	87.7(2)	C(3)-Co-C(4)	89.9(2)
C(1)-Co-C(5)	88.1(2)	C(3)-Co-C(5)	89.1(2)
		C(4)-Co-C(5)	175.7(2)

the previously-discussed crowding of the water molecules.

An intriguing facet of this structure lies in the Co-C distances. These range from 1.875(4) Å to 1.913(3) Å , and average 1.895 Å. The shortest of these is the _trans_ distance, which is considered significantly shorter than the equatorial average 1.900 Å; an octahedral _trans_ influence is indicated. The situation is not so simple; however, as a shortened _trans_ bond with respect to chemically and structurally equivalent _cis_ bonds. Significant differences exist within the equatorial Co-C distances themselves, which correlate well with close contacts to the water molecules hydrogen bonded to the peroxo group. Table IV-3 lists Co-C distances for each of the equatorial ligands along with close contacts to water molecules for each (N-O distances less than 3.4 Å).

Ligand	Co-C	Contact(s)
C(2)-N(2)	1.913 Å	3.03 Å to O(5), 3.33 Å to O(6)
C(3)-N(3)	1.900 Å	3.24 Å to O(5)
C(5)-N(5)	1.895 Å	3.27 Å to O(6)
C(4)-N(4)	1.890 Å	No contacts < 3.4 Å to H_2O

Table IV-3

The order of decreasing contact with water molecules is seen to be the same as the order of decreasing Co-C distances. This seems to be an example of the effects of intermolecular forces upon bond distances.

The C-N distances in the binuclear anion range from 1.136 to 1.163 Å and average 1.149(6) Å, which is a quite typical distance for a cobalt cyano complex. The Co-Co distance, always a subject of interest in binuclear structures, is 4.899(2) Å.

The nitrate ion and its surroundings are shown in Figure IV-5, distances and angles within the ion are given in Table IV-4. The nitrate ion is ordered in this structure, which seems to be the exception rather than the rule in structures of binuclear cobalt ions. Hydrogen bond donation from the water molecule O(6) no doubt aids in bringing about this fortunate state of affairs. The hydrogen bond is rather strong, with an O···O distance of 2.87 Å, an H···O distance of 2.22 Å and an O-H···O angle of 137°. While nitrate oxygen atom O(4) is engaged in a hydrogen bond, the other two oxygen atoms of this ion make close contacts with neighboring nitrate ions related by a 2_1 operation along y. The interionic nonbonded O···O distance is surprisingly short, 2.97 Å.

Within the precision of this experiment, the three oxygen atoms of the nitrate ion form a perfectly equilateral triangle with side 2.157(3) Å, and the ion is perfectly planar. The central nitrogen atom is removed within the plane from the center of the triangle by an amount of borderline statistical significance.

TABLE IV-4. GEOMETRY OF THE NITRATE ION

Atoms	Distance or Angle
N(6)-O(2)	1.236(5) Å
N(6)-O(3)	1.243(5)
N(6)-O(4)	1.258(5)
O(2)-N(6)-O(3)	120.6(4)°
O(2)-N(6)-O(4)	119.9(4)
O(3)-N(6)-O(4)	119.5(4)

TABLE IV-5. CLOSEST CONTACTS (LESS THAN 3.3 Å) TO THE POTASSIUM IONS IN $K_8\{(CN)_5CoO_2Co(CN)_5\}(NO_3)_2 \cdot 4H_2O$

Contact	Distance (Å)	Contact	Distance (Å)
K(1)···O(4)	2.75	K(3)···O(5)	3.08
K(1)···O(5)	2.69	K(3)···O(6)	2.68
K(1)···N(1)	2.79	K(3)···O(6')	3.21
K(1)···N(1')	2.93	K(3)···N(2)	2.95
		K(3)···N(2')	3.01
K(2)···O(2)	2.83	K(3)···N(4)	3.01
K(2)···O(3)	2.91	K(3)···N(5)	2.80
K(2)···O(3')	2.98		
K(2)···O(4)	2.80	K(4)···O(2)	2.89
K(2)···N(1)	3.09	K(4)···O(3)	2.88
K(2)···N(3)	2.81	K(4)···O(5)	3.01
K(2)···N(4)	3.21	K(4)···O(6)	2.97
K(2)···N(5)	2.95	K(4)···N(2)	2.96
K(2)···N(6)	3.20	K(4)···N(3)	2.88
K(2)···N(6')	3.26	K(4)···N(4)	2.93
		K(4)···N(5)	2.94

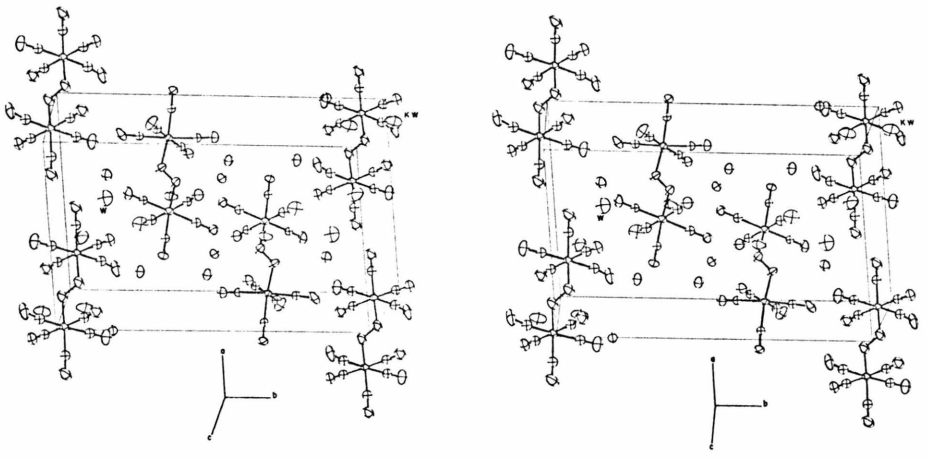
The four independent potassium ions of the structure have irregular coordination spheres, and any attempt to classify them as distorted forms of idealized polyhedra would be pointless. Closest contacts to the K^+ ions are listed in Table IV-5. These ions are anisotropic to varying degrees, however, their thermal amplitudes are by no means extreme.

The two independent water molecules of the structure have quite normal geometries. In both cases, as seen in Figures IV-3 and IV-5, the thermal motion of the oxygen atom is essentially normal to the molecular plane. The molecule containing O(5) has O-H distances of 0.73(5) and 0.76(5) Å, with an H-O-H angle of 106(4)°. That containing O(6) has O-H distances of 0.80(4) and 0.90(4) Å, with an H-O-H angle of 111(3)°.

B. $K_5\{(CN)_5CoO_2Co(CN)_5\}\cdot H_2O$

The crystal structure of this salt consists of a nearly parallel arrangement of two crystallographically distinct binuclear ions in a 2:1 ratio, one acentric and the other centric, with K^+ ions and water molecules surrounding the anions. Figure IV-6 illustrates the packing of ions and molecules in the unit cell. The hypersymmetry of this arrangement has been described briefly in the structure solution section and is clearly illustrated here. Along the body diagonal of the unit cell, crystallographic centers of symmetry

Figure IV-6



The crystal packing, with the unit cell outlined. The atom labelled W and its inversion equivalent are ordered water molecules; the atom labelled KW and its symmetry equivalents are $1/2(K^+ + H_2O)$ "atoms". Ellipsoids enclose 40% probability.

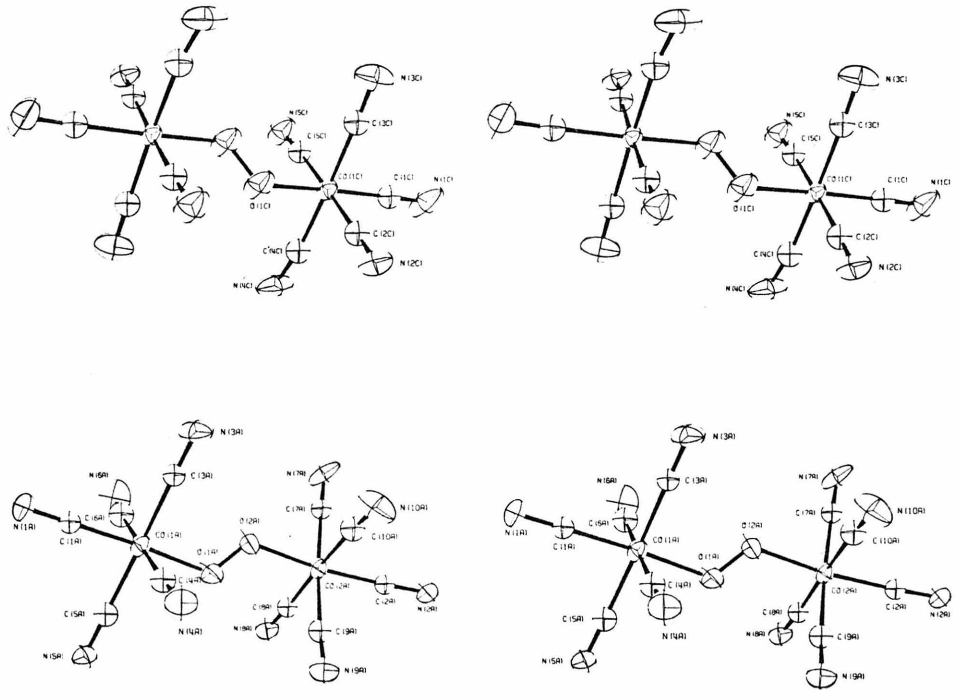
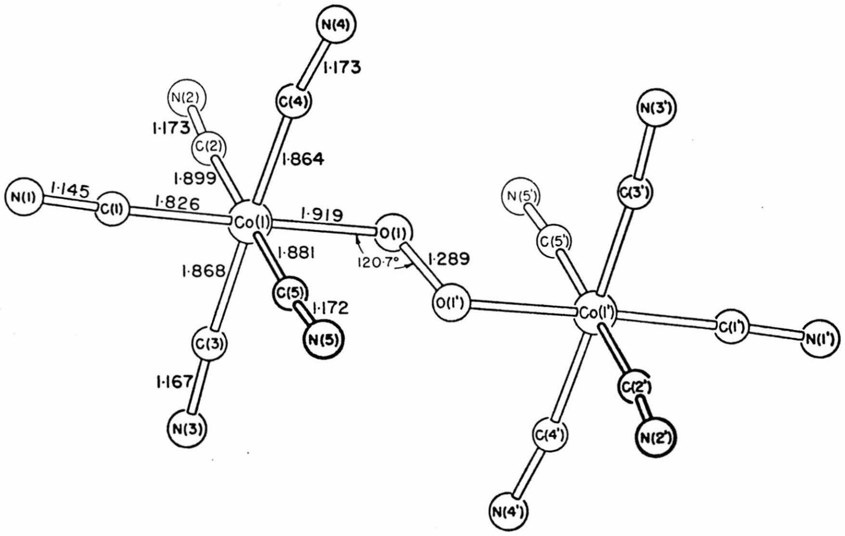


Figure IV-7
ORTEP stereopairs of anions C (above) and A. Ellipsoids enclose 40% probability.

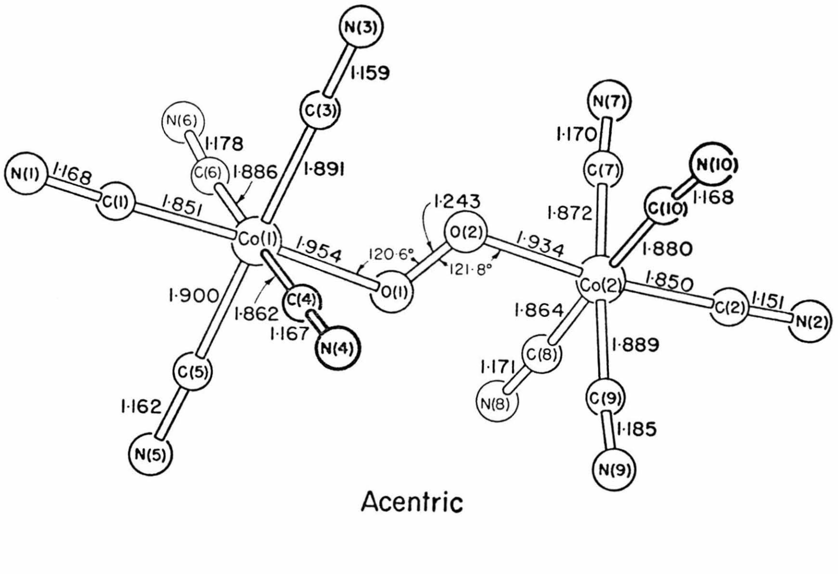
are located at zero and ½ the diagonal length. Pseudocenters are located at 1/6, 1/3, 2/3 and 5/6, causing a rough hypersymmetric array of binuclear ions which has a repeat unit 1/3 as large as the actual unit cell.

The $\{(CN)_5CoO_2Co(CN)_5\}^{5-}$ ion is seen in this structure to come in two delicious flavors, one which lies on a center of symmetry, hereafter referred to as the centric anion or anion C, and another of no symmetry which will be hereafter referred to as the acentric anion or anion A. Conformations and thermal ellipsoids of the two distinct anions are seen in Figure IV-7, and interatomic distances within these ions are given in Figure IV-8. The centric anion, which has rigorous C_i symmetry, deviates only slightly from C_{2h}, the O-O grouping being nearly eclipsed with respect to the equatorial ligand C(5)-N(5). Neglecting the off-set due to the O-O bridge, the equatorial ligands of the two cobalt centers are eclipsed, as is usually found to be the case in 2:1 dioxygen-bridged complexes, and the Co-O-O-Co linkage is, of course, exactly planar. The acentric anion has a quite different conformation, having no crystallographic symmetry nor even any close correspondence to non-crystallographic, idealized symmetry. In this ion, the equatorial ligands about the two cobalt centers are staggered by about 35°; in addition, there is a twist about the O-O bond, making the superoxide group Co-O-O-Co non-planar and the planes of the two sets of equatorial ligands non-parallel. The torsion angle about the O-O bond is 166°.

Figure IV-8



Centric



Acentric

Bond distances and bridging angles for anions A and C. In anion C, esd's are 0.02 Å for O-O and C-N, 0.009 Å for Co-O, and 0.015 Å for Co-C. Values are similar for anion A except for C-O, which has an esd of 0.013 Å.

Table IV-6 Bond Angles in the $[(CN)_5CoO_2Co(CN)_5]^{5-}$ Ions

The Centric Ion	
O(1C) - Co(1C) - C(1C)	177.3(6)°
C(2C) - Co(1C) - C(5C)	178.7(6)°
C(3C) - Co(1C) - C(4C)	177.4(7)°
O(1C) - Co(1C) - C(2C)	84.6(5)°
C(3C)	92.5(5)°
C(4C)	87.0(7)°
C(5C)	94.2(5)°
C(1C) - Co(1C) - C(2C)	92.8(6)°
C(3C)	88.4(6)°
C(4C)	92.2(6)°
C(5C)	88.4(7)°
C(2C) - Co(1C) - C(3C)	91.6(7)°
C(4C)	90.9(7)°
C(5C) - Co(1C) - C(3C)	88.8(7)°
C(4C)	88.7(7)°
Co(1C) - C(1C) - N(1C)	178.7(14)°
C(2C) - N(2C)	177.6(12)°
C(3C) - N(3C)	176.8(15)°
C(4C) - N(4C)	171.7(14)°
C(5C) - N(5C)	176.8(14)°
Co(1C) - O(1C) - O(1C′)	120.7(10)°

The Acentric Ion	
O(1A) - Co(1A) - C(1A)	176.2(5)°
C(3A) - Co(1A) - C(5A)	173.6(5)°
C(4A) - Co(1A) - C(6A)	179.1(6)°
O(1A) - Co(1A) - C(3A)	93.6(5)°
C(4A)	88.0(5)°
C(5A)	89.9(5)°
C(6A)	91.2(6)°
C(1A) - Co(1A) - C(3A)	89.1(6)°
C(4A)	89.4(6)°
C(5A)	87.2(6)°
C(6A)	91.4(6)°
C(3A) - Co(1A) - C(4A)	88.1(6)°
C(6A)	91.5(6)°
C(5A) - Co(1A) - C(4A)	86.6(7)°
C(6A)	93.8(7)°
Co(1A) - C(1A) - N(1A)	177.0(14)°
C(3A) - N(3A)	176.6(13)°
C(4A) - N(4A)	177.7(14)°
C(5A) - N(5A)	173.3(13)°
C(6A) - N(6A)	175.0(12)°
Co(1A) - O(1A) - O(2A)	120.6(6)°
O(2A) - Co(2A) - C(2A)	173.1(5)°
C(7A) - Co(2A) - C(9A)	175.2(7)°
C(8A) - Co(2A) - C(10A)	176.3(6)°
O(2A) - Co(2A) - C(7A)	87.4(5)°
C(8A)	93.0(5)°
C(9A)	94.8(5)°
C(10A)	87.6(5)°
C(2A) - Co(2A) - C(7A)	86.3(6)°
C(8A)	90.2(6)°
C(9A)	91.3(6)°
C(10A)	89.7(6)°
C(7A) - Co(2A) - C(8A)	94.1(6)°
C(10A)	89.6(6)°
C(9A) - Co(2A) - C(8A)	90.1(6)°
C(10A)	86.2(6)°
Co(2A) - C(2A) - N(2A)	176.3(13)°
C(7A) - N(7A)	178.3(14)°
C(8A) - N(8A)	176.0(12)°
C(9A) - N(9A)	173.2(13)°
C(10A) - N(10A)	172.9(13)°
Co(2A) - O(2A) - O(1A)	121.8(7)°

Torsion Angles	
C(2C) - Co(1C) - O(1C) - O(1C′)	150.5°
C(3A) - Co(1A) - O(1A) - O(2A)	-15.7°
C(8A) - Co(2A) - O(2A) - O(1A)	54.6°
Co(1A) - O(1A) - O(2A) - Co(2A)	165.9°

The presence of both a planar and a non-planar μ-superoxo group in the same structure indicates very strongly that packing forces are a very important factor in determining the O-O torsion angle. Anion A is in an ordered environment, and presumably adopts a slightly non-planar conformation to enable it to fit best among the fixed cations. Anion C, however, has as close neighbors two pairs of disordered potassium ions and water molecules (KW); presumably this slight disorder puts less constraint on the anion, and it can adopt the more favored planar conformation.

The fact that two different conformations of the same ion are present in the same structure also presents us with an opportunity to explore the effects of conformation upon bond lengths, but unfortunately, the somewhat low precision of our determination limits us in this respect. We are not, at this level of precision, able to definitively distinguish any differences in bond lengths between the two ions. The Co-Co distances are identical, having values of 4.634(8) Å for the centric ion and 4.637(6) Å for the acentric ion. The largest difference between ions A and C is the O-O bond length, the determination of which is a primary interest in this investigation. The centric O-O distance, 1.289(20) Å, is among the least precisely known distances of the structure, and differs from that of the acentric anion by 0.046 Å, about twice the esd of the difference. Thus the difference is of marginal significance at this level of precision. The average O-O distance is 1.262 Å.

Co-O distances range from 1.919(9) to 1.954(9) Å, and average 1.936 Å. The difference between the largest and smallest of these values is 0.035 Å, which cannot be said to be significant at this level of precision. Accompanying this rather long Co-O distance, we also find a shortening of almost 0.04 Å in the trans Co-C distance (average 1.842(7) Å) relative to the average equatorial distance, 1.880(4) Å. This difference is formally about 5σ and is considered significant.

The C-N distances of the cyanide ligands range from 1.145(19) to 1.185(23) Å and average 1.167(8) Å. Co-C-N angles deviate from linearity by amounts up to about eight degrees; such deviations are common in terminal cyanide ions coordinated to transition metals.

