

EXPERIMENTS IN NUCLEAR MAGNETIC
RESONANCE

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ABSTRACT

I. Proton and cobalt resonances were observed in single crystals of $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. The cobalt spectrum consists of a maximum of seven lines whose separation follows a $(3\cos^2\theta - 1)$ dependence quite closely where θ is the angle between the c-axis of the crystal and H_0 . The spectrum is fully explained on the basis of quadrupole interaction. Two sets of doublets were found for the proton resonances; an inner, very narrow set following a dependence similar to the cobalt resonance, and a pair of outer broad peaks which overlap the sharp peaks. The narrowness of the central peaks is attributed to internal rotation of one of the proton bearing groups.

II. A summary is given of various high resolution spectra of compounds related to phosphine.

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I. ANISOTROPIC EFFECTS IN THE NMR SPECTRA OF SINGLE CRYSTALS OF COBALTIC COMPLEXES

INTRODUCTION AND PREVIOUS WORK

It was felt that a study of the anisotropic effects in the nuclear magnetic resonance spectra of single crystals of trivalent cobalt complexes might give some insight as to the nature of the crystalline fields existing within the crystals. Hence observations were undertaken on the proton and cobalt resonances in a number of various cobaltic complexes, and in particular $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$.^{*} The complexes of trivalent cobalt, containing no unshared electrons, are all diamagnetic thus eliminating any complications due to paramagnetic effects.

Previous work has been done on cobaltic complexes, though in the powdered, dehydrated state, by J. S. Waugh (1) and H. L. Richter (2). For powdered $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ at room temperature Waugh found a rather narrow proton peak about 3.4 gauss wide and concluded that the $\text{Co}(\text{NH}_3)_6^{+3}$ ion underwent rapid rotation in the lattice. For $\text{Co}(\text{en})_3\text{Cl}_3$ he found a broad line and concluded that there was no rotation of the $\text{Co}(\text{en})_3^{+3}$ ion in the lattice. Richter corroborated these results for the case of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$; indeed he showed that the group rotated at temperatures down to -80 deg.C. For the case of

*The ethylenediamine groups, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, will henceforth be abbreviated to read "en."

the ethylenediamine, however, he could get no consistent results. His first measurements indicated a narrow peak of about 1.3 gauss in width at room temperature which did not begin to broaden until the temperature was reduced to about -60 deg.C. Waugh later obtained a narrow line superimposed upon a broad line with the NMR Spectrometer at MIT (3), however, no explanation has been advanced. These two previous studies covered only the proton resonances, and made no attempt to work with the cobalt resonance as was done here.

COMPOUNDS AND CRYSTAL GROWTH

A number of compounds have been prepared during the course of this work following procedures in the standard reference works (4). These include: $\text{Co}(\text{NH}_3)_6\text{X}_3$ (X = Cl, I, NO_3 , ClO_4) (5); racemized $\text{Co}(\text{en})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Co}(\text{en})_3\text{Br}_3 \cdot 3\text{H}_2\text{O}$ (6); dextro- and levo $\text{Co}(\text{en})_3\text{Br}_3 \cdot \text{H}_2\text{O}$ prepared from the racemized chloride following the method of Werner (7); and $\text{Co}((\text{NH}_3)_5\text{Cl})\text{Cl}_2$ (8). The crystal forms included in this list are: cubic (the hex[^]amine iodide and perchlorate); trigonal (the racemized ethylenediamine chloride and bromide); tetragonal (the dextro- and levo- ethylenediamine bromide, and the hex[^]amine nitrate); monoclinic ($\text{Co}(\text{NH}_3)_6\text{Cl}_3$); and orthorhombic ($\text{Co}((\text{NH}_3)_5\text{Cl})\text{Cl}_2$) (9). In view of the fact that the growth of large crystals is a selfpurifying process it was not felt necessary to purify the prepared compounds beyond the levels stipulated in the references mentioned.

To verify the complete resolution of the $\text{Co(en)}_3\text{Br}_3 \cdot \text{H}_2\text{O}$ into its respective optically active isomers, the specific rotation was checked against the literature value. The experimental value of 116.5° was in excellent agreement with Werner's value of 115° for the dextro form (10). The levo-form was not checked.