Although hydrogen atoms were not located, hydrogen bonds can be postulated from examination of distances between the water molecules and cyanide nitrogen atoms. The ordered water molecule O(4) occupies a position in proximity to (i.e., less than 3.3 Å distant from any atom in) three different binuclear anions, but only one contact can be found indicative of hydrogen bonding; the O(4)-N(6A) distance is 2.86 Å. The disordered water molecule exhibits more possibilities for hydrogen bonding. The "KW" atom, an artifact half-populated with both K^+ and O, is disordered about (0,0,½), and thus is

Table IV-7 Closest Contacts[a] (less than 3.3 Å) to the Potassium Ions

K(1) -	N(5A)	3.21 Å	K(2) -	N(4C)	2.75 Å	K(3) -	O(4)	2.83 Å	K(4) -	N(4C)	3.21 Å
	N(1A)	2.90 Å		N(6A)	3.01 Å		N(2C)	2.93 Å		O(1C)	3.03 Å
	N(2A)	3.06 Å		N(2C)	3.01 Å		N(3A)	2.91 Å		N(1A)	2.91 Å
	N(8A)	2.98 Å		N(1A)	3.08 Å		N(1C)	2.86 Å		N(10A)	2.79 Å
	N(9A)	2.88 Å		N(2A)	3.02 Å					N(7A)	2.85 Å
	N(8A′)	3.04 Å									
K(5) -	N(3A)	3.03 Å	K(6) -	N(5A)	2.78 Å	K(7) -	N(6A)	3.15 Å	KW -	N(4C)	3.11 Å
	N(7A)	3.04 Å		N(4A)	2.71 Å		N(8A)	2.87 Å		N(2C)	2.93 Å
	N(1C)	2.80 Å		N(2A)	2.80 Å		N(4A)	2.75 Å		N(3C)	3.11 Å
	O(2C)	3.24 Å		N(5A)	3.22 Å		N(10A)	3.10 Å		KW′	2.70 Å
	O(4)	2.87 Å		N(9A)	3.01 Å		N(9A)	3.08 Å		N(5C)	2.82 Å
	N(3C)	2.82 Å		O(1A)	2.88 Å		N(5A)	3.17 Å			
	N(5C)	2.92 Å									

[a] Where both C and N atoms of a cyanide ligand are closer than 3.3 Å, only the N atom is listed.

located between two centric anions related by a unit translation along z. The actual position of the water molecule is poorly known, as its position was constrained to exactly correspond with that of the half-potassium atom, which is probably not realistic. Possible hydrogen bonding distances are 2.93 Å to N(2C), 3.11 Å to N(3C), 3.11 Å to N(4C), and 2.82 Å to N(5C). The distance of 2.70 Å from KW to its inversion-related equivalent represents in principle another possibility for hydrogen bonding, if in any particular unit cell both positions are simultaneously occupied by water molecules. Each such configuration would, however, require that in another area of the crystal, two K^+ ions also occupy adjacent positions separated by 2.70 Å, which is unreasonably short; therefore, we believe that the statistical centers are due only to the configurations $K^+\cdots H_2O$ and $H_2O\cdots K^+$ in equal populations.

Close contacts to the potassium ions are listed in Table IV-7. The coordination of these ions follows no regular pattern, and cannot easily be described in terms of regular or distorted polyhedra. The number of atoms within 3.3 Å of the potassium ions is seen to vary from four to seven among the eight independent K^+ ions within the unit cell.

C. $\{(NH_3)_5CoO_2Co(NH_3)_5\}(SCN)_4$

The results of this structure determination agree well with the original investigation in terms of the general shapes and arrangements of ions. The new refinement has resulted in several improvements, however, over the older model. In addition to confirming the planarity of the binuclear ion and locating the hydrogen atoms, this work has resulted in a much higher precision in interatomic distances, and in particular, revealed the peroxo O-O distance to be normal. This structural determination was carried out primarily because the O-O distance found by Vannerberg,[29] 1.65(3) Å, appeared to be anomalous with respect to those found in similar complexes and even in the same cation crystallized with another counterion.[30] The distance found here is 1.469(6) Å, a much more reasonable value.

We find the $\{(NH_3)_5CoO_2Co(NH_3)_5\}^{4+}$ cation to have crystallographic C_{2h} symmetry. Bond distances and angles are given in Figure IV-9 and Table IV-8. The conformations of the ammine ligands as well as a representation of the thermal parameters are given in Figure IV-10. The Co-O-O-Co group in this ion is rigorously planar, and thermal ellipsoids of the bridging oxygen atoms and axial nitrogen ammine ligand are of reasonable orientation and size to suggest that this planarity is not due to a statistical disorder of forms with a torsion angle smaller than 180°.

The Co-O distance, 1.879(3) Å, is quite normal for this type of complex. The Co-ammine distances are reasonable for

TABLE IV-8. ANGLES IN $\{(NH_3)_5CoO_2Co(NH_3)_5\}^{4+}$

Cation	
Atoms	Angle (Degrees)
N(1)-Co-O	89.5(1)
N(2)-Co-O	88.1(1)
N(3)-Co-O	178.3(5)
N(1)-Co-N(1')	88.6(2)
N(1)-Co-N(2)	91.5(2)
N(1)-Co-N(2')	177.6(4)
N(1)-Co-N(3)	91.7(2)
N(2)-Co-N(2')	88.3(2)
N(2)-Co-N(3)	90.7(2)

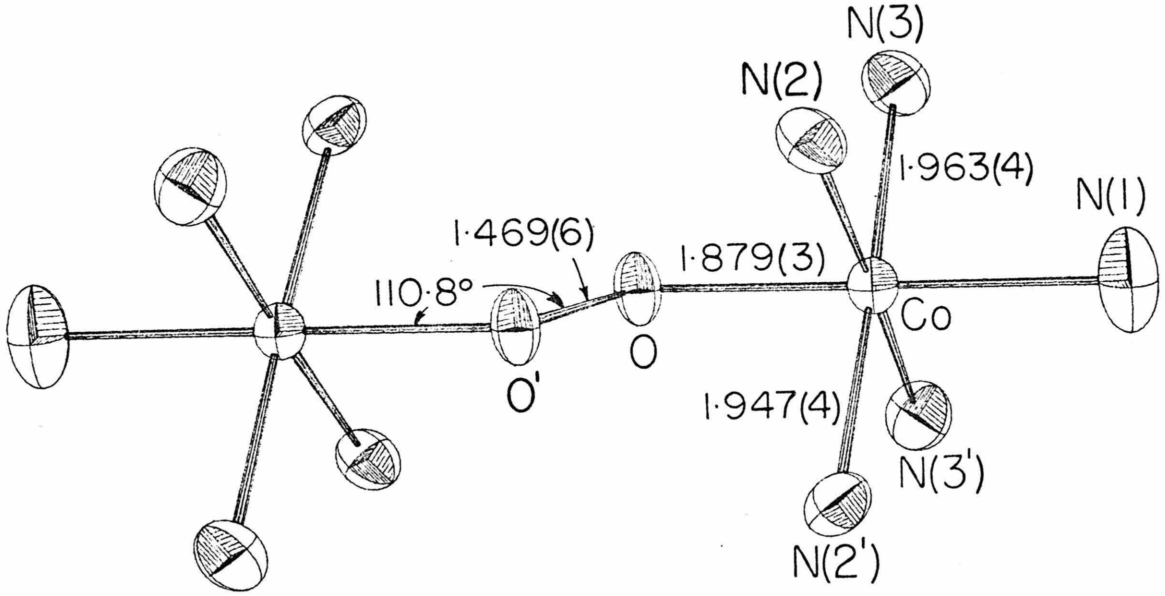


Figure IV-9
The non-hydrogen atoms of the cation, with interatomic distances and their esd's. Thermal ellipsoids enclose 40% probability.

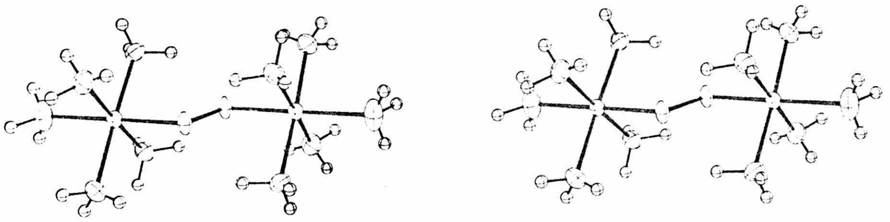


Figure IV-10
Stereopair of the cation. Thermal ellipsoids enclose 40% probability, and hydrogen atoms are represented by spheroids of arbitrary radius.

a Co(III) complex. They vary from 1.947(4) to 1.971(7) Å, and this range is outside the limits of experimental error. As the equatorial distances vary significantly, no special significance can be placed upon the fact that the axial Co-N distance is the longest such bond. Comparison to similar compounds suggests that this trans lengthening may in fact be real, as will be discussed later.

The ordered thiocyanate ion is found to be linear, with bond distances tabulated in Table IV-9. These bond lengths indicate normal S-C≡N bonding. Speculations made in the earlier work about bonding within this group should be disregarded, as they are based upon an erroneous carbon position. The disordered thiocyanate groups are both linear; however, the interatomic distances of that containing SN(2) are simply not reasonable. This is clearly due to the fact that, after the failure of ΔF refinement, as discussed in the section involving structure solution and refinement, the sulfur atom and the nitrogen atom of the alternate arrangement were constrained to exactly the same position in order to facilitate least squares refinement. Except by accident, this procedure cannot lead to a model which approximates reality, and such a happy accident has not befallen us in this case. The large thermal parameters of atom SN(2) are a further indication that the model for this disordered ion is inadequate. The intensity data have been fit well by this model; however,

TABLE IV-9. GEOMETRIES OF THE THIOCYANATE IONS

Ordered Thiocyanate		Disordered Thiocyanates	
Atoms	Angle or Length	Atoms	Angle or Length
S-C(3)	1.626(7) Å	SN(1)-C(1')	1.63(4) Å
C(3)-N(4)	1.16(1) Å	C(1)-C(1')	0.64(8) Å
S-C(3)-N(4)	179.8(2)°	SN(1)-C(1)-SN(1')	179(1)°
		SN(2)-C(2')	1.70(2) Å
		C(2)-C(2')	0.76(4) Å
		SN(2)-C(2)-SN(2')	178(1)°

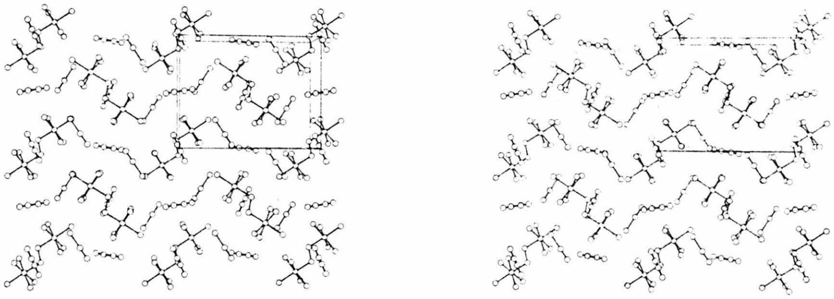
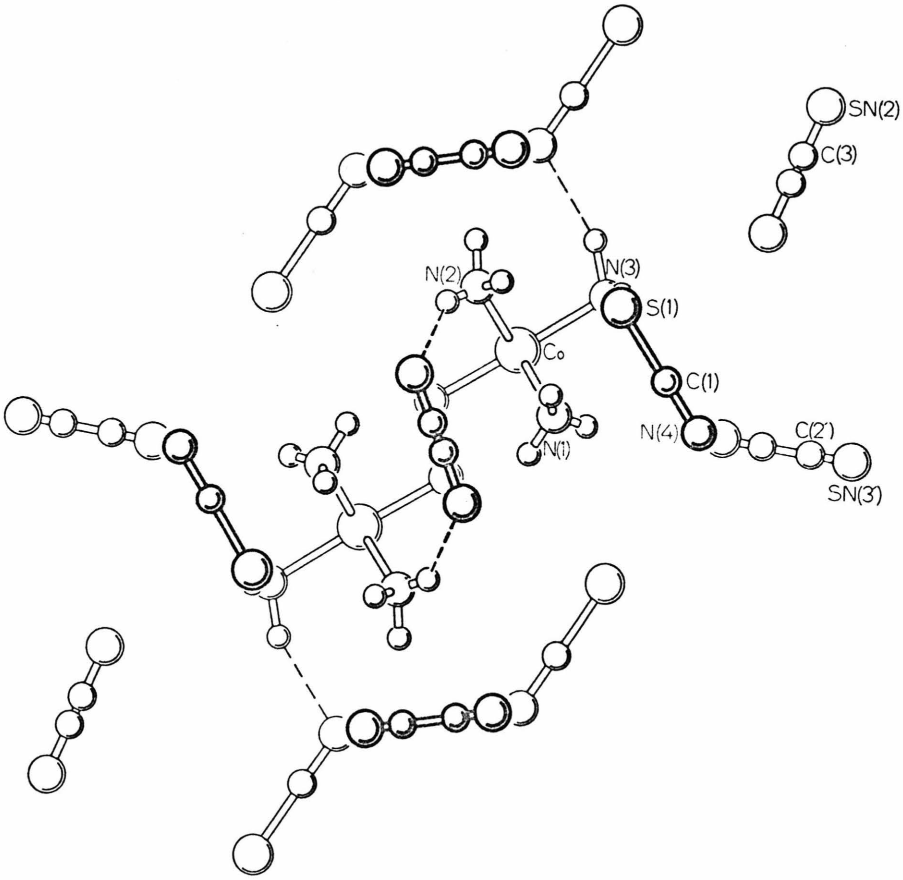


Figure IV-11

ORTEP stereopair of the crystal packing, viewed down the c axis. Two unit translations are shown in the a and b directions, and 1/2 unit translation is shown in the vertical direction. The outlined area is 1/2 unit cell.

Figure IV-12



The configuration of the thiocyanate ions around the cation, illustrating the lack of extensive hydrogen bonding. Closest contacts are indicated by dashed lines. The four-atom groups are SN-C-C-SN disordered thiocyanate ions.

as a difference map of this region calculated after the conclusion of the refinement was essentially flat.

The packing of ions in this structure is illustrated in Figure IV-11, and the manner in which the thiocyanate ions surround the binuclear cation is shown in the simplified illustration, Figure IV-12. The cation is seen to be surrounded by 18 anions, of which only two are situated in reasonable positions to suggest hydrogen bonding. Good hydrogen bonding parameters exist between the axial ammine nitrogen atom N(3) and the nitrogen atom N(4') of the ordered thiocyanate ion lying on the (001) mirror plane. The N···N distance is 3.10 Å, and the N-H···N angle is 160°. Other contacts illustrated in Figure IV-12 are too long to be considered as hydrogen bonds. Lack of favorable circumstances for hydrogen bonding to the disordered thiocyanate ions allows us to understand their ambivalence, as an ammine donating a hydrogen bond would certainly prefer the nitrogen end of thiocyanate as an acceptor.

Planar chains of 14 atoms SCN···(cation)···NCS exist lying on the (001) mirror plane, with no bonding connecting these chains out of plane. This accounts for the ease with which crystals can be cut normal to the c axis.

D. $K_6\{(CN)_5CoSSO_2Co(CN)_5\}\cdot 6H_2O$

The crystal structure of this salt consists of discrete potassium ions, water molecules, and binuclear anions containing the thiosulfito bridging group. One potassium ion and virtually all the solvent molecules are affected by disorder; however, the interesting part of the structure, the μ-thiosulfitodecacyanodicobalt(III)ate anion, appears to be completely ordered and well-behaved.

An ORTEP representation of this ion is seen in stereopair in Figure IV-13, which illustrates the orientations of the thermal ellipsoids as well as the overall conformation of the ion. Bonding interatomic distances and a few important angles are given in Figure IV-14, and other bonding angles are listed in Table IV-10. The coordination about both cobalt centers is seen to be essentially octahedral, with only minor distortions, and the distances from cobalt to coordinated ligands support the formulation of both as Co(III). Figure IV-15 is a view of the binuclear ion approximately down the Co-Co vector, illustrating the deviations from the C_s (mirror) symmetry which is conceivably possible for this ion.

The S-S distance of the coordinated thiosulfite ligand, 2.064(3) Å, is indicative of a single bond. It agrees well with the average value of 2.07 Å found in polysulfides and polythionates,[59] the value of 2.059 Å found in orthorhombic S ,[60] and the average value of 2.062 Å found in thiosulfate complexes in which only the terminal sulfur atom is coordinated.[61-63] The thiosulfite ligand is coordinated as a

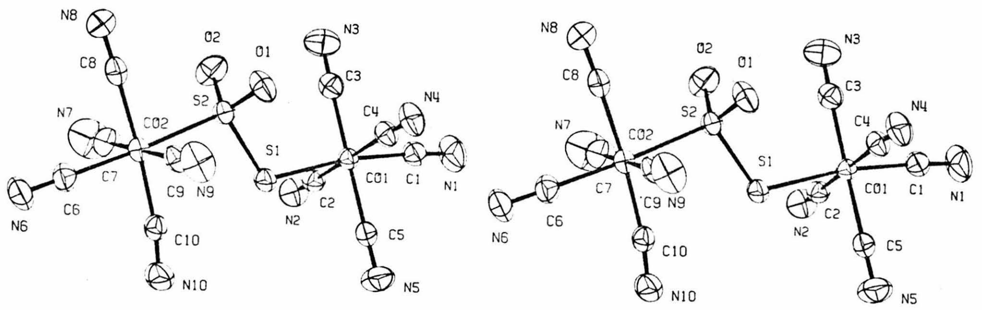
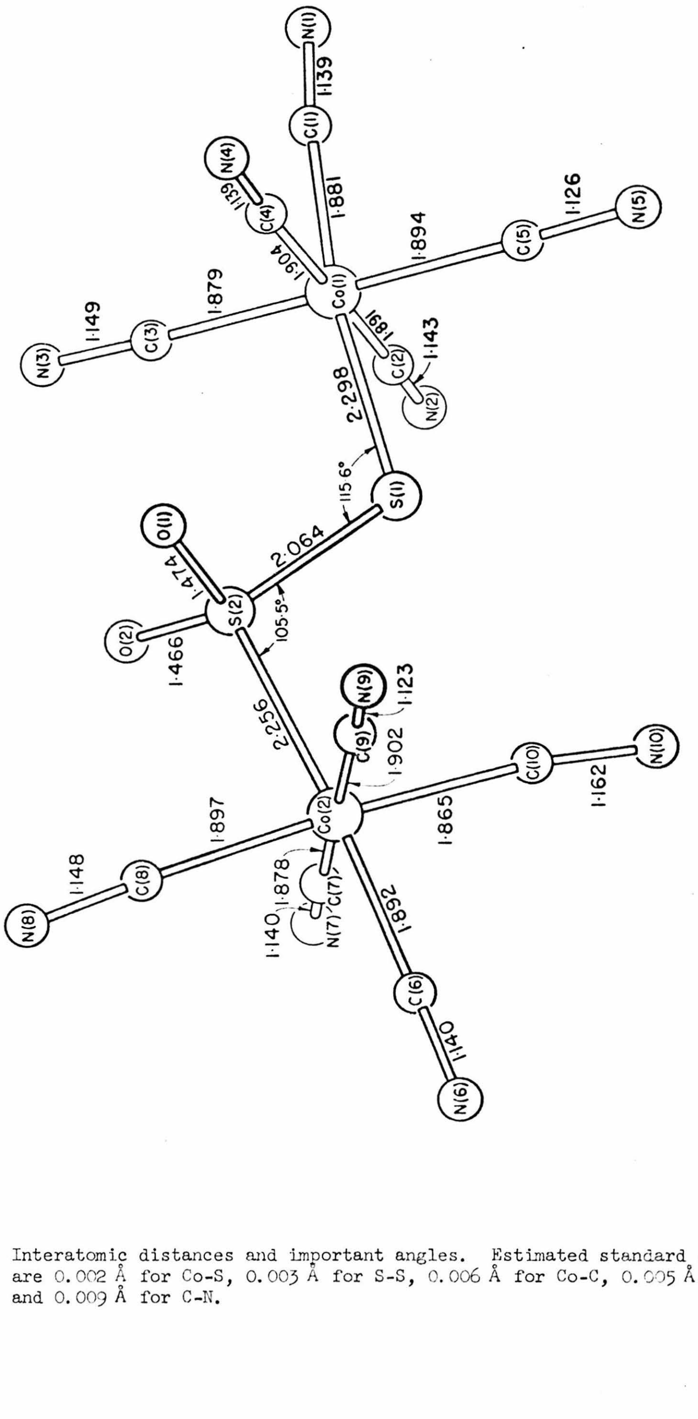


Figure IV-13

The decacyano-μ-thiosulfitodicobalt(III)ate anion in stereopair. Atoms are represented by thermal ellipsoids enclosing 50% probability.

Figure IV-14

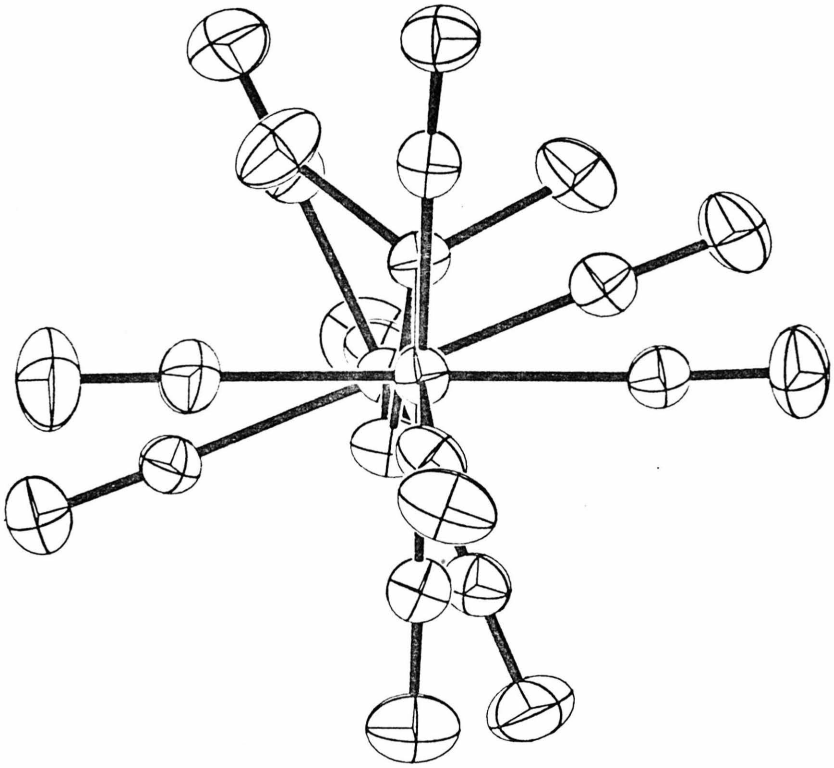


Interatomic distances and important angles. Estimated standard deviations are 0.002 Å for Co-S, 0.003 Å for S-S, 0.006 Å for Co-C, 0.005 Å for S-O, and 0.009 Å for C-N.

TABLE IV-10. BONDING ANGLES

Atoms	Angle (Degrees)	Atoms	Angle (Degrees)
S(1)-Co(1)-C(1)	171.0(3)	S(2)-Co(2)-C(6)	175.9(2)
S(1)-Co(1)-C(2)	87.4(2)	S(2)-Co(2)-C(7)	89.2(2)
S(1)-Co(1)-C(3)	97.7(2)	S(2)-Co(2)-C(8)	87.4(2)
S(1)-Co(1)-C(4)	93.2(2)	S(2)-Co(2)-C(9)	89.5(2)
S(1)-Co(1)-C(5)	83.5(2)	S(2)-Co(2)-C(10)	97.3(2)
C(1)-Co(1)-C(2)	88.6(3)	C(6)-Co(2)-C(7)	92.5(3)
C(1)-Co(1)-C(3)	90.3(3)	C(6)-Co(2)-C(8)	88.8(3)
C(1)-Co(1)-C(4)	90.8(3)	C(6)-Co(2)-C(9)	89.0(3)
C(1)-Co(1)-C(5)	88.4(3)	C(6)-Co(2)-C(10)	86.5(3)
C(2)-Co(1)-C(3)	88.9(3)	C(7)-Co(2)-C(8)	92.1(3)
C(2)-Co(1)-C(4)	179.3(3)	C(7)-Co(2)-C(9)	178.2(3)
C(2)-Co(1)-C(5)	89.6(3)	C(7)-Co(2)-C(10)	88.8(3)
C(3)-Co(1)-C(4)	90.8(3)	C(8)-Co(2)-C(9)	89.1(3)
C(3)-Co(1)-C(5)	178.0(2)	C(9)-Co(2)-C(10)	175.2(2)
C(4)-Co(1)-C(5)	90.7(3)	C(9)-Co(2)-C(10)	90.1(3)
Co(1)-C(1)-N(1)	175.9(7)	Co(2)-C(6)-N(6)	175.7(6)
Co(1)-C(2)-N(2)	178.4(6)	Co(2)-C(7)-N(7)	178.1(7)
Co(1)-C(3)-N(3)	177.0(4)	Co(2)-C(8)-N(8)	176.1(4)
Co(1)-C(4)-N(4)	178.0(6)	Co(2)-C(9)-N(9)	176.2(6)
Co(1)-C(5)-N(5)	179.0(4)	Co(2)-C(10)-N(10)	172.8(6)
Co(1)-S(1)-S(2)	115.6(1)		
Co(2)-S(2)-S(1)	105.5(1)		
Co(2)-S(2)-O(1)	111.8(2)		
Co(2)-S(2)-O(2)	111.6(2)		
S(1)-S(2)-O(1)	109.2(2)		
S(1)-S(2)-O(2)	108.5(2)		
O(1)-S(2)-O(2)			

Figure IV-15



View of the anion $Co_2SSO_2(CN)_{10}{}^{6-}$ approximately down the Co-Co vector. Thermal ellipsoids enclose 40% probability.

bridging group to the two cobalt atoms through the two sulfur atoms, with the two distinct Co-S distances differing significantly. The bond to the thiosulfur atom is greater than 0.04 Å (14σ) longer than the bond to the sulfito sulfur atom, and the Co-S-S angles differ as well. The Co-S(thio) bond, with length 2.298(2) Å, compares favorably with the value of 2.284(6) Å found in $\{(NH_3)_5CoSSO_3\}^+$,[61] being perhaps slightly longer, and the Co-S(sulfito) bond, with length 2.256(2) Å, is somewhat longer than the corresponding distance of 2.203(6) Å in $Co(en)_2SO_3NCS$.[64] The distance observed in the present complex is very close to the sum of the covalent radii of Co(III) and tetrahedral sulfur, 2.26 Å. The angles about this sulfur atom are slightly distorted tetrahedral, the smallest being Co(2)-S(2)-S(1), which has a value of 105.5(1)°. The thio sulfur atom S(1) is the apex of a very large angle 115.6(1)°; this angle is outside the normal range for two-coordinate sulfur (100-111°), and approaches that expected for sp^2 hybridization.

The two S-O distances of the thiosulfite ligand are equal within experimental error and average 1.470(5) Å. This is comparable to the values found for coordinated sulfites in other metal complexes. The average S-O distance in $Co(en)_2SO_3NCS$ is 1.485(9) Å , and the average in $Pd(NH_3)_3SO_3$ is 1.494(10) Å.[64,65] The nonbonded O-O distance is 2.41 Å, a typical value for various sulfur oxides. The structural unit Co-S-S-Co is essentially planar, having a torsion angle about the S-S bond of about 179°. No particular bonding implications are drawn from this observation, since it is the conformation to be expected from steric considerations alone.

Co-C distances vary from 1.865(6) to 1.904(6)Å ; this range is outside statistical variation. The different bonding environments of Co(1) and Co(2) appear to have no detectible effect upon the coordinated cyanide ligands, as the average Co-C distances about both cobalt atoms are the same within experimental error. These distances about Co(1) average 1.890 Å; and the corresponding average about Co(2) is 1.887 Å. The overall average Co-C distance is 1.888 Å, very close to the expectation value of 1.890 Å (see discussion in later section). No structural <u>trans</u> influence is apparent at either cobalt center; in both cases the <u>trans</u> distance is indistinguishable from the average value.

All cyanide ligands coordinate to cobalt in the usual "linear" fashion, with the maximum deviation from ideal linearity being about seven degrees. All are coordinated via the carbon atom, as indicated by the normal temperature factors derived from this model. Individual C-N distances range from 1.123(9) to 1.162(9) Å and average 1.141(3) Å , very close to the expectation value of 1.148 Å .

A description of the crystal packing is somewhat confused by the disorder and partial occupancy associated with K(7) and most of the water molecules. In general, it can be said that the highly charged (6-) anions are well separated from each other by an envelope of potassium counterions and water molecules hydrogen bonded to each other and to the anions. The anions, which are about 12 Å in the longest dimension, are spaced at least 9 Å apart, each being surrounded by 22 K^+ ions and 27 water sites within 3.5 Å.

Contacts less than 3.4 Å to the potassium ions are listed in Table IV-11. Their environments are seen to consist of primarily cyanide ligands and water molecules, with an occasional contact to a sulfito oxygen atom. All contacts are greater than or equal to 2.6 Å. The potassium ions are seen to be predominantly eight-coordinate, with the notable exception of K(1), which sits astride a twofold axis and has only six close contacts to cyanide ligands of two binuclear ions related by that axis.

Table IV-12 lists close contacts to the water sites, excluding those to potassium ions. While some of these contacts may be considered as indicative of hydrogen bonding, few appear to be particularly strong. For no particular water molecule is it clear from examination of its intermolecular contacts where its hydrogen atoms should "prefer" to locate themselves. This, in conjunction with the fact that most sites are only partially populated, eradicates any surprise one might feel from failure to locate definite positions for these hydrogen atoms. Examination of distances from water

TABLE IV-11. CONTACTS LESS THAN 3.4 Å TO THE POTASSIUM IONS

Contact	Distance (Å)	Contact	Distance (Å)
K(1)-N(4)	2.82	K(5)-O(1)	2.76
N(6)	3.02	O(1')	2.92
N(8)	3.23	N(4)	3.06
		N(8)	3.03
K(2)-O(1)	2.79	N(9)	3.00
O(2)	3.38	N(9')	3.37
N(3)	2.94	O(4W)	2.84
N(5)	2.81	O(5W)	2.96
N(6)	2.86	O(9W)	2.62
N(9)	2.75	O(10W)	2.76
O(4W)	2.93		
O(5W)	3.02	K(6)-O(2)	2.73
		N(1)	2.80
K(3)-O(2)	2.74	N(2)	2.88
N(2)	3.22	N(8)	3.20
N(2')	2.92	N(10)	3.01
C(3)	3.36	O(2W)	3.18
N(7)	3.32	O(5W)	3.27
O(2W)	2.86	O(8W)	2.91
O(8W)	2.74		
O(11W)	2.81	K(7)-N(1)	2.98
		N(1')	3.01
K(4)-N(4)	3.29	N(7)	2.80
N(5)	3.34	O(6W)	2.75
N(6)	3.30	O(7W)	2.60
N(8)	2.95	O(7W')	3.40
N(10)	2.93	O(11W)	3.25
O(1W)	2.87	O(12W)	3.05
O(1W')	2.80		
O(12W)	3.22		

TABLE IV-12. CLOSE CONTACTS TO THE WATER MOLECULES

Contact	Distance(Å)	Contact	Distance(Å)
O(1W)-N(6)	3.40	O(6W)-N(3)	3.18
N(9)	3.27	N(5)	3.09
O(1W')	3.27	N(7)	2.98
O(9W)	2.81	O(7W)	3.26
O(10W)	2.74	O(11W)	2.50
O(2W)-N(3)	3.27	O(7W)-N(3)	2.87
N(10)	3.23	N(5)	3.40
O(3W)	3.03	N(7)	3.06
O(8W)	3.37		
O(11W)	3.16	O(8W)-O(2)	3.26
		N(3)	3.00
O(3W)-N(1)	2.99	N(5)	3.09
N(3)	3.18		
N(7)	3.32	O(9W)-O(9W')	3.01
O(6W)	2.49	O(10W)	3.29
O(7W)	2.56		
O(7W')	3.03	O(10W)-S(1)	3.29
O(12W)	2.70	C(4)	3.38
		C(5)	3.32
O(4W)-N(10)	2.98		
O(9W)	3.29	O(11W)-N(2)	3.26
O(9W')	2.81	N(3)	2.81
O(10W)	2.74	N(5)	3.30
		N(2)	2.65
O(5W)-N(8)	3.40		
N(10)	2.81	O(12W)-N(1)	3.19
O(9W)	2.91	N(5)	2.71
O(10W)	2.84	N(6)	3.32
		C(7)	3.27
		N(10)	3.19

molecules to potassium ions, listed previously, suggests that the cations, in packing closely around the highly charged binuclear anion, prevent water from approaching the cyanides too closely, and the resulting hydrogen bonds are weak. The primary purpose of water in this crystal is to occupy the voids left by the packing of the ionic species, and since these voids are not in all cases particularly well-defined or small, disorder of the solvent results. Good examples of the ill definition of the solvent regions are the pairs O(4W), O(5W) and O(9W), O(10W). Each pair represents two water sites which are less than one Angstrom apart and are normalized to contain a total of one water molecule, with the major site (80% occupancy) listed first. In both cases, although the major site has slightly more favorable contacts, the minor site represents a large void in the structure in the absence of occupancy of the major site. Partial population of these minor sites is not surprising. As mentioned in the refinement section, there are probably in reality several more sites of minor occupancy of solvent water, and in fact, it is not clear that the solvent is stoichiometric, as it has been treated here.

E. $(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$

This structure is a molecular crystal rather than an ionic salt as all those previously described have been. As mentioned before, it is isostructural with its linkage isomer $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$. Our structure determination confirms that it is indeed a binuclear molecule with cobalt(III) atoms in $(C)_5(N)$ and $(N)_5(C)$ environments, as was its characterization based on infrared, visible, and ultraviolet spectroscopy. In addition to confirmation of the original characterization, this determination has revealed details of geometry which, when compared with those of the cyano isomer, lead to a better understanding of bonding in cyano complexes. The effect of switching the bridging ligand from the cyano to the isocyano orientation appears to be generally a weakening of metal-ligand bonding and a strengthening of C-N bonding both in the terminal and bridging cyanide ligands.

Figure IV-16 is a stereoscopic view of the isocyano molecule, exhibiting the thermal ellipsoids and the conformations of the ammine ligands. Figure IV-17 is a comparison of the cyano and isocyano molecules in the same orientation as Figure IV-16. The thermal motions of the two isomers are seen to be quite similar, with RMS amplitudes roughly 30% larger in the isocyano structure. The conformations of the ammines in the two structures are seen to be essentially the same except for that at N(9). This ammine group was not particularly clear in the difference maps calculated at various stages in the refinement; the conformation in the cyano structure fits the intricate hydrogen bonding system much better. We attribute our failure to determine the positions of these hydrogen

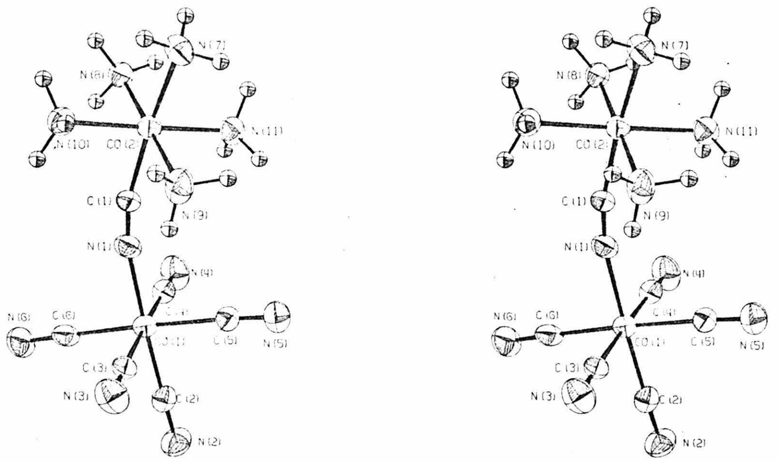
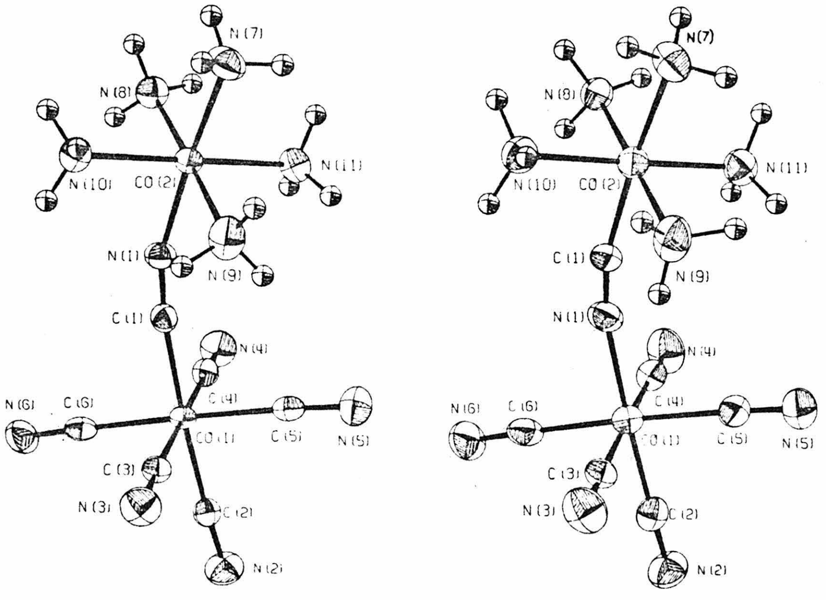


Figure IV-16
An ORTEP stereopair of the isocyano molecule. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are represented by spheroids of arbitrary radius.