Crystals were grown by slowly lowering the temperature of a seeded aqueous solution saturated initially at about 15 to 20 degrees above ambient temperature (that is about 40 deg.C. in the laboratory and about 25 deg.C. in the 4 deg.C. cold room). The seeds, of the order of a millimeter in size, were prepared by saturating a solution at about 15 degrees above room temperature, and allowing the solution to cool to room temperature over night. The solution was then poured off, and the best seeds extracted with a pair of forceps. To grow the large single crystals, the seeds were suspended in the saturated solutions by gluing them to a length of 4mm pyrex tubing drawn out to a capillary point with duco cement. The tubes were then joined to the glass stoppers of the flasks with shellac.

To provide a slow but constant rate of cooling, a "constantly variable" constant temperature bath was constructed. The heart of the bath lay in a large mercury thermoregulator with an adjustable upper tungsten contact. By means of a screw mechanism the upper electrode was lowered by a clock motor to give a rate of cooling of about one degree centi-

grade per day. The crystals were removed and dried with filter paper as soon as they had reached the required size.

No noteworthy success has been achieved with this method except for the cases of $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $d\text{-Co(en)}_3\text{Br}_3 \cdot \text{H}_2\text{O}$. With these two compounds large crystals of the order of a centimeter in dimensions with well developed faces have been prepared in a period of about a week. It is with the former of these that we shall be primarily concerned. Some reasonable success was obtained with the $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, however, the crystals were not nearly as large as the ethylenediamines nor were the faces as well developed. The $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ forms hexagonal prisms, the hexagonal cross section being somewhat irregular; the $d\text{-Co(en)}_3\text{Br}_3 \cdot \text{H}_2\text{O}$ forms a tetragonal prism capped on either end by tetragonal pyramids composed of (111) planes. No attempt was made to grow crystals of the levo- isomer. In all other cases the crystals failed to grow properly or even to cap. A possible source of difficulty is slight decomposition of the compounds, in which case a lowered operating temperature should help greatly. With this in mind the temperature bath was transferred to a 4 deg.C. cold room. Results were not much better under these conditions; however, it is felt that time did not permit a proper sustained effort along these lines, and it is quite possible that further attempts might well be successful. Another factor to take into consideration is stirring. It might well be that stirring of the seed crystal might give greatly enhanced results,

however, it is also possible that the results might be worse.

SPECTRA AND SPECTRAL MEASUREMENTS--DATA

NMR spectra of both hydrogen and cobalt nuclei have been observed in $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. In both cases there is a marked anisotropy. To align the crystal at various angular orientations a simple goniometer was constructed consisting of a full circle protractor marked off at intervals of ten degrees mounted in the stopper of a standard taper test tube which served as the sample holder. The crystal was aligned by eye with the zero line on the protractor; a length of masking tape stretched across the pole faces of the magnet served as a reference for alignment at various angles.

The proton spectra of figure 1 were taken at 16 megacycles corresponding to a field of 3760 gauss, while those of figures 2 and 3 and table I were taken at 6.4 megacycles corresponding to a field of 1500 gauss. The field scan rate was rather low and assumed linear. The scan rate was calibrated by measuring the chemical shift between Tl^{203} and Tl^{205} in thallic acetate at the same magnetic field value and scan rate at the corresponding frequency for the thallium nucleus.

The proton spectra gives rise to two sets of lines visible in figure 1. The form of each set is dependent upon angular orientation. The central, sharper peak is in reality a doublet as is clearly obvious from figure 2; under the conditions of modulations for figure 1 the two lines remain