Figure IV-17



-CYANO- **-ISOCYANO-**

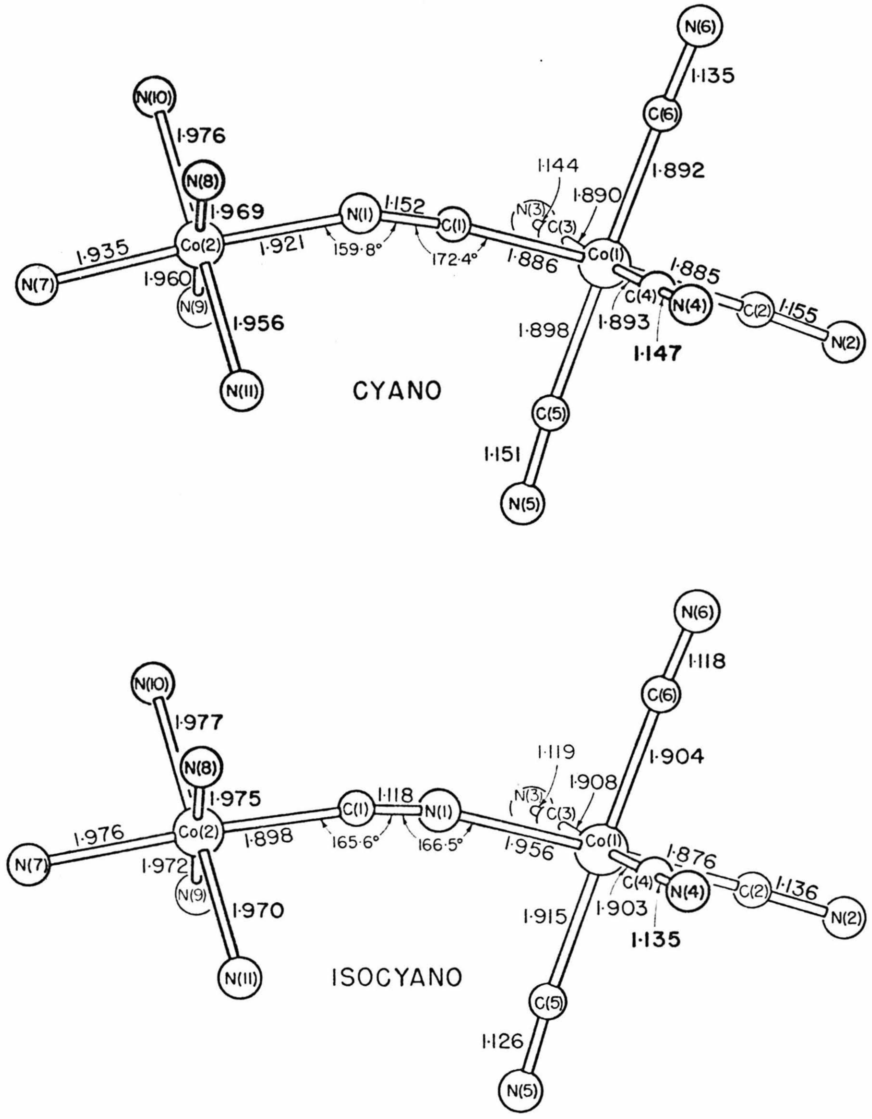
ORTEP drawings of both isomers. Thermal ellipsoids are drawn at the 50% probability level.

atoms unambiguously to the fact that N(9) has the largest thermal motion of the ammine nitrogen atoms, and seems to be moving in and out of the "pocket" formed by cyanide ligands C(3) - N(3) and C(5) - N(5). Figure IV-18 exhibits the bond distances and bridging angles of both the cyano and isocyano molecules. Standard deviations are estimated to be 0.005 Å for Co-ligand distances and 0.007 Å for C-N distances in the cyano structure. Corresponding esd's in the isocyano structure are 0.007 Å for Co-ligand distances and 0.010 Å for C-N distances. Bond angles for the isocyano molecule are given in Table IV-13. A detailed comparison of bond distances for the two structures will be given in a later section of this document; however, a description of the isocyano molecule itself will be made here.

It should first be noted that the C-N distance of the bridging cyano group is rather short, having a value of 1.118 Å. Comparison to the terminal cyano distances, however, indicate that it is not special in this respect, as all C-N distances are rather short. Terminal C-N distances range from 1.118 Å to 1.136 Å and average 1.127 Å. All are equal within the limits of experimental uncertainty, and this includes the bridging group. The average of all C-N distances is 1.125 Å.

The Co-C (bridging) is seen to be almost 0.06 Å shorter than the Co-N (bridging) distance. It should be noted that this is opposite of the trend we would expect for single

Figure IV-18



Bonding distances and bridging angles for both cyano-bridged isomers.

TABLE IV-13

Bond Angles

Atoms	Angle, Degrees	Atoms	Angle, Degrees
N(1)-Co(1)-C(2)	177.6(3)	C(1)-Co(2)-N(7)	175.2(3)
N(1)-Co(1)-C(3)	91.5(3)	C(1)-Co(2)-N(8)	92.6(3)
N(1)-Co(1)-C(4)	91.0(3)	C(1)-Co(2)-N(9)	86.3(3)
N(1)-Co(1)-C(5)	89.1(3)	C(1)-Co(2)-N(10)	92.9(3)
N(1)-Co(1)-C(6)	93.1(3)	C(1)-Co(2)-N(11)	88.2(3)
C(2)-Co(1)-C(3)	89.2(3)	N(7)-Co(2)-N(8)	91.1(3)
C(2)-Co(1)-C(4)	88.3(3)	N(7)-Co(2)-N(9)	89.9(3)
C(2)-Co(1)-C(5)	88.7(3)	N(7)-Co(2)-N(10)	90.1(3)
C(2)-Co(1)-C(6)	89.1(3)	N(7)-Co(2)-N(11)	88.9(3)
C(3)-Co(1)-C(4)	177.4(3)	N(8)-Co(2)-N(9)	178.9(3)
C(3)-Co(1)-C(5)	89.2(3)	N(8)-Co(2)-N(10)	90.5(2)
C(3)-Co(1)-C(6)	90.2(3)	N(8)-Co(2)-N(11)	88.9(3)
C(4)-Co(1)-C(5)	91.2(3)	N(9)-Co(2)-N(10)	89.8(3)
C(4)-Co(1)-C(6)	89.3(3)	N(9)-Co(2)-N(11)	90.9(3)
C(5)-Co(1)-C(6)	177.8(3)	N(10)-Co(2)-N(11)	178.7(3)
C(1)-N(1)-C(1)	166.5(6)		
Co(2)-C(1)-N(1)	165.6(7)		

Atoms	Angle, Degrees
Co(1)-C(2)-N(2)	178.1(7)
Co(1)-C(3)-N(3)	177.2(6)
Co(1)-C(4)-N(4)	179.0(7)
Co(1)-C(5)-N(5)	177.7(7)
Co(1)-C(6)-N(6)	178.5(6)

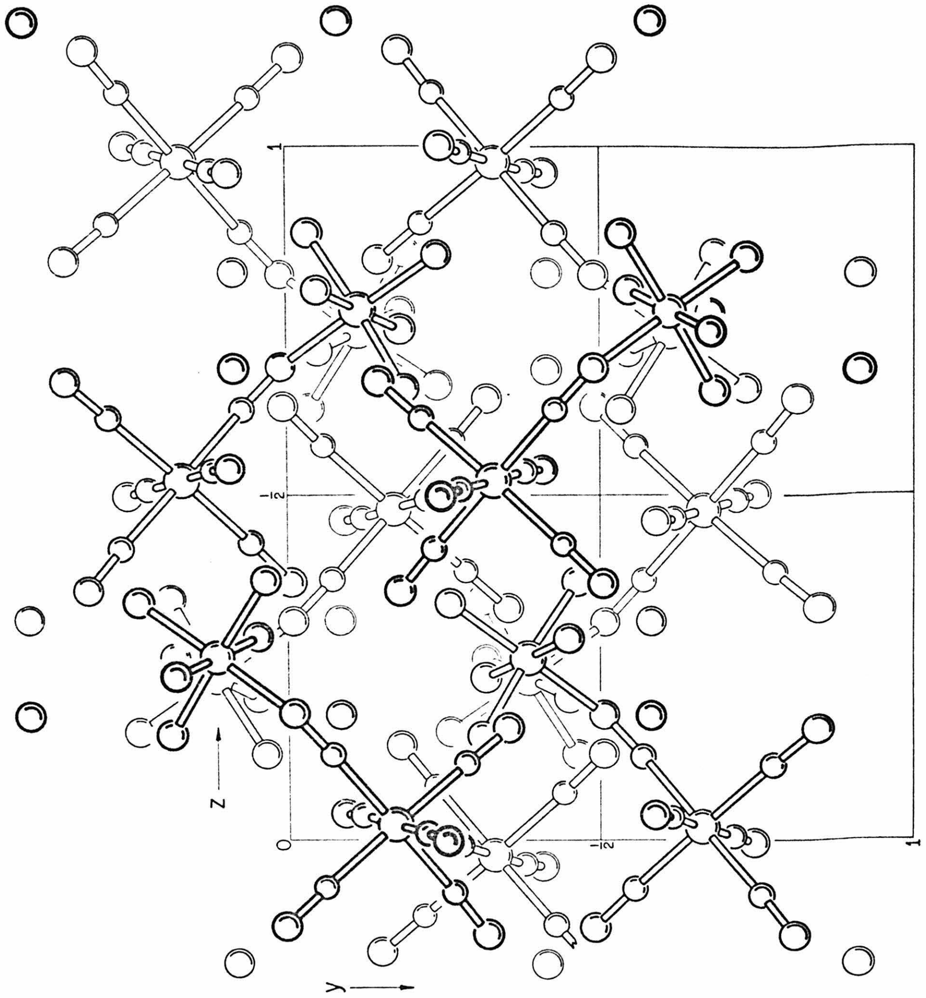
covalent bonds. Co-C π bonding is probably the cause of this effect, as will be discussed in detail later. The bending of the molecule was somewhat of a surprise when revealed in the structural solution of the cyano molecule, but was fully anticipated when discovered here. This effect is in all probability mostly due to intramolecular Coulombic attraction due to the asymmetric charge distribution of this neutral molecule. Bending at both coordination sites of the bridging cyano group allows the positively charged pentaamminecobalt(III) and negatively charged pentacyanocobalt(III) ends of the molecule to approach each other. Of course, intermolecular interactions may also cause some of the observed bending, but it is improbable that any contribution from a structure such as $:C=N:^-$ gives rise to the bending, since this form would have a long C-N distance, and the C-N distance found is quite short. The total deviation from linearity is about 28° in both isomers; however, the individual angles are quite different in the cyano molecule and more symmetric in the isocyano molecule. This is in line with the overall weaker metal-ligand bonding in the isocyano molecule. Differences in the bond lengths and angles cause the Co-Co distance in the cyano isomer, 4.767 Å, to be considerably shorter than that found in the isocyano isomer, 4.843 Å.

Co-N(ammine) distances in the isocyano molecule are amazingly constant, ranging from 1.970 to 1.977 Å, and exhibit absolutely no hint of the _trans_ shortening observed in the cyano molecule. The average Co-N value, 1.974(2) Å, is about that which is generally expected for Co(III) ammine complexes; this claim will hopefully be merely noted at this point, as it will be substantiated and discussed more fully in subsequent comments (see Discussion of Results).

Co-carbon distances vary from 1.876 to 1.915 Å, with the shortest being _trans_ to the bridging group. Equatorial Co-C distances are fairly constant and average 1.908 Å, not a significantly longer value than the Co(2)-C(bridging) distance. The _trans_ Co-C distance of the pentacyanocobalt fragment is 0.032 Å shorter than this average; this difference is formally 4σ and is probably significant and real. While such effects are generally referred to as a "shortening" of the _trans_ distance, this terminology may be misleading, as will be clarified later. It should be noted here that while in the cyano isomer, the _trans_ distance was also the shortest found, the difference in that case was insignificant on statistical grounds.

The packing of molecules into the structure appears to be dictated by maximization of hydrogen bonding possibilities. The packing is illustrated in projection down _a_ in Figure IV-19, which is actually that for the cyano molecule, which packs in exactly the same manner. Figures IV-20 and IV-21 are also illustrations of intermolecular contacts found in the cyano

Figure IV-19



Crystal packing for the cyano molecule.

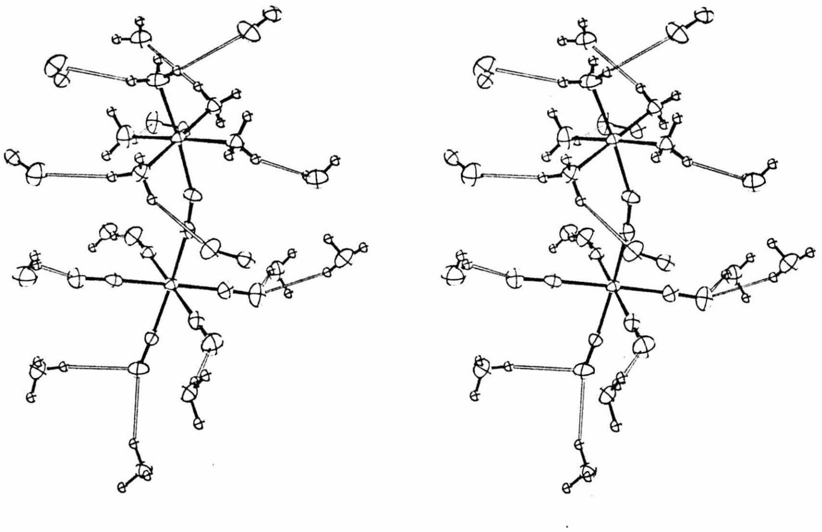


Figure IV-20
Surroundings of the cyano molecule, in stereopair.

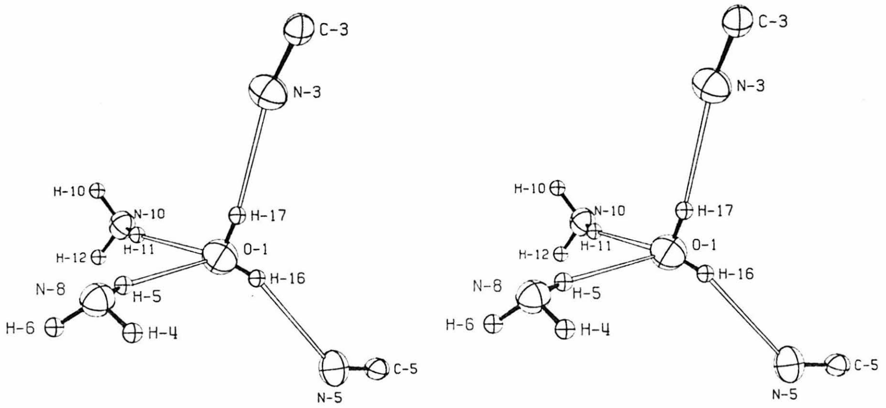


Figure IV-21
Environment of the water molecule in the cyano structure.

TABLE IV-14. INTERMOLECULAR N-N OR N-O CONTACTS LESS THAN 3.2 Å

Donor	Acceptor	D···A Distance	H···A Distance	D-H···A Angle
N(7)	N(2)	3.14 Å	2.28 Å	146°
	N(3)	3.22	2.47	134
	N(6)	2.97	2.45	112
N(8)	N(6)	3.20	2.32	148
	O(1)	3.04	2.19	143
N(9)	N(4)	3.16	2.26	151
	N(6)	3.12	2.63	111
N(10)	O(1)	3.17	2.21	164
N(11)	N(2)	3.01	2.15	146
	N(4)	3.04	2.08	166
O(1)	N(3)	2.84	1.86	169
	N(4)	3.17	2.53	123
	N(5)	3.06	2.22	144

structure which are applicable here. Table IV-14 lists the intermolecular contacts which may be interpreted as hydrogen bonds. Approximately half of the ammine hydrogen atoms act as donors in hydrogen bonding, and all terminal cyanide ligands act as acceptors for at least one hydrogen bond. The function of the water molecule appears to be that of "bridging" the positive and negative ends of different molecules when the arrangement of these molecules does not allow a direct contact. As shown in Figure IV-21, the water molecule is centered in a tetrahedral environment, accepting two hydrogen bonds from ammine donors and donating two hydrogen bonds to cyanide ligands.

F. $(NH_3)_5CoNCSCo(CN)_5\cdot H_2O$

Our structural study of this molecule confirms the formulation of Buckley and Wardeska[46] as a singly thiocyanate-bridged, nonionic binuclear complex containing the bridging ligand in the more favorable isomeric configuration. In this isomer, the "hard" nitrogen end of the thiocyanate is coordinated to the hard pentaamminecobalt(III) group, and the "soft" sulfur end is coordinated to the softer pentacyanocobalt(III), leading to $(N)_6$ and $(C)_5(S)$ environments around the two cobalt atoms.

An ORTEP representation of the configuration and thermal motion of the molecule is shown in Figure IV-22, and interatomic distances within the molecule are given in Figure IV-23.

The most striking feature of the $(NH_3)_5CoNCSCo(CN)_5$ molecule is its overall "bent" configuration. The coordination angle at the sulfur atom is 101°, and at the bridging nitrogen atom is 169°. Deviations from linearity of up to 10° are not at all uncommon for isothiocyanates, and angles at coordinated sulfur have been observed over a range of 90° to 109°. This range probably reflects more the steric differences between various complexes than relative stabilities due to hybridization changes in sulfur orbitals. Nonbonded contacts with the thiocyanate carbon atom C(1) occur with equatorial cyanide ligands. Distances are 2.91 Å to C(3) and 3.21 Å to C(6) of the same molecule; a smaller angle at sulfur would lead to severe nonbonded repulsions.

It should be noted that the nonlinearity of the coordination of the nitrogen end of the thiocyanate group is in roughly the same sense as the angle at sulfur. In other words, the molecule is bent in such a manner as to bring the two ends as close together as possible, a circumstance which was also noted in the closely related compounds $(NH_3)_5CoCNCo(CN)_5$ and $(NH_3)_5CoNCCo(CN)_5$. More flexibility is possible with thiocyanate than with cyanide, and in this structure, the bending manifests itself in an intramolecular hydrogen bond. Ammine ligand N(11) donates to cyanide ligand N(3) through hydrogen

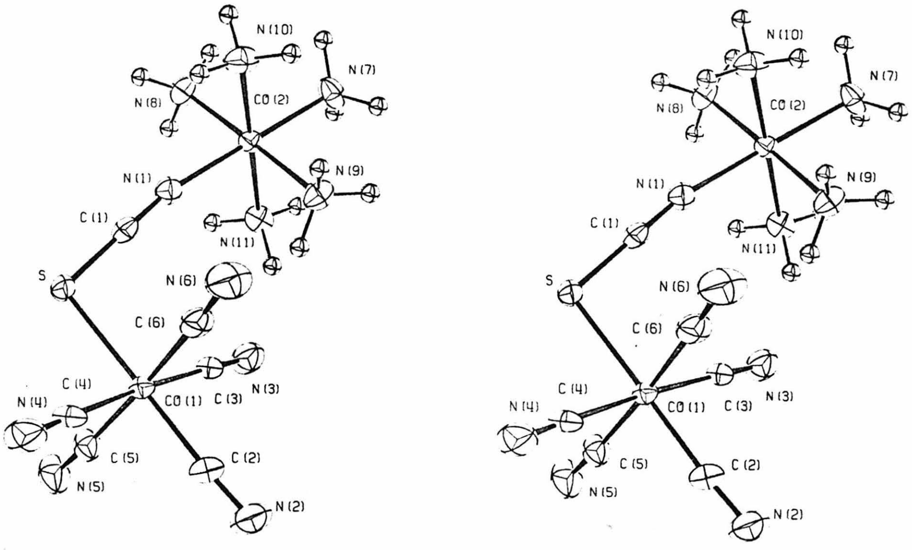
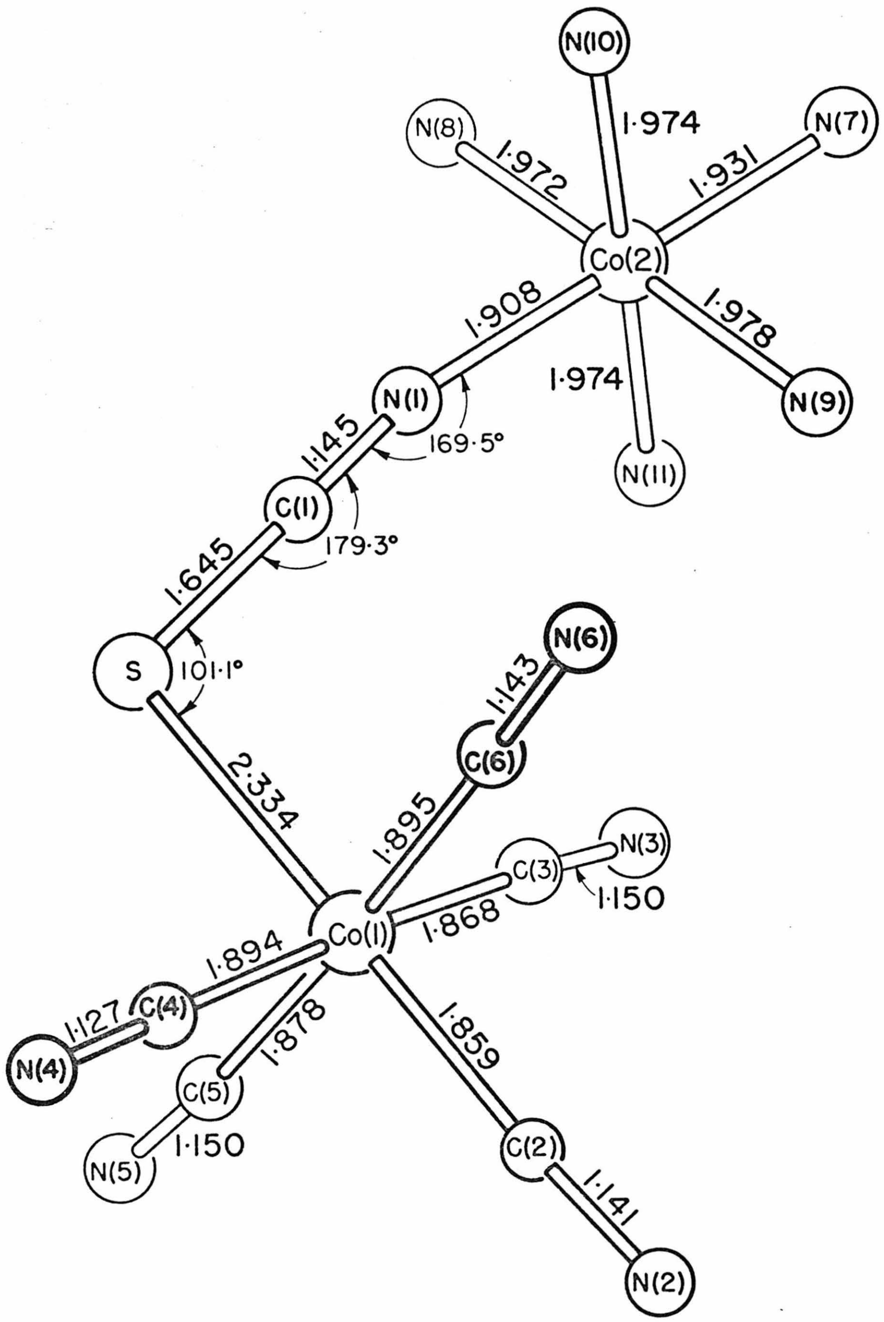


Figure IV-22

An ORTEP representation of the $(NH_3)_5CoNCSCo(CN)_5$ molecule. Thermal ellipsoids are drawn at the 40% probability level, and the hydrogen atoms are represented by spheroids of arbitrary radius.

Figure IV-23



Interatomic distances and some important angles in the μ-SCN molecule. Esd's are 0.002 Å for Co-S, 0.004 Å for Co-N, 0.005 Å for Co-C and S-C, and 0.007 Å for C-N.

atom 11H(3). The hydrogen bond is reasonably strong, having an N···N distance of 3.03 Å and an N-H···N angle of 154°. An adjacent ammine ligand N(9) also has a close contact to N(3), with an N···N distance of 3.40 Å.

The bridging thiocyanate ligand is essentially linear with interatomic distances typical of those found in coordinated and free thiocyanate ions. The Co-S bond has a length of 2.334(2) Å, which is perhaps longer than might be expected. The Co-NCS distance of 1.908(4) Å is indistinguishable from the value of 1.921(5) Å found in $(NH_3)_5CoNCCo(CN)_5$ for Co-NC.

Distances within the pentaamminecobalt(III) fragment of the molecule are given in Figure IV-23. All equatorial Co-N distances are identical within experimental error, with an average value of 1.975(2) Å. The axial Co-NH_3 bond is 0.044 Å shorter than this average; this difference is formally 10σ, and is thus considered quite significant. An octahedral trans influence is clearly in effect.

The situation with regard to the cyanide ligands is not so simple. Dimensions of the $Co(CN)_5$ fragment of the molecule may be found in Figure IV-23 and Table IV-15. The Co-C distances range from 1.859 Å to 1.895 Å, with the shortest trans to the bridging group. While the trans distance is 0.025 Å shorter than the equatorial average and significantly shorter than most of the equatorial distances, statistically significant differences exist among the equatorial Co-C distances

TABLE IV-15. BONDING ANGLES IN $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$

Atoms	Angle (degrees)	Atoms	Angle (degrees)
S-Co(1)-C(2)	179.5	N(1)-Co(2)-N(7)	179.5
S-Co(1)-C(3)	92.7	N(1)-Co(2)-N(8)	90.0
S-Co(1)-C(4)	90.1	N(1)-Co(2)-N(9)	88.5
S-Co(1)-C(5)	86.9	N(1)-Co(2)-N(10)	90.1
S-Co(1)-C(6)	90.3	N(1)-Co(2)-N(11)	89.2
C(2)-Co(1)-C(3)	87.3	N(7)-Co(2)-N(8)	90.5
C(2)-Co(1)-C(4)	90.0	N(7)-Co(2)-N(9)	90.9
C(2)-Co(1)-C(5)	92.6	N(7)-Co(2)-N(10)	89.9
C(2)-Co(1)-C(6)	90.2	N(7)-Co(2)-N(11)	90.9
C(3)-Co(1)-C(4)	176.3	N(8)-Co(2)-N(9)	178.5
C(3)-Co(1)-C(5)	87.9	N(8)-Co(2)-N(10)	89.4
C(3)-Co(1)-C(6)	93.0	N(8)-Co(2)-N(11)	90.9
C(4)-Co(1)-C(5)	89.8	N(9)-Co(2)-N(10)	90.3
C(4)-Co(1)-C(6)	89.5	N(9)-Co(2)-N(11)	89.4
C(5)-Co(1)-C(6)	177.1	N(10)-Co(2)-N(1)	179.2
Co(1)-C(2)-N(2)	175.3	Co(1)-S-C(1)	101.1
Co(1)-C(3)-N(3)	176.8	S-C(1)-N(1)	179.3
Co(1)-C(4)-N(4)	178.9	C(1)-N(1)-Co(2)	169.5
Co(1)-C(5)-N(5)	174.9		
Co(1)-C(6)-N(6)	177.9		

Esd's are 0.1° for angles involving S and Co, 0.2° for angles between lighter ligands coordinated to cobalt, and 0.3° for Co-C-N.

themselves, due to their vastly varying environments. In view of all the inter- and intramolecular interactions in effect here, one cannot conclude nor dismiss the possibility that this short trans distance represents an octahedral trans influence. If it exists, it is small. The average (of all five) Co-C distances is 1.879 Å, which agrees satisfactorily with typical values found in cobalt(III) cyanide complexes.

All C-N distances of the cyanide ligands are statistically indistinguishable, averaging 1.142 Å, which is in excellent agreement with similar values found in cobalt(III) cyanide complexes. All cyanides coordinate linearly to within about five degrees, and such variations are generally found for terminal cyanide ligands.

The arrangement of molecules within the unit cell is represented in Figure IV-24. This molecule would be expected to employ a great deal of hydrogen bonding in the crystalline state, since one end of the complex is composed of good donor ammine ligands, and the other end consists of good acceptor cyanide ligands. The packing does indeed appear to be determined by hydrogen bonding. Intramolecular hydrogen bonding has previously been discussed. Table IV-16 lists intermolecular N···N contacts, many of which should certainly be considered as hydrogen bonds. The water molecule, which can act both as donor and acceptor, is located in the vicinity of three ammine ligands and three cyanide ligands; this geometry

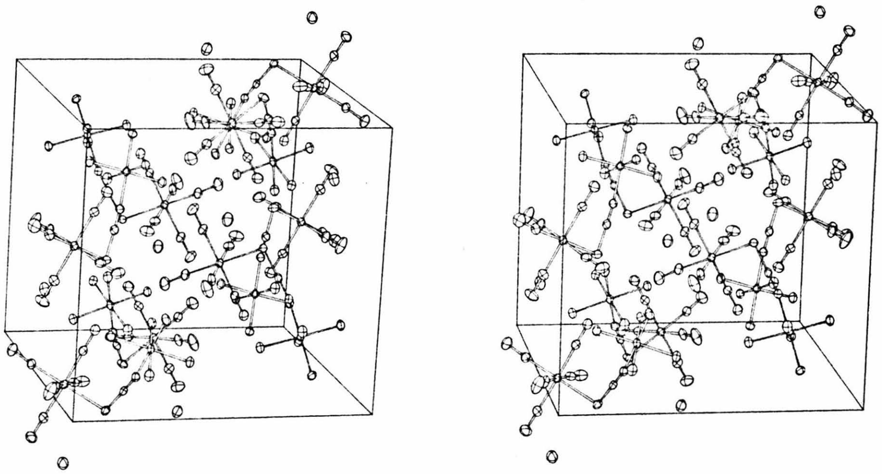


Figure IV-24

A stereoscopic representation of the contents of the unit cell. Atoms are represented by thermal ellipsoids enclosing 40% probability. The origin of the coordinate system is at the lower left (foreground). The a axis is vertical, and the b axis is horizontal.

TABLE IV-16. INTERMOLECULAR N···N CONTACTS LESS THAN 3.3 Å

A-H···B	Dist. A···B	Dist. H···B	Angle
N(7)-7H(1)-N(2)	3.00 Å	2.38 Å	120°
N(7)-7H(1)-N(5)	3.12	2.29	141
N(7)-7H(3)-N(6)	3.05	2.04	101
N(8)-8H(3)-N(4)	3.08	2.12	153
N(8)-8H(2)-N(5)	3.10	2.13	165
N(9)-9H(3)-N(2)	3.26	2.86	104
N(9)-9H(1)-N(5)	3.11	2.09	172
N(10)-10H(1)-N(2)	3.14	2.23	150
N(10)-10H(3)-N(3)	3.18	2.23	154
N(11)-11H(2)-N(4)	3.09	2.11	171
N(11)-11H(1)-N(6)	3.17	2.39	136

is summarized in Table IV-17. It is clear that the water molecule has several orientations to choose from, and is not surprising that no discrete positions were determined for its hydrogen atoms, which are no doubt disordered, with varying occupancies, into several orientations.

Another close intermolecular contact involves the sulfur atom and the <u>trans</u> ammine N(7). The S···N distance is 3.39 Å, and the N-H···S angle is 126°, which places the hydrogen atom 2.7 Å from the sulfur atom, as compared to a van der Waals distance of 3.05 Å. A contact with such a small angle should probably not be considered as a bona fide hydrogen bond at this interatomic separation.

TABLE IV-17. CLOSE CONTACTS TO THE WATER MOLECULE

Ammines:

A-H	Dist. N···O	Dist. H···O	Angle	Cyanides	Dist. N···O
N(8)-8H(1)	3.09 Å	2.16 Å	161°	N(3)	3.31 Å
N(9)-9H(3)	3.05	2.05	171	N(4)	3.28
N(10)-10H(1)	3.13	2.55	116	N(6)	3.01

CHAPTER V. DISCUSSION OF RESULTS

A. Dioxygen-Bridged Dicobalt Complexes

1) The decaammine complexes

At the time work described herein was initiated, dioxygen-bridged dicobalt ammine complexes were well characterized and reasonably well understood with one exception. The reported structure of the thiocyanate salt of the diamagnetic peroxo ion appeared to have an internuclear O-O separation, 1.65(3) Å, which was much out of line with that found in similar complexes, and no reason for this anomaly was apparent, the only unique feature of the binuclear ion in that structure being the planarity of the CoOOCo group. It is quite doubtful that the repulsion between eclipsed lone pairs on the two oxygen atoms in the planar peroxo group could cause a lengthening of the O-O distance of 0.16 Å. The new structural determination of the thiocyanate salt proves that the O-O distance is normal, and this ion is in harmony with results of other determinations. The story of μ-dioxygen decaammine complexes now appears complete and congruous, and bonding implications can be drawn. The structure[66] of $\{Co_2O_2(en)_2(dien)_2\}^{4+}$ will be discussed along with the structures of the four decaammine crystals which have been analyzed, due to its obvious similarity and applicability.

The oxidation state of the cobalt atoms is of primary interest, and this in all cases appears to be Co(III) in more than just a formal sense, as shown by the Co-NH_3 distances. These, along with other structural data, are listed in Table V-1, and are segregated into axial and equatorial varieties, for convenient speculation about octahedral trans effects. The equatorial distances are seen to be typical of Co(III) complexes, and to be quite invariant in both peroxo and superoxo complexes. The average equatorial Co-N distance in the peroxo complexes is 1.955 Å, and in the superoxo complexes is 1.950 Å; the difference is certainly not significant. Discussion of the trans distances will be momentarily postponed.

The Co(III) atom in all these complexes is in a nearly octahedral environment, and both Co atoms are equivalent, either by crystallographic symmetry or virtually identical coordination spheres not related by symmetry. The CoOOCo unit is in all cases staggered, and may or may not be planar. The Co-O distances are reasonably invariant and independent of the oxidation state of the bridging group. The average Co-O distance in these five structures is 1.889 Å; the expected Co-O distance for a single bond is about 1.95 Å, so some degree of multiple bond character (π donating or accepting character) is indicated. For peroxides, only π donation is possible, while superoxides have unfilled π^* orbitals, allowing the possibility of π acceptance as well, thus it is a bit

TABLE V-1. GEOMETRIES OF μ-DIOXYGEN DICOBALT AMMINES

Compound	Co-O	O-O	Co-O-O	eq. Co-N	axial Co-N
$Co_2O_2(NH_3)_{10}(SO_4)_2 \cdot 4H_2O$	1.882 Å	1.473 Å	112.7°	1.957 Å	1.983 Å
$Co_2O_2(NH_3)_{10}(SCN)_4$	1.879	1.469	110.8	1.955	1.971
$Co_2O_2(en)_2(dien)_2(ClO_4)_4$	1.896	1.488	110	1.952	1.998
$Co_2O_2(NH_3)_{10}SO_4(HSO_4)_3$	1.894	1.312	117.6	1.943	1.958
$Co_2O_2(NH_3)_{10}(NO_3)_5$	1.895	1.317	117.3	1.957	1.955

surprising that the two types of ions have so nearly the same Co-O distances.

The Co-O-O angle for the peroxo complexes ranges from about 110° to about 113° in the complexes listed in Table V-1, the average value being 111.2°. This is somewhat smaller than the 117.5° angle found in the superoxo complexes. Although not an ideal way of thinking about dioxygen complexes, as mentioned earlier, different hybridizations of the oxygen atoms in the two cases seems to do a reasonably good job of explaining the difference here. Two lone pairs in sp^3 hybrids localized on each oxygen atom of the peroxo group would be expected to produce an angle Co-O-O of slightly smaller than 109°; and the angle found resembles this situation. Hybridization of sp^2 in the superoxo group would produce one lone pair on each oxygen atom, leading to π overlap of the unhybridized p orbitals normal to the molecular plane and a Co-O-O angle slightly smaller than 120°, which is exactly what is observed.

The O-O distances in this class of complexes fall into two distinct groups, corresponding to idealized peroxo and superoxo ions. The compounds normally thought of as peroxo complexes have O-O distances ranging from 1.469(6) to 1.488(6) Å and averaging 1.477 Å. Those which can best be described as superoxo complexes have O-O distances averaging 1.315 Å. Comparison of these values to those found in simple dioxygen compounds is illuminating. The distance for a single oxygen-

oxygen bond has long been considered to be about 1.48 Å, based upon measurements of twenty years or more ago. The O-O distance in H_2O_2 was reported in 1943 to be 1.47 Å,[67] and the corresponding distance in BaO_2 was found in 1954 to be 1.49 Å.[68] It now appears that the O-O single bond distance may be a slight bit shorter than this, as the most precise determination of H_2O_2 to date places the distance at 1.453(7) Å.[69] The distance in the peroxo ammine complexes appears to be significantly longer. The O-O distance corresponding to free superoxide is not as well known, the best measurement being based on powder diffraction data of KO_2, 1.28(2) Å.[70] Large thermal parameters found in that determination have been interpreted as a rotational disorder of the superoxide ion, with a predicted O-O distance in the range 1.32-1.35 Å.[71] Powder work on several polymorphs of NaO_2 indicates disordered and twinned structures with estimates of the O-O distance being 1.33(6) Å and 1.28(10) Å.[72,73] Clearly, the superoxo O-O distance found in the decaammine complexes is not distinguishable from these values.

More evidence for π-bonding in both the peroxo and superoxo complexes is the fact that in both types, the Co-O-O plane bisects the angle between the equatorial ligands. This configuration allows π overlap between the π* orbital of the O_2 group and the equivalent d_{xy} and d_{yz} orbitals of the metal. Co-O π bonds seem to be an intrinsic feature of the decaammine system, even when π orbitals of the oxygen atoms are filled and localized on the atoms.

The matter of planarity or nonplanarity of Co-O-O-Co groups deserves some discussion. For a peroxo group, simple MO theory predicts the formation of two lone pairs of electrons on each oxygen atom, such that when it bridges two metal atoms the most stable configuration is predicted when the lone pairs, and thus also the coordinated metal atoms, are skewed.[74] For the sterically unhindered hydrogen peroxide, the torsion angle about the O-O bond is 90.2(6)° in the crystal.[69] For a superoxo group, net π overlap is expected, such that the O-O torsion angle should be the planar 180°. $H_2O_2^+$ is unknown, such that direct experimental evidence is lacking. When the oxygen atoms are coordinated to bulky groups such as $Co(NH_3)_5$, the torsion angle would be expected, in the peroxo case, to be somewhat larger on steric grounds, and have an even stronger tendency to be 180° in the superoxo case. It might be considered to be unfortunate that for the first complexes unambiguously characterized, these predictions were confirmed, for confirmation of preconceived notions led to suspicion when results to the contrary were obtained. It now seems clear that planar peroxo complexes and nonplanar complexes which have O-O distances close to the superoxo separation are quite common. Torsion angles in all known dioxygen-bridged dicobalt structures are listed in Table V-2.

TABLE V-2. DIOXYGEN-BRIDGED DICOBALT COMPLEXES

Complex	O-O	O-O Torsion	Ref.
$\{Co_2O_2(CN)_{10}\}^{5-}$	1.262 Å	180, 166°	This work
Co(F-salen) tetramer	1.308	122	76
$\{Co_2O_2(NH_3)_{10}\}(SO_4)(HSO_4)_3$	1.312	175	27
$\{Co_2O_2(NH_3)_{10}\}(NO_3)_5$	1.317	180	28
$\{Co_2O_2NH_2(NH_3)_8\}^{4+}$	1.320	0	77
$Co_2O_2(salen)_2(DMF)_2$	1.339	110	78
$\{Co_2O_2NH_2(en)_2\}^{4+}$	1.353		79
$Co_2O_2(salen)_2(pip)_2$	1.365	121	80
$\{Co_2O_2(CN)_{10}\}^{6-}$	1.447	180	This work
$Co_2O_2(DDP)_2$	1.45	149	81
$\{Co_2O_2NH_2(en)_2\}^{3+}$	1.458	63	82
$\{Co_2O_2(NH_3)_{10}\}(SCN)_4$	1.469	180	This work
$\{Co_2O_2(NH_3)_{10}\}(SO_4)_2 \cdot 4H_2O$	1.473	146	30
$\{Co_2O_2(en)_2(dien)_2\}^{4+}$	1.488	180	66
$\{Co_2O_2(en)_4(NO_2)_2\}^{2+}$	1.529	180	83

Intermolecular interaction, particularly the hydrogen bonding is of much more importance in determining the torsion angle about O-O in peroxo complexes than lone pair repulsions within the peroxo group. The conformational energy maximum occurs at 180° for H_2O_2, and is of magnitude about 1 kcal/mol.[75] For charged binuclear complexes which form a crystal structure with little or no hydrogen bonding to distribute for charge away from the cobalt atoms, simple Coulombic repulsion causes a conformational energy minimum at 180° which outweighs the small stability obtained by staggering the peroxo lone pairs. The most striking example of this phenomenon is the μ-peroxo decaammine ion, which has a torsion angle of 146° in the disulfate tetrahydrate and is planar in the tetrathiocyanate. The sulfate structure contains an extensive array of hydrogen bonds, while the thiocyanate structure contains only two hydrogen bonds. The planar $\{Co_2O_2(en)_2(dien)_2\}^{4+}$ ion participates in only two good intermolecular hydrogen bonds. (Four intramolecular hydrogen bonds are also present in this structure; however, these do not serve to distribute charge away from the ion.) The planar $\{Co_2O_2(en)_4(NO_2)_2\}^{2+}$ ion contains in the dinitrate tetrahydrate structure four good intermolecular hydrogen bonds, and the planar $\{Co_2O_2(CN)_{10}\}^{6-}$ ion participates in only four intermolecular hydrogen bonds in the nitrate double salt.

Nonplanar superoxo complexes are a bit more perplexing. Small deviations from perfect planarity such as found in the decaammine sulfate tris-bisulfate and the decacyano structures may be easily imagined to be due to optimization of intermolecular interactions without costing too much in π overlap; however, an increasing number of reversible oxygenated complexes with ligands such as salen are being found to have distinctly nonplanar Co-O-O-Co groups and O-O distances which look like slightly long superoxides. In particular, it is difficult to understand how, in the apparent absence of π overlap within the dioxygen ligand, the short O-O distance (indicating a bond order greater than one) is accomplished. It does seem that the torsion angle in these complexes is somehow controlled by optimization of intermolecular interactions.

2) The decacyano complexes

The obvious question one might ask in relation to complexes of the type $\{(CN)_5CoO_2Co(CN)_5\}^{n-}$ is: "What is the effect of the cyano ligands on the electronic distribution in the CoOOCo group?" Since the structures of the corresponding peroxo and superoxo ammine complexes are known, the question might be reformulated to ask what the effect upon the geometry of the decaammine complexes would be if the ammine ligands are replaced by cyanides. This is actually more than just an aid to visualization, since the μ-superoxo decacyanide complex can be synthesized quite nicely in just this manner.

First, the most important single result of studies of the μ-peroxo and μ-superoxo decacyanodicobalt(III) ions is that the bridging group in both is end-on bonded and staggered, qualitatively the same arrangement as seen in the decaammine systems. This indicates a similarity of the metal-dioxygen bonding. The "stagger angle" (Co-O-O) is systematically larger in the cyano systems; however, being about 4° larger for the superoxo system and some 8° larger for the peroxo system. These angles indicate a breakdown in the sp^2-sp^3 hybrid approximation for the oxygen atom which holds approximately in the decaammine system; clearly the bonding cannot be thought of in such simple terms. An angle of 119° between bonding pairs in the presence of two lone pairs of electrons is a poor approximation to sp^3 hybridization.

A practically invariant Co-O distance of 1.889 Å was found in the decaammine system; here the corresponding bonds are much longer. The superoxo decacyano ion has a Co-O distance of 1.936 Å (average of three individual bonds); this is almost 0.05 Å longer than the ammine distance, and much closer to the predicted single bond distance. Apparently a much smaller amount of multiple bonding is present in this complex. For the peroxo system, in which no ligand-to-metal π bonding is possible, the Co-O distance for the cyano ion is extremely long, 1.985(3) Å. This is a good deal longer than what would be expected for a single bond, such that we can almost certainly rule out any kind of π interaction between the metal and bridging ligand in this complex. We cannot conclude from this that a species with no π overlap is the lowest energy form of the isolated ion, because the length of the Co-O bond is probably affected somewhat by the distortions imposed upon the ion by the water molecules hydrogen bonded to the bridging group. It should also be noted that this is the highest charged ion of the μ-dioxygen type, and this may have some lengthening effect upon the metal-to-dioxygen linkage.

Comparison of O-O distances in the cyano ions with those found in the ammine ions disclose significant and systematic differences. As mentioned earlier, peroxo and superoxo distances in the ammine system are 1.477(4) and 1.315(10) Å, respectively. Corresponding values found in the decacyano ions are 1.447(4) and 1.262(11) Å. These are the shortest distances to be found in binuclear cobalt complexes described as peroxo and superoxo. It is clear that an O-O shortening of cyano complexes versus ammine complexes is in effect in both the peroxo and superoxo linkages; the relationship these distances hold to those in the free dioxygen ions is not so clear. The peroxo O-O separation in H_2O_2 is apparently identical to that found in the cyano complex, but due to the ambiguity in the O-O distance in free superoxide, the same statement cannot definitely be made in the superoxo case. It seems a good guess, by analogy to the behavior of the peroxo system, that the O-O distance in free superoxide is closer to that found in the cyano complex than in the ammine complex.

Bonding implications of the behavior of the O-O distance are consistent with π-bonding in both the peroxo and superoxo systems. Competition for π-symmetry orbitals of the cobalt atom between the axial ligand and the dioxygen group nicely rationalizes the observed behavior. In the cyano systems, the axial cyanide ligand, which is a much better π acid than dioxygen, dominates metal-to-ligand π bonding with the appropriate metal d orbital, leaving little multiple bond character in the M-O bond, which would use the same metal orbital for any π bonding. This predicts a long Co-O bond, a shortened trans Co-C bond, and no lengthening of the O-O distance versus the free ion, all of which are observed in the cyano complexes. For ammine systems, the metal d orbital is no longer dominated by the trans ligand, and is available to donate electron density into the π* molecular orbitals of the dioxygen ligand. For superoxo complexes, this works nicely, predicting a shorter Co-O bond, a lengthened (more π* character) O-O bond, and perhaps a small trans lengthening of the ammine ligand, all of which are observed. This reasoning breaks down for the peroxo ammine complex, which cannot accept electron density into the filled π* orbitals of dioxygen. For the peroxo ligand, it is necessary to invoke ligand-to-metal π interaction (π donation) in the ammine case which is not present in the cyano case. This explanation seems reasonable on grounds of charge distribution, as, in its quest for electroneutrality, the ammine system, with its positive charge, is not able to arrive at a stable configuration through sigma interaction alone. The negatively charged pentacyano system is reasonably not as prone to π donation from a negatively charged ligand. The π donor orbitals of the peroxo ligand would normally be expected to be the high energy, filled π^*_g antibonding levels. If the energy of the metal d orbital happens to fall close to the π_u bonding orbitals of the peroxo group (MO calculations have not been performed), some donation from these might be expected. Miskowski considers this a "faint possibility" due to the unimportance of such interactions in CO complexes, where the analogous orbital is of similar energy.[84] Our results indicate that this effect might be significant, since involvement of the π_g orbitals would lead to a shortening of the O-O distance while involvement of the π_u orbitals would lead to a lengthening, and we observe longer O-O distances in the ammine complexes than in the cyano complexes.

Further evidence for the observation that π effects present in the ammine complexes have disappeared in the cyano complexes is that the invariant relationship between the orientation of the Co-O-O plane and the equatorial ammines does not hold in the cyano systems. In fact, the other extreme (eclipsing of Co-O-O and Co-C-N) is more common.

B. The $(NH_3)_5Co\text{-}L\text{-}Co(CN)_5$ System

The pentaamminecobalt(III)-ambidentate ligand-pentacyanocobalt(III) system presents a good opportunity for the study of coordination of ambidentate ligands to both the pentaamminecobalt(III) and pentacyanocobalt(III) systems from the structural point of view. To date, four compounds of this type are known, both isomers of the μ-CN type, and both isomers of the μ-SCN type. Prior to this thesis work, the structure of only one of these, the μ-cyano compound, was known. Two more structures, those of the isocyano and thiocyanato compounds, are reported here. Attempts were made to grow crystals of the isothiocyanato compound, which met with no success; no stable crystals suitable for X-ray diffraction work were obtained. It is unfortunate that the structure of the isothiocyanate compound $(NH_3)_5CoSCNCo(CN)_5$ has not been determined yet, as it is conceptually more interesting than the thiocyanato isomer, being the less favored of the two from the hard-soft point of view. Direct comparison of structural parameters derived from the μ-SCN and μ-NCS structures would be perhaps illuminating in terms of the phenomenon of "inorganic symbiosis";[85] present structural information does not suffice, as will be shown later in this discussion.

Interpretation of results of diffraction studies of transition metal cyanides in terms of bonding is in general not straightforward, since a metal-carbon bond length is a function of both ligand-to-metal sigma bonding and metal-to-ligand back donation. The importance of π bonding is usually difficult to assess, since there is no information at hand about what this bond distance would be if no such π bonding were present. As if this confusing situation were too straightforward yet, things are usually further complicated by the fact that molecular packing can have real and noticeable effects upon molecular geometry, obscuring small changes in bond lengths due to electronic rearrangements. Fortunately, crystals of the isocyano isomer were almost accidentally obtained which are isostructural with those for which diffraction work was done in the cyano system, such that we can assume that any differences noted between the two structures are due solely to differences in the bonding in the two molecules, since packing effects are closely the same. A detailed inspection of these differences, then, should give clues as to the bonding of cyanide by both the carbon and nitrogen atoms. In addition, comparison of the effects of the two modes of coordination upon the pentacyano and pentaamminecobalt(III) systems should illuminate the bonding within these fragments. Comparison of the structure of the μ-SCN compound with the others should give information about bonding of the SCN^- and its relation to cyanide.

A fair question to ask before delving into detailed comparisons is "what sort of distances are normal for ammine and cyano complexes of cobalt(III)?" Structures of a number of monomeric pentaammine complexes have been determined; those which do not exhibit substantial disorder are listed in Table V-3, including the mean Co-N distance in each. These are seen to vary from about 1.94 to 2.00 Å, the weighted mean value being 1.969 Å. Table V-4 includes binuclear complexes containing the $(NH_3)_5CoX$ fragment, all but one having been structurally characterized in this laboratory. The Co-N distances in this class of compounds varies over a slightly smaller range, about 1.94 to 1.98 Å, but the weighted mean of these values is 1.968 Å, which agrees beautifully with the average value in the mononuclear compounds. The nice agreement between these two values and the fact that the more precise determinations seem to have Co-N values clustered in the range 1.965-1.975 Å indicate that 1.970 Å is a good expectation value for the length of the $Co\text{-}NH_3$ bond.

Sufficient data are also available for arriving at expectation values for Co-C and C-N distances in Co(III) cyano complexes. While these distances were not well known until very recently, a flurry of activity within the past five years has resulted in the fact that the $Co(CN)_6^{3-}$ ion is one of the best characterized transition complexes from the structural point of view. This is partially because, being a very stable and large anion, it is convenient for use as a counterion for large cations in crystallographic studies. Early work on salts of the $Co(CN)_6^{3-}$ ion did not determine

TABLE V-3. PENTAAMMINE COBALT(III) STRUCTURES

Compound	Co-N(Å)	Reference
$\{(NH_3)_5CoCN\}Cl_2$	1.967(12)	86
$\{(NH_3)_5CoCN\}Cl_2$	1.986(15)	87
$\{(NH_3)_5CoCN\}(ClO_4)_2\cdot\frac{1}{2}H_2O$	1.980(20)	87
$\{(NH_3)_5CoCl\}Cl_2$	1.974(14)	88
$\{(NH_3)_5CoCl\}(SiF_6)$	1.995(16)	89
$\{(NH_3)_5CoN_3\}(N_3)_2$	1.968(9)	90
$\{(NH_3)_5CoNO_2\}Br_2$	1.978(6)	91
$\{(NH_3)_5CoCO_3\}Br\cdot H_2O$	1.96 (2)	92
$\{(NH_3)_5CoNO_2\}Cl_2$	1.960(10)	93
$\{(NH_3)_5CoSCN\}Cl_2$	1.942(10)	94
$\{(NH_3)_5CoS_2O_3\}Cl\cdot H_2O$	1.964(8)	61

Average=1.969 Å

TABLE V-4. BINUCLEAR COMPLEXES CONTAINING PENTAAMMINECOBALT(III)

Complex	Co-N (Å)	Reference
$\{Co_2O_2(NH_3)_{10}\}(SO_4)_2\cdot4H_2O$	1.962(12)	30
$\{Co_2O_2(NH_3)_{10}\}(SCN)_4$	1.959(10)	This work
$\{Co_2O_2(NH_3)_{10}\}SO_4(HSO_4)_3$	1.946(19)	27
$\{Co_2O_2(NH_3)_{10}\}(NO_3)_5$	1.956(10)	28
$\{Co_2NH_2(NH_3)_{10}\}(NO_3)_5$	1.969(20)	95
$\{Co_2N_2O_2(NH_3)_{10}\}(Br,NO_3)_3$	1.94 (2)	96
$\{(NH_3)_5CoNCCo(CN)_5\}\cdot H_2O$	1.965(8)	8
$\{(NH_3)_5CoCNCo(CN)_5\}\cdot H_2O$	1.974(3)	This work
$\{(NH_3)_5CoNCSCo(CN)_5\}\cdot H_2O$	1.975(5)	This work

Average= 1.968 Å

interatomic distances with any great degree of precision; however, very recently at least eight precise structures containing this ion have been reported. These are listed in Table V-5. The Co-C distances listed vary from 1.87 to 1.91 Å, and average 1.890 Å. The C-N distances actually vary quite a bit less, averaging 1.150 Å. The C-N distance would be expected to be less sensitive to both steric and electronic constraints than the Co-C distance, and the fact that these are more constant, even with the inherent lower precision of measurement of C-N, instills confidence that the observed variation in Co-C distances in the hexacyanides is real.

A smaller number of binuclear complexes containing the $Co(CN)_5$ unit have been determined by crystallographic methods, most of which are reported in this thesis. Mean equatorial Co-C and C-N distances in these compounds are 1.891 and 1.147 Å, respectively. These values are in excellent agreement with those found in the hexacyanides, and expectation values of these two distances can confidently be said to be 1.890 Å for Co-C and 1.149 Å for C-N. It should be noted that these values are expected specifically for terminal (nonbridging) equatorial ligands, as bridging or trans influence would be expected to affect them.

Inorganic symbiosis considerations predict that the molecule $(NH_3)_5CoCNCo(CN)_5$ will be less stable than its linkage isomer $(NH_3)_5CoNCCo(CN)_5$, since in the isocyano isomer, the harder, more electronegative nitrogen atom is bonded to

TABLE V-5. COBALT HEXACYANIDES AND BINUCLEAR COBALT CYANIDES

Compound	Av. Equat. Co-C(Å)	Av. Axial Co-C(Å)	Av. C-N(Å)	Ref.
$H_3\{Co(CN)_6\}$	1.885(3)	-	1.154(4)	97
$D_3\{Co(CN)_6\}$	1.883(9)	-	1.147(10)	98
$Cd_3\{Co(CN)_6\}$	1.893(5)	-	1.151(7)	99
$Cs_2Li\{Co(CN)_6\}$	1.886(3)	-	1.148(5)	100
$\{CrCN_3\}\{Co(CN)\}_6 \cdot H_2O$	1.869(8)	-	1.155(8)	101
$\{Co(NH_3)_5\}\{Co(CN)_6\}$	1.894(1)	-	1.157(2)	102
$\{Co(penten)\}\{Co(CN)_6\} \cdot 2H_2O$	1.915(8)	-	1.136(11)	103
$\{Co(dien)_2\}\{Co(CN)_6\} \cdot 2H_2O$	1.889(2)	-	1.148(3)	104
$K_5\{Co_2O_2(CN)_{10}\} \cdot H_2O$	1.880(4)	1.842(7)	1.167(8)	This work
$K_8\{Co_2O_2(CN)_{10}\}(NO_3)_2 \cdot 4H_2O$	1.900(4)	1.875(4)	1.149(6)	This work
$(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$	1.893(2)	1.885(5)	1.144(3)	8
$(NH_3)_5CoCNCo(CN) \cdot H_2O$	1.908(3)	1.876(7)	1.125(5)	This work
$(NH_3)CoNCSCo(CN)_5 \cdot H_2O$	1.879(5)	1.859(5)	1.142(5)	This work
$Ba_3\{Co_2(CN)_{10}\} \cdot 13H_2O$	1.885(3)	1.951(5)	1.153(5)	31,32
Averages =	1.890(11)		1.148(10)	

the soft pentacyano group, and the softer carbon atom is bonded to the hard pentaammine group. From the results of the isocyano refinement, the bonding does appear to be slightly weaker in the isocyano molecule than in the cyano molecule. The results of the cyano structure determination were interpreted as indicating that the carbon end of cyanide is a better π-accepting ligand than the nitrogen end, and that conclusion is borne out by the results of the isocyano refinement also. While for a single bond, one would expect the Co-C bond to be <u>longer</u> than Co-N, the opposite trend is noted in both structures. The difference is 0.035 Å for cyano and 0.058 Å for isocyano, both values being highly significant. While Co-C in isocyano is longer than in cyano, the difference (0.013 Å) is not statistically significant, although it is probably real. The Co-N distance in isocyano is significantly longer than in cyano, the difference being 0.035 Å. This indicates weaker overall bonding to the bridging group in the isocyano molecule than in the cyano molecule. This weaker bonding to the ligand is accompanied by a strengthening of the bonding within the cyano bridge itself. The C-N distance in the isocyano structure is shortened by 0.034 Å relative to cyano; the shortening is 4σ and is thus significant. The observed C-N distances in the two isomers correlate well with C-N stretching frequencies in the infrared spectra of these two complexes, supporting the significance of the observed shortening. The C-N stretch for the cyano complex occurs at 2180 cm^{-1}, while the corresponding frequency for the bridging cyanide of the isocyano complex is 2202 cm^{-1}. Lengthening of the metal-cyanide distance coupled with a C-N shortening is consistent with the observation that decreased d-π^* back-bonding has the effect of removing electron density from antibonding orbitals of the cyanide group and thus increasing the bond order.

The overall geometry of the $(NH_3)_5CoCN$ group of the isocyano molecule agrees fairly well with that of the $\{(NH_3)_5CoCN\}^{2+}$ ion as determined by X-ray studies of the chloride[86,87] and perchlorate[87] salts. Co-N values average 1.974(2) Å for the isocyano complex and 1.965(8) Å for the cyano complex, both close to the expectation value of 1.970 Å. All individual distances in isocyano are longer than the corresponding distances in the cyano molecule; while no particular distance is longer by a statistically significant amount, the term-by-term trend is quite striking and hints at reality.

In the cyano structure, a 0.03 Å shortening in the <u>trans</u> ammine distance was noted, and rationalized by Wang in terms of some π-accepting character on the part of the nitrogen end of cyanide. Since carbon-bonded cyanide is a better π-acceptor than isocyanide, as evidenced by the relative lengths of bonds to the bridging group, we would expect that this effect would be even more pronounced in the isocyano complex. This prediction, however, turns out to be totally wrong: absolutely no hint of a trans influence is noted in the pentaammine end of the isocyano molecule. A trans shortening is, in fact, quite rare in pentaamminecobalt(III) structures. Since π effects do not seem to be the cause of the shortening, it must be due to sigma bonding, in particular competition between the cyanide and ammine for sigma-bonding e_g orbitals of the metal. A similar situation is seen in the $\{Co_2(CN)_{10}\}^{6-}$ dimer, in which the Co-Co σ bond is thought to compete successfully with the trans cyanide, causing an elongation of the axial Co-C bond. In the present system, the ammine appears to compete about equally with the C-bonded cyanide and win the competition with the isocyanide. This explanation forces the conclusion that not only is cyanide a better π-acceptor than isocyanide, but also a better σ-donor. This accounts for the fact that no stable isocyanides with a bare carbon atom are known.

The pentaamminecobalt(III) group in the thiocyanato-bridged complex is identical with that found in the cyano isomer. Not only is the Co-NCS distance indistinguishable from the Co-NC distance, but exactly the same sort of trans shortening is evident in $(NH_3)_5CoNCSCo(CN)_5$. The axial Co-N distance, 1.931(4) Å of the thiocyanato molecule is identical to the axial Co-N distance of 1.935(5) Å in the cyano molecule. It is evident that the bonding within the $Co(NH_3)_5N$ fragment is identical in the two compounds, and one may conclude that inserting a neutral sulfur atom into the bridge three atoms distant from the metal has no detectable effect upon the bonding within pentaamminecobalt(III).

The average equatorial Co-C and C-N distances in the isocyano molecule are 1.908(4) Å and 1.125(7) Å, respectively. In the cyano molecule, the corresponding distances are 1.893(2) Å and 1.144(5) Å. While the individual differences are not significant statistically in all cases, the term by term trend appears clear: the effect of switching the bridging ligand to the isocyano form lengthens the equatorial Co-C distances and shortens the equatorial C-N distances. The sums of the two are the same within experimental error in all cases. While both Co-C σ and π bonding lead to shortening of the Co-C distance, Co-C σ bonding results in a decrease in the C-N distance, while Co-C π bonding leads to a compensatory increase in the C-N distance, resulting in very uniform terminal C-N distances in a wide variety of cyanides. In this system the observed differences indicate similar metal-ligand σ bonding in both isomers and greater π bonding in the equatorial ligands of the cyano isomer. Since the effect is rather small, this is not inconsistent with results of MO calculations and vibrational studies which indicate that π bonding in $\{Co(CN)_6\}^{3-}$ is relatively unimportant with respect to σ bonding.[105,106] This observed shortening of equatorial C-N distances caused by N-bonding to the bridging group is also consistent with the infrared spectra of the two isomers. The terminal cyanide stretching frequency for the cyano isomer occurs at 2120 cm^{-1}, while the corresponding absorption in the isocyano spectrum occurs at 2131 cm^{-1}, indicating stronger C-N bonding in the isocyano molecule.[43,45,107]

In the cyano molecule, all Co-C distances of the pentacyanocobalt group are equivalent; however, in the isocyano molecule, a shortening of the axial Co-C distance by 0.032 Å relative to the equatorial distances is noted. This shortening is 4σ and therefore quite significant. This observation seems to support the contention that nitrogen-bonded cyanide is a poorer σ donor than carbon-bonded cyanide, since the C-bonded terminal ligand competes successfully for cobalt e_g orbitals with the N-bonded bridging group. The significance of this apparent shortening is diminished, however, when the two isomers are compared. This distance is insignificantly different from the corresponding distance in the cyano isomer, which has normal equatorial Co-C distances. The overall effect upon the pentacyanocobalt system caused by switching the bridging group to the isocyano form is best thought of as a lengthening of the cis ligand distances only, with no effect on the trans distance.

In the pentacyano portion of the thiocyanato molecule, significant differences in Co-C distances exist both between the equatorial and axial ligands and within the equatorial distances themselves. Neglecting the axial cyanide, which is probably suffering from the effects of a trans influence, the Co-C distances average 1.884 Å, which agrees well with the expectation value. The average C-N distance is 1.142 Å, which is also in satisfactory agreement with the expectation value.

That the possible trans effect is real although not particularly clear is suggested by the Co-S distance. From past experience with complexes exhibiting trans influence phenomena, we would expect a shortened axial Co-CN distance to be accompanied by a lengthened Co-S distance, due to orbital competition. This sort of effect has been noted in three of the other complexes described in this thesis. The Co-S bond does appear to be elongated with respect to what is observed in cobaltammine complexes. The distance here, 2.334(2) Å, is more than 0.05 Å longer than the essentially identical values of 2.272(7) and 2.284(6) Å found in pentaamminecobalt(III) complexes of -SCN and -S_2O_3, respectively.[94,61] The difference is about 10σ, and is undoubtedly significant. It would be surprising to observe this difference between the ammine and cyano complexes without an accompanying trans shortening in the cyano complex, thus the ill defined shortening is judged to be probably real.

The fact that the Co-S bond in the $(CN)_5$Co-SCN fragment is longer and therefore presumably weaker than the Co-S bond in the corresponding ammine complex is at first glance a bit surprising, in view of the fact that $(CN)_5CoSCN^{3-}$ is known to be the stable linkage isomer while the $(NH_3)_5CoSCN^{2+}$ ion is not stable with respect to isomerization. It must be remembered, however, that the important consideration is not the relative bond strengths between these two complexes, but rather the stability of each with respect to its own linkage isomer. We would, therefore, like to compare the difference between the Co-S and Co-N bond lengths in the ammine system with the corresponding difference in the cyano system to see if any insight about how symbiosis works is developed. Unfortunately, not all these data are available, but fortunately, good estimates are available for those which are not. The Co-N distance for the ammine system and the Co-S distance for the cyano system are both available from the structure of $(NH_3)_5CoNCSCo(CN)_5$. The Co-S distance for the ammine system is available from the determination of the crystal structure of $\{(NH_3)_5CoSCN\}Cl_2$. No data are available for the Co-N distance in the cyano system; however, it is probable that the distance sought is about the same as Co-NC in the compound $(NH_3)_5CoCNCo(CN)_5$, by analogy to the fact that the $N\text{-}Co(NH_3)_5$ groupings are virtually identical in the molecules $(NH_3)_5CoNCCo(CN)_5$ and $(NH_3)_5CoNCSCo(CN)_5$, indicating identical bonding to -NC and -NCS. The distances to be compared, then, are given in the table below:

	Co-S	Co-N
pentaammine	2.27 Å	1.91 Å
pentacyano	2.33 Å	1.96 Å

We see that the Co-S bond is 0.36 Å longer than the Co-N bond in the pentaammine system, and the number is virtually identical in the pentacyano system (0.37 Å). Thus our results have shed no light upon the question of how symbiosis works. It is clear, however, that the π-competition effects which presumably lead to the antisymbiotic behavior of the soft metals Pt(II) and Pd(II) are still in effect in the Co(III) systems, and the reason for the opposite behavior of the two classes of metals must be attributed to something other than a magical disappearance of π effects in the cobalt(III) complexes.

C. The Complex $\{(CN)_5CoSSO_2Co(CN)_5\}^{6-}$

The synthesis and structural characterization of the μ-thiosulfitodecacyanodicobalt(III)ate ion were somewhat serendipitous, in that formation of this complex arose out of attempts to crystallize the closely related ion $\{(CN)_5CoS_2Co(CN)_5\}^{6-}$, and the identity of the new complex was not discovered until the mid-stages of the structural refinement. It appears that the thiosulfito complex was formed by very slow air oxidation of the pre-formed dithio bridge, in which the oxidant becomes trapped in the product (oxidative addition). Attempts to prepare the complex conveniently by rapidly bubbling oxygen through a solution of the dithio complex yields no detectible formation of the product after two days at -15°, and to the formation of $(CN)_5CoOH_2^{2-}$ at room temperature. Hydrogen peroxide as the oxidant reacts within hours at -15° to form an unidentified product or products.

The μ-thiosulfitodecacyanodicobalt(III)ate ion is interesting because it is a complex of a "nonexistent" ligand. Thiosulfite ion has never been demonstrated to exist either independently or in complexed form. Analogy can be drawn to the dithio ligand, which exists as free S_2 only in the gaseous form at high temperatures, but is stabilized by complexation to transition metal ions, forming several known compounds which are stable at room temperature.[108,109,41] Thiosulfite also appears to be stabilized by complexation to Co(III), as the complex can exist in aqueous solution at room temperature for several days. The dithio complex disproportionates within minutes under the same conditions unless the solution is highly basic.

Thiosulfite ion is a new example of an ambidentate ligand, which has several possibilities for bonding mode. As is shown by this structural study, it can function as a bridging group through both sulfur atoms, and thus nonbridging coordination through either sulfur atom seems possible. Bonding to this ion is expected to be similar to that exhibited by sulfite when coordinated through the sulfito sulfur atom, and somewhat similar to that exhibited to thiosulfate when coordinated through the thio sulfur atom. In the present complex, we see examples of both.

Sulfite as an S donor is classed as a π-acceptor ligand based upon its strong trans labilizing power in cyanocobaltate(III) complexes, and because of its high position on the spectrochemical series.[110,111] This characterization is supported by the facts that sulfite-cobalt(III) bonds are much shorter than Co-S bonds in other complexes, and sulfite exerts a strong structural trans influence as well. For instance, the complex $Co(en)_2SO_3NCS$ exhibits a Co-S distance of 2.203(6) Å, as opposed to 2.26 Å for the sum of the covalent radii, and a very long Co-NCS distance of 1.974(18) Å trans to the sulfite. The Co-NCS distance in a more "normal" sort of isothiocyanate complex, $(NH_3)_5CoNCSCo(CN)_5$, is 1.908(4) Å, almost 0.07 Å shorter.

We should expect the $Co-SO_2S$ bonding in thiosulfite complexes to resemble that in ordinary sulfites, that is, a tendency toward π-acceptor behavior. What is observed in the structure determination of the μ-SSO_2^{2-} dimer is a $Co-SO_2S$ distance of 2.256(2) Å, and no indication of a shortening of the trans Co-C distance. This seems consistent with the characterization of SSO_2^{2-} ion as a π-acceptor for the following reasons:

a) $(CN)_5CoSCNCo(NH_3)_5$ exhibits a somewhat long Co-S distance (2.334(2) Å) and some hint of a shortening of the trans Co-C distance.

b) The Co-S bond in $(CN)_5CoSCN^{3-}$ has little or no π character.[21] The ligand $-SO_2S^{2-}$ in the present binuclear complex apparently competes equally well with the trans cyanide for orbitals of the cobalt of π symmetry, whereas $-SCN^-$ does not, accounting for the observed bond lengths. The fact that the Co-S distance is considerably longer in this complex than in sulfite complexes is a consequence of the strong ligand field strength of cyanide, rather than a lesser degree of π-accepting character on the part of sulfito-bound thiosulfite.

The length of the $Co-SSO_2$ bond, as mentioned in the section on structure descriptions, is 2.298(2) Å. Cobalt-sulfur bond lengths can, due to the high electron density at both atoms, be determined to a good degree of precision by X-ray methods, even when the overall precision of the structural determiniation is not particularly high. This is pointed out because reference will presently be made to Co-S bond lengths in similar coordination compounds, the structures of which were determined by photographic methods.

The length of the Co-S bond in the pentaammine thiosulfato cobalt(III) complex[61] is 2.284(6) Å, only 0.014 Å shorter than the length found here. This difference is not statistically significant, and the temptation is to attribute the bonding of thiosulfite through this sulfur atom to a scheme very similar to that of S-bonded thiosulfate. The near -coincidence of the two bond lengths is misleading, however, because of the high trans influence of the cyanide ion; in a pentaammine complex, the Co-SSO_2 distance would be expected to be a great deal shorter than what we observe here. Since the structure of the complex $(CN)_5CoSSO_3{}^{4-}$ has not been worked out, the thiosulfate and thiosulfite ions cannot be compared directly and confidently with respect to their bonding through the thio sulfur atom, but analogies can be drawn to formulate a good guess as to what the Co-S bond length in $(CN)_5CoSSO_3{}^{4-}$ should be.

Comparisons of pentacyanocobalt(III) to pentaammine-cobalt(III) complexes of the same ligand, based partly on work reported in this thesis, indicate that the Co-ligand distance is systematically longer in the cyano complexes by several hundredths of an Angstrom. This difference is greater than 0.06 Å for Co-SCN, about 0.05 Å for Co-$O_2{}^-$, and about 0.04 Å for Co-NC. A difference of 0.04 Å thus seems appropriate for the difference between Co-S bonds in the pentacyano and pentaammine thiosulfate ions. This supposition places the

Co-S distance tentatively at about 2.33 Å in $(CN)_5CoSSO_3{}^{4-}$, about the same found in the thiocyanato-bridged complex, and our Co-thio distance in the μ-$SSO_2{}^{2-}$ complex looks significantly shorter. Thus, if the above assumptions are correct, thiosulfite and thiosulfate differ somewhat in their bonding to cobalt, which is reasonable, since the thio sulfur atom in thiosulfite is undoubtedly in a more reduced state.

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PROPOSITIONS

I. I propose to carry out complete three-dimensional X-ray crystal structure determinations of salts of three somewhat controversial metal-cyano complex anions in order to elucidate questions regarding bonding in each. The ions are $Co(CN)_5{}^{3-}$, $Fe_2(CN)_{10}{}^{6-}$, and $\{Co(CN)_5\}_2N_2O_2{}^{6-}$.

II. I propose to attempt to prepare transition metal complexes containing carbon monosulfide as the sole ligand by direct reaction of the CS molecule in a reaction similar to those resulting in the formation of group VIB hexacarbonyls.

III. I propose to investigate the potential use of X-ray photoelectron spectroscopy as a tool for determining the bonding mode of ambidentate ligands, particularly for ligands such as sulfite, for which several modes are possible.

IV. I propose to investigate by X-ray diffraction methods, the structure of a reportedly stable intermediate ozone complex formed in the ozonolysis of triethyl stannic chloride, to provide information about such usually transitory structures.

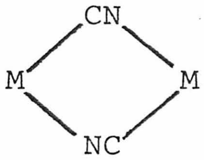
V. I propose that the unique arrangement of olefinic bonds in tricyclo [5.2.1.$0^{4,10}$] deca-2,5,8-triene (triquinacene) makes it an ideal triene for the formation of octahedral π-metal complexes with d^6 molybdenum. I propose to prepare the complex $(C_{10}H_{10})Mo(CO)_3$ and other complexes of triquinacene.

Proposition I. Structural Problems in Cyanide Chemistry

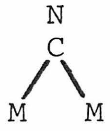
Although much structural work has been done recently on transition metal cyano complexes, many questions remain, and a number of these can probably be answered relatively easily by the use of X-ray diffraction.

A) Structure of the $Co(CN)_5^{3-}$ ion: The structure of the coordination compound formed in cyano solutions of Co(II) with CN:Co greater than 5 has been a subject of interest and controversy for several decades. The complex was long formulated as the hexacyanide $Co(CN)_6^{4-}$, but the pentacyanide formulation was proposed in 1949 as a result of a polarographic study.[1] Green solutions of the ion are paramagnetic, but the crystalline product obtained from such solutions are purple and diamagnetic; the dimer $Co_2(CN)_{10}^{6-}$ has been shown to have approximate D_{4d} symmetry, consisting of two square pyramidal $Co(CN)_5^{3-}$ groups joined by a metal-metal bond.[2,3] This dimer is presumed to exist in rapid equilibrium with the monomer in solution, and thus all attempts to crystallize the monomer from aqueous solution have resulted in the dimer as the sole product. A recent study of tetraalkylammonium pentacyanocobaltates in acetonitrile has reported a method of crystallizing the monomer as such.[4] Presumably the large tetrabutyl ammonium cations effectively shield the cyano monomers from one another to allow crystallization without dimerization as a yellow solid. Single crystal X-ray analysis of these air-sensitive yellow crystals should settle the question of the structure of the monomer.

B) Solutions of the aquopentacyanoferrate(II) ion have been shown[5] to equilibrate within a few hours at 10°C. to a mixture containing the original $(CN)_5FeOH_2{}^{3-}$ ion and a presumably binuclear species having the empirical formula $Fe(CN)_5{}^{3-}$. The electronic spectrum of this complex is consistent with iron(II) in an octahedral field of the chromophore C_5N.[6] Emschwiller et. al have interpreted this situation in terms of the existence of a dimer $Fe_2(CN)_{10}{}^{6-}$ which contains two bridging cyanides and is centrosymmetric. This formulation, if correct, represents the only example of a complex containing the structure

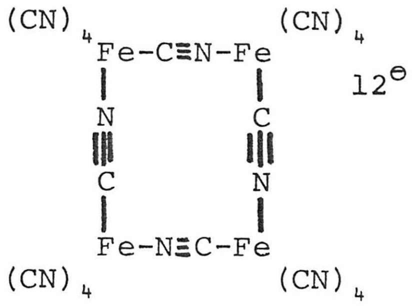


which would be inherently interesting in itself, for the following reasons: 1) Nonlinear bridging cyanides are known, but are usually not too far deviant from linearity. The M-C-N angles in this compound would have to be in the area of 140°, which seems far-fetched for sp-hybridized C and N atoms. 2) This compound might be expected to stabilize a form with sp^2 hybridized C and N atoms to accommodate the small M-C-N angle, leading to an increase in the C-N distance. Infrared spectroscopy would be an interesting tool to give evidence about this matter, as the decrease in the frequency of the C-N stretching vibration due to the weakening of the C-N bond would counter the increase normally observed for bridging cyanides, and little or no shift might be seen in a complex containing bridging cyanides. 3) A slight possibility exists that cyano bridges analogous to carbonyl bridges are present in this complex,



which has not been previously observed. This seems unlikely, since carbonyl bridges of this type appear to be too weak to hold clusters together without the accompanying presence of M-M bonds, and such interactions are not to be expected in d^6 Fe(II) complexes.

None of the above alternatives appear too satisfying; however, there is an alternate structure which Emschwiller et. al have apparently overlooked. It is possible to maintain $Fe(CN)_5$ stoichiometry, C_5N environments about all the Fe atoms and maintain linear CN bridges in the tetranuclear structure:

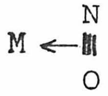


This polymerization is easily imagined by nucleophilic substitution of a coordinated cyanide for the water molecule of another aquopentacyano ferrate ion:

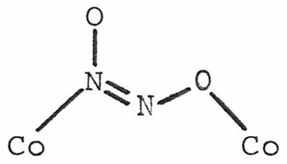
$$(CN)_5FeOH_2{}^{3-} + NCFe(CN)_4OH_2{}^{3-} \longrightarrow (CN)_5FeNCFe(CN)_4OH_2{}^{6-} + H_2O$$

Continued polymerization leads to the product when cyclization occurs. A tetramer seems likely from the symmetry of the problem, but higher order polymers are certainly not ruled out. Low molecular weight polymers stand a good chance of crystallizing well with the proper cation, which would not only conceal their polymeric nature from the casual observer, but make an X-ray analysis possible.

C) Nitrosyl complexes of the type $(CN)_5MNO^{n-}$ have been the subject of extensive investigations, and are generally found to contain the nitrosyl bonded linearly to the metal ion.[7] The NO adduct of $Co(CN)_5{}^{3-}$ is expected to be structurally different, due to the electronic configuration $t_{2g}{}^6e_g{}^1$ of the pentacyanocobaltate which differs from the normal $t_{2g}{}^6e_g{}^0$ configuration of most ions of this type. Strange and wonderful types of coordination for the nitrosyl have from time to time been suggested for this complex, including such beasts as oxygen-coordinated nitrosyl[8] and pi-bonded nitrosyl[9]



The recent elucidation of the structure of the "red nitrosylpentaammine cobalt" complex as a dimer containing the hyponitrite ion[10] prompted Jezowska-Trzeblatowska et al.[11] to interpret the infrared spectrum of the cyano analog in terms of the same structure:



This formulation is probably correct; however, nagging doubts are present. There appears to be an equilibrium between the monomer and dimer in solution, which is not the case for the ammine system. Also, three sharp peaks in the 900-1200 cm^{-1} region of the IR spectrum of the ammine complex[12] have been attributed to the bridging $N_2O_2{}^{2-}$ group, and for the cyano complex, only one sharp peak and one broad peak appear in this region, suggesting a difference in structure.

An X-ray structure determination would conclusively settle the controversy about this ion, and good crystallization is probably merely a matter of finding the suitable cation.

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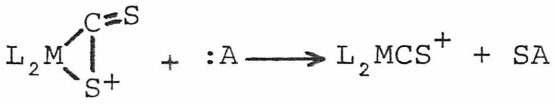
Proposition II. Preparation of Hexathiocarbonyl Metal Complexes

Carbon monosulfide (CS) is a molecule which does not exist under ordinary conditions in any form which allows convenience in the study of its chemistry, and thus its chemistry has not been extensively studied. The free CS molecule is an intermediate in the photolysis[1] of CS_2, and has been detected in the upper atmosphere in small concentrations;[2] however, until very recently, gram quantity samples of the compound have not been easily available for use in synthesis of metal complexes.

Thiocarbonyl complexes have been known for less than a decade, and all the well-characterized examples were formed by reactions of the coordinated CS_2 ligand rather than by a preparation involving CS itself as a reactant. These reactions are thought to involve attack of a nucleophilic reagent upon the coordinated sulfur atom of an oxidatively added CS_2 ligand:[3]



An example[4] of this type of reaction is the formation of trans-$RhCl(CS)(P\phi_3)_2$

$$(\phi_3P)_2RhCS_2^+ + P\phi_3 \longrightarrow SP\phi_3 + (\phi_3P)_2RhCS^+ \xrightarrow{Cl^-} RhCl(CS)(P\phi_3)_2$$

A number of complexes of this type have been made, and all contain only one thiocarbonyl ligand.

Richards has reported calculations (SCF wavefunctions) leading to orbital energies for the CS molecule.[5] The relative energies indicate that a lone pair of sigma symmetry localized on the carbon atom is of more favorable energy for donation to metal ions than is the corresponding lone pair on carbon monoxide, and the lowest energy empty π^* orbital is of lower energy than the corresponding CO orbital. In short, CS looks like an extremely good ligand for synergistic bonding to metals. This expectation is supported by the fact that CS cannot be displaced by CO in the thiocarbonyl complexes previously described.[6] A crystal structure determination[7] of the complex $Rh(P\phi_3)_2ClCS$ has demonstrated the Rh-CS bond length to be quite short, 1.787(10) Å, and thus presumably quite strong.

The only reported synthesis of a metal complex containing CS as the sole ligand was rather disappointing in view of the above expectations. $Ni(CS)_4$ was reportedly detected by mass spectrometry as an unstable product of the direct reaction of CS upon metallic nickel.[8] This result, if correct, is unexpected, and complexes of CS containing no other ligands deserve further investigation.

Klabunde et al. have recently reported a convenient method of producing gram quantities of CS for synthetic use by high voltage ac discharge through CS_2 in a vacuum flow system.[9]

They report that the CS gas thus formed can be moved at least five meters in gas phase, making its use as a reagent feasible.

To guess what CS complexes should be most stable, and thus which we should wish to attempt to synthesize, analogy to the corresponding carbonyl complexes may be helpful. The hexacarbonyl complexes of the group VIB metals exhibit remarkable stability as compared to other metal carbonyls, being inert with respect to oxygen at ordinary temperatures and sublimable at temperatures up to 120°. It is thus desired to synthesize the complexes $Cr(CS)_6$, $Mo(CS)_6$ and $W(CS)_6$.

Klabunde et al.[9] report the failure of CS to replace CO in carbonyl complexes at low (otherwise unspecified) temperatures, and thus this sort of reaction is eliminated. Any reaction in which the metal is reduced at high temperature or pressure should be avoided, since carbon monosulfide is known to polymerize at high temperatures. The most promising reaction to use appears to be the Grignard synthesis, which may be carried out at room temperature or below. This involves reduction of the metal halide by alkylmagnesium halide in the presence of CS followed by hydrolysis of the product.[10]

Successful preparation of metal hexathiocarbonyl complexes would logically lead to attempts to prepare polynuclear complexes and thiocarbonyl-arene metal complexes. Hexathiocarbonyl complexes would also be the ideal starting product for studies of the reactions of coordinated carbon monosulfide.

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Proposition III. ESCA and the Bonding Mode in Ambidentate Ligands

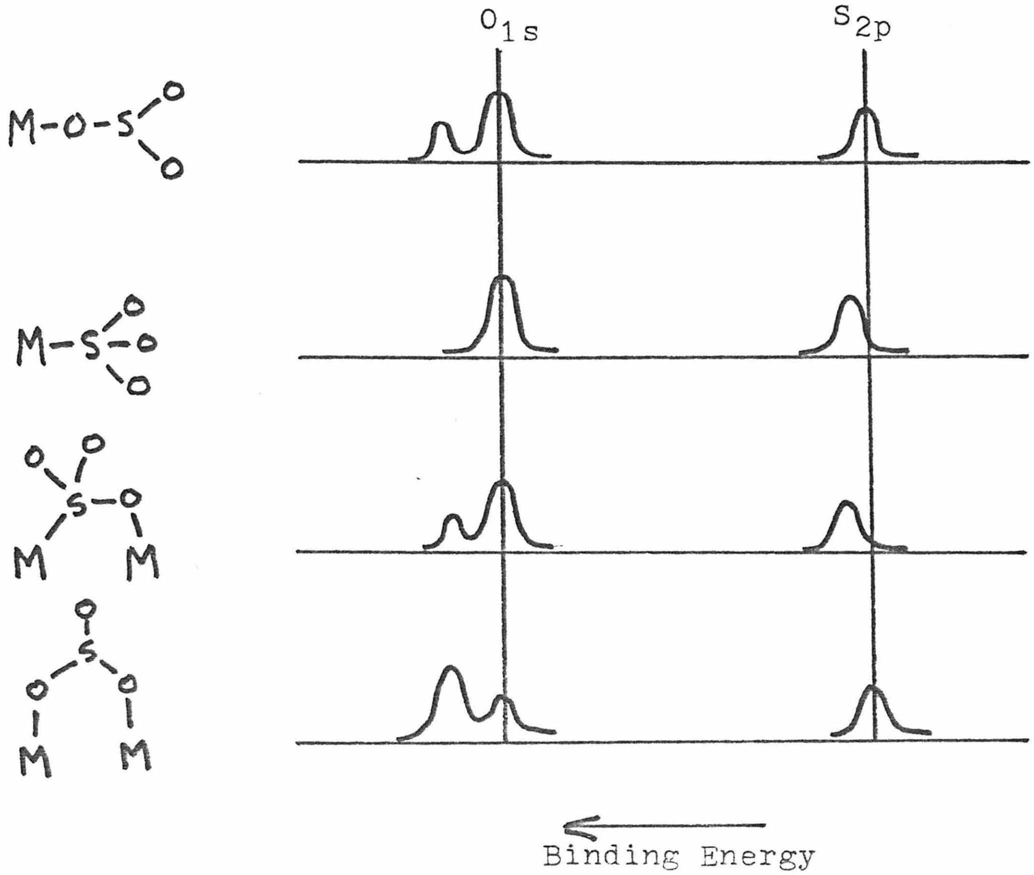
Short of full X-ray diffraction analysis, the most useful methods of determining which atom or atoms coordinate to transition metals when the ligand in question is ambidentate in nature have been infrared and ultraviolet-visible spectroscopy. Infrared absorption gives information about force constants of bonds considered as oscillators as well as information about the symmetry of the complex in many cases. Positions of bands observed in UV-VIS spectra yield clues as to the ligand field strength of ligands coordinated to the metal. This information, when unambiguous, is generally sufficient to determine the bonding mode of the ambidentate ligand, and many such predictions have been confirmed when X-ray structure determinations have become available.

Both methods mentioned have drawbacks which can sometimes be serious and tend only to obscure the issue. Shifts of absorption lines in IR spectra are sometimes quite small, and the lines themselves weak. Line counting, for purposes of point symmetry considerations, can be difficult due to overlap with other bands in the same region of the spectrum. The indexing of the individual absorptions is crucial but sometimes ambiguous. Electronic absorption spectroscopy suffers from similar problems; overlap of bands due to poor resolution and contribution from different portions of the molecule. Ambiguity in assigning specific transitions to observed bands also generally arises. The net result of these problems is that the literature is sprinkled generously with incorrect predictions about bonding mode of ligands.

X-ray photoelectron spectroscopy (ESCA) has several advantages over the more traditional methods as a tool for determination of bonding mode. First, for a fairly simple complex, the ESCA spectrum will be manifestly uncluttered. Peaks are sharp, and correlation of peaks to specific orbitals of specific elements is anambiguous. Shifts in ionization energies of inner core electrons are reasonably sensitive to chemical environment, and peak areas are approximately proportional to the number of atoms in specific environments.[1]

To demonstrate the potential use of ESCA for determination of binding mode, sulfite will be discussed as the ambidentate ligand, since several coordination modes are possible for it.[2] The method depends upon the fact that upon coordination to a metal ion, donation of ligand valence electrons to the metal causes a slight increase in the effective nuclear charge of the donor atom upon its core electrons, resulting in a slight increase in the binding energy of the core electrons. Particular core electrons to be monitored are somewhat arbitrary, but 1s for oxygen and 2p for sulfur have been found to yield best results in ESCA studies.[3]

Modes of binding for sulfite are monodentate O donor, monodentate S donor, bridging S,O and bridging O,O. Expected ESCA spectra for these four modes are illustrated below:



All are easily discernible except for monodentate O vs. bridging S,O; the only difference between these two configurations being a slight chemical shift of the S2p peak. In view of this problem, it is heartening to note that very recently, Su and Faller[4] were able to distinguish S-bonded from O-bonded sulfoxide complexes on the basis of chemical shifts alone, by examining the differences O1s-S2p.

Spectral differences for other ambidentate ligands, while usually not as dramatic as those expected for sulfite, may be sufficient to determine bonding mode. ESCA spectra should be recorded for complexes in which the bonding mode is well established from other evidence in order to test their usefulness as a mode criterion.

It is not suggested that X-ray photoelectron spectroscopy should be used as a substitute for more conventional methods of analysis, for to do so would ignore a vast accumulation of past experience, and could be counterproductive; however ESCA indications in agreement with those from IR and UV-VIS spectra would certainly allow binding mode to be assigned with a higher degree of confidence.

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Proposition IV. A Stable Intermediate in the Ozonolysis of Triethyl Stannic Chloride

The cleavage of carbon-carbon double bonds by reaction with ozone is a time-honored technique for synthesis and analysis in organic chemistry;[1] however, more recently renewed interest in the ozonolysis of other types of bonds to carbon has arisen. Interest in ozone-organic chemistry is perhaps due in part to potential synthetic uses, but more because of its application to environmental problems of the times, the role of ozone in air pollution and its use in sewage treatment.

The polar ozone molecule is able to act as an electrophile, nucleophile, or 1,3 dipole, and thus is able to form complexes with aromatic compounds, olefins, hydrocarbons, and various types of organometallic compounds as intermediates in degrading them to simpler products.[2] The initial complex formed between ozone and an organic or organometallic molecule is in general quite unstable and either rearranges or causes bond scission very quickly, such that these intermediates are somewhat difficult to study structurally. This is particularly true for the organics, in which the ozone complex is probably a transition state which is five-coordinate at a carbon atom in the ozonolysis of a C-X bond.

Heavier congeners of carbon are somewhat happier than carbon with higher coordination numbers, therefore, a stable ozone complex might rationally be expected to be more stable for the metallic members of group IVA. For instance, Sn(IV) is known to exist in stable complexes which are four, five, and six coordinate.[3] The reaction of ozone with $Sn(C_2H_5)_4$ yields acetaldehyde, Et_2SnO and an unidentified organotin peroxo compound; the initial ozone complex is not stable.[4] The substitution of chloride for an ethyl group has a marked effect upon the ozone reaction, as the ozonolysis of Et_3SnCl is reported to yield an intermediate complex of ozone as a fairly stable crystalline product.[5] Aleksandrov and Sheyanov report the products of bubbling a 0.02% O_3 in O_2 mixture through a hexane solution of Et_3SnCl as acetaldehyde and a crystalline organotin compound with formula $Sn_3O_4Et_7Cl_3$. Reaction with iodide suggest that 3 of the 4 oxygen atoms comprise a bonded ozone. These crystals slowly and spontaneously decompose to form acetaldehyde and an organotin compound which does not contain ozone, $Sn_2OEt_4Cl_2$.

The crystals of the alleged ozone complex apparently survive for a length of time on the order of several days, such that an X-ray crystal structure determination should be possible. This compound allows us, then, to structurally study the ozone-organometallic complex, in the hope of generating some insight into the mechanism of ozonolysis of the Sn-C bond, with its obvious applicability to organic compounds.

References for Proposition IV

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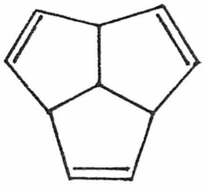
Proposition V. Metal Complexes of Triquinacene

The tricyclic triene triquinacene (I=II) was first prepared by Woodward and coworkers[1] in 1964, and was of interest then because it appeared to be an attractive precursor of the unknown but long-pursued hydrocarbon dodecahedrane (III).



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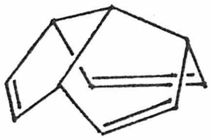

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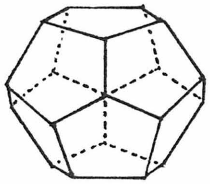

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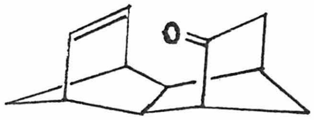
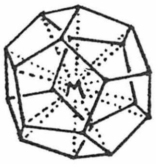


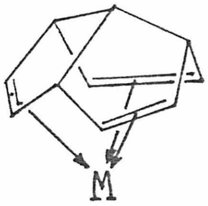
IV

The multistep synthesis produced triquinacene in 1.7% yield starting from the tetracyclic alcohol (IV). A few years later, a more direct, higher yield synthesis was found by Jacobson,[2] beginning with 1,4-bisdiazobutane Jacobson mentioned the possibility of formation of octahedral 2:1 π-complexes with "certain transition metals for which carbon-metal bond distances to be expected of this kind of compound probably permit nonbonded interactions between the olefinic hydrogens of the two organic entities to remain relatively small." Jacobson even proposes a valence tautomerism model of the 2:1 complex reminiscent of dodecahedrane:



Predictably, Jacobsen's pseudo-dodecahedrane has not appeared in the literature; however, neither have other metal π-complexes of triquinacene, and certain complexes do indeed seem possible.

Arene-metal complexes and most nonaromatic polyene complexes bond through ligand orbitals which are really not ideally geometrically suited for overlap with metal d orbitals. Monoolefins coordinate to metals with the olefinic plane normal to a metal d orbital, allowing good overlap of π-bonding orbitals with empty metal d orbitals and π* orbitals with filled metal d orbitals. In most polyene-metal complexes, however, this condition is not met exactly, and donation of π-bonding orbitals forms bent bonds because of nonideal overlap. Triquinacene allows a reasonably good approximation to ideal overlap conditions with an octahedral metal complex because the olefinic planes are bent inward toward the C_3 axis of the organic molecule, which has C_{3v} symmetry:



It would be of interest to attempt to prepare a metal complex of triquinacene which takes advantage of this favorable situation.

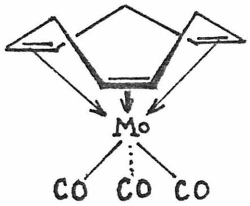
In designing this complex, those variables which must be decided upon are which metal or metal ion should be used, and what other ligands should be bonded to that metal (2:1 complexes with triquinacene are impossible due to repulsion between hydrogen atoms between the two triquinacene molecules). Ideal overlap should occur for a metal atom for which M-C is about 2.5 Å. This is slightly too large for transition metals, so some deviation from ideality will have to be tolerated; in any case, a second or third row metal should be picked over a first row metal. Anticipating the use of carbonyl ligands (2 electron donors) for the other three positions, a d^6 metal will be necessary to satisfy the empirical EAN rule, and a neutral d^6 is preferable to an ionic species, thus we are restricted to metals of group VIB. Third row W is only slightly larger than second row Mo, so there is little advantage in choosing it. The carbonyl ligands are chosen not only for stability of the complex, but for ease of preparation. Owing to the strongly electronegative character of the carbonyl ligand and its suitability for π-acceptance from the metal, olefin→metal→CO transfer is known to stabilize the olefin-metal bond in unsubstituted olefin-metal carbonyl complexes,[3] and these complexes are easily prepared from the corresponding hexacarbonyl complexes.[4]

Thus the complex to be prepared is $(C_{10}H_{10})Mo(CO)_3$, which is probably best prepared from molybdenum hexacarbonyl:

$$C_{10}H_{10} + Mo(CO)_6 \longrightarrow (C_{10}H_{10})Mo(CO)_3 + 3CO\uparrow$$

by ultraviolet irradiation of the reactants in a high-boiling hydrocarbon solvent. UV irradiation has been a successful technique in preparing π-olefin molybdenum carbonyl complexes.[5]

The complex is expected to be reasonably but not extremely stable. A similar compound, cis,cis,cis-1,4,7-cyclononatriene molybdenum tricarbonyl (V), is air stable and decomposes at 155°; however, acetone or more polar solvents displace the ligand at room temperature.[6] The triquinacene complex (VI) is expected to be somewhat more stable, because it lacks the three apical hydrogen atoms, repulsion between which tend to distort the maximum overlap conditions and weaken the bonding to the metal.



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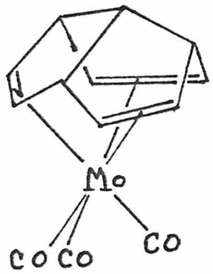
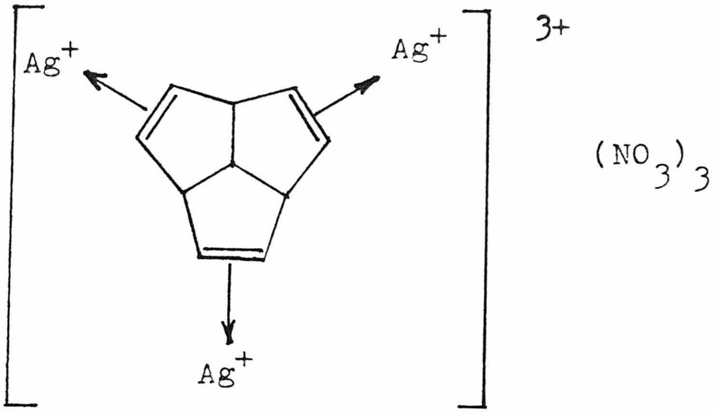


VI

Structural proof of the triquinacene carbonyl complex could be made by IR, PMR, and of course X-ray diffraction if suitable crystals could be prepared. We would expect to see in the infrared spectrum a shift to lower wavenumbers of the C=C stretching band, corresponding to the weakening of the double bonds. This is brought about by donation from the olefinic π-bonding orbitals to the empty d orbitals of the metal and π back donation from the filled metal orbitals to the π* antibonding orbitals of the olefinic bond. Those processes effectively remove electrons from bonding orbitals into antibonding orbitals of the π bond. The PMR spectrum of the complex would be expected to be very similar to that of the uncomplexed ligand, showing three absorptions: a quartet with relative area 1, due to the axial proton, a doubled triplet (6 lines) with relative area 3, and a triplet with relative area 6, corresponding to the methylene protons.

A less aesthetically pleasing complex than the molybdenum triquinacene derivative, but one which is almost sure to form is the 1:3 silver nitrate adduct. In this complex, the outer π* lobes of the olefinic bonds are employed in the back bonding rather than the inner ones as in the octahedral complex, and a silver ion complex with each of the olefinic bonds, retaining the C_{3v} symmetry:



This complex could probably be formed in an analogous manner to the formation of the similar cyclononatriene complex,[6] that is, by shaking a water solution of $AgNO_3$ with a carbon tetrachloride solution of the olefin. Confidence that the triquinacene complex will form is based upon the properties of the analogous cis,cis,cis-1,4,7-cyclononatriene complex, which is a stable solid at the melting point of silver nitrate (212°).

Other triquinacene complexes seem possible, particularly complexes including d^6 ions of other metals. Also, further substitution for carbon monoxide by another sort of polyene in the tricarbonyl molybdenum complex may yield complexes containing triquinacene as well as other polyolefins. In these it would be of interest to compare the preference of the metal for either the "parallel" sort of π orbitals found in, for instance, planar arenes, or the "converging" π orbitals found in triquinacene.

References for Proposition V

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