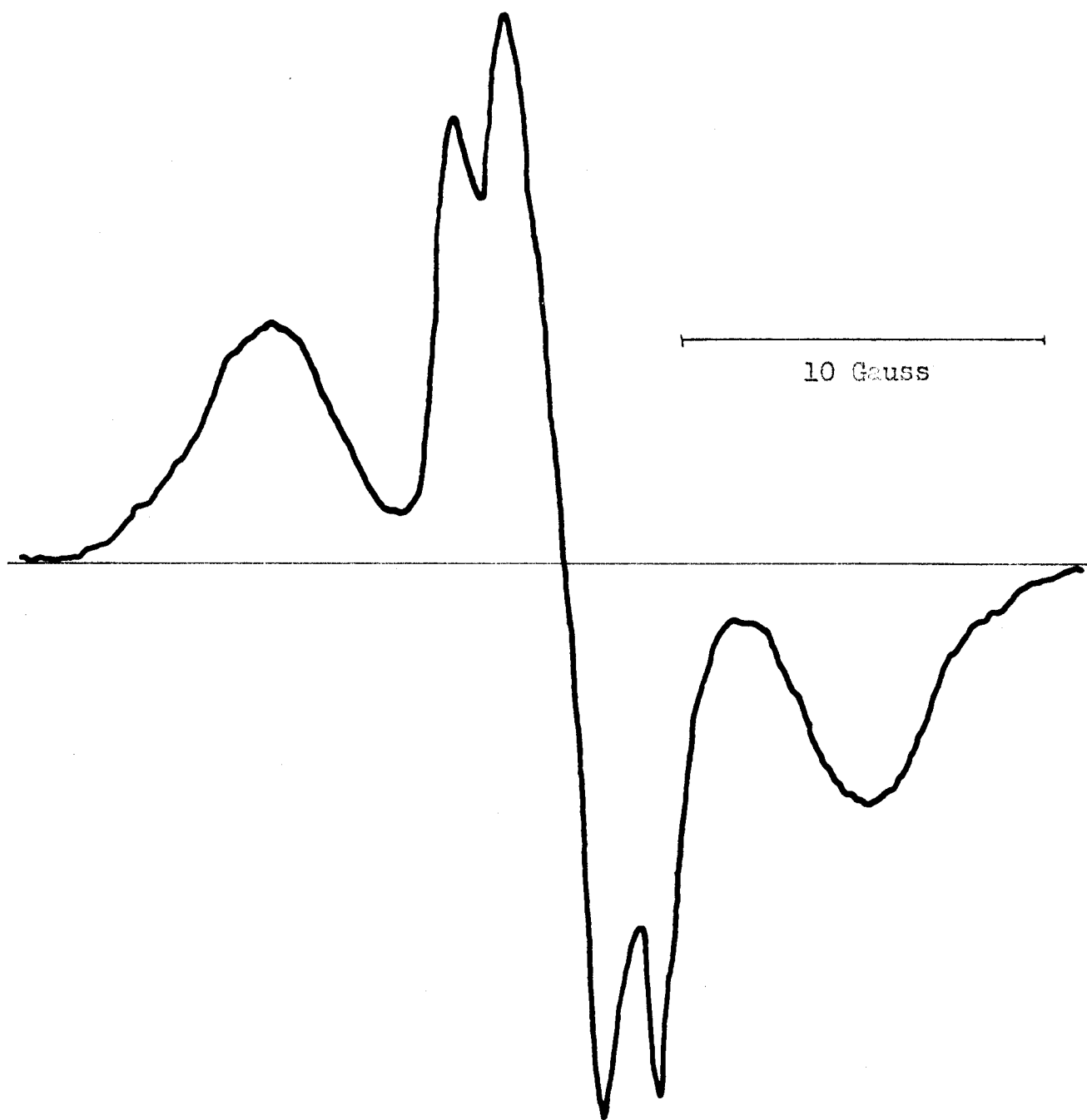


Fig. 1: Proton resonance in a single crystal of $\text{Co}(\text{en})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ where the c-axis is parallel to H_0 .

unresolved. The inner lines have a width of the order of 0.4 gauss while the outer, much broader peaks are approximately 7 gauss wide. Any attempt to measure the characteristics of the broad outer peaks would be vitiated by the overwhelming influence of the central peaks. Two points may be brought out with regard to these outer peaks. Firstly, the geometry of the derivative curve in figure 1 seems to indicate that it is a doublet; and secondly, spectra taken at other angular orientations clearly indicate that the peaks are dependent upon orientation.

At narrower field modulation amplitudes the outer peaks are not observed while the inner peaks form a clearly resolved doublet whose separation is greatly dependent upon orientation. The geometry of the crystal was such that the c-axis and H_0 always formed a plane parallel to the floor of the laboratory. To change the angular orientation of the crystal it was rotated about an axis in space perpendicular to the plane formed by the c-axis and H_0 . For the spectra in figure 2 the axis of rotation coincided with an a-axis of the crystal, however, other experiments indicated that the orientation of the a-axis with respect to H_0 is completely irrelevant, the results being unchanged if the crystal is rotated about the c-axis. The two lines in the doublet have a separation ranging from a maximum of 1.7 gauss at zero degrees when the c-axis is parallel to H_0 , to zero gauss at 50-60 degrees where the lines are coincident. Figure 2 contains traces of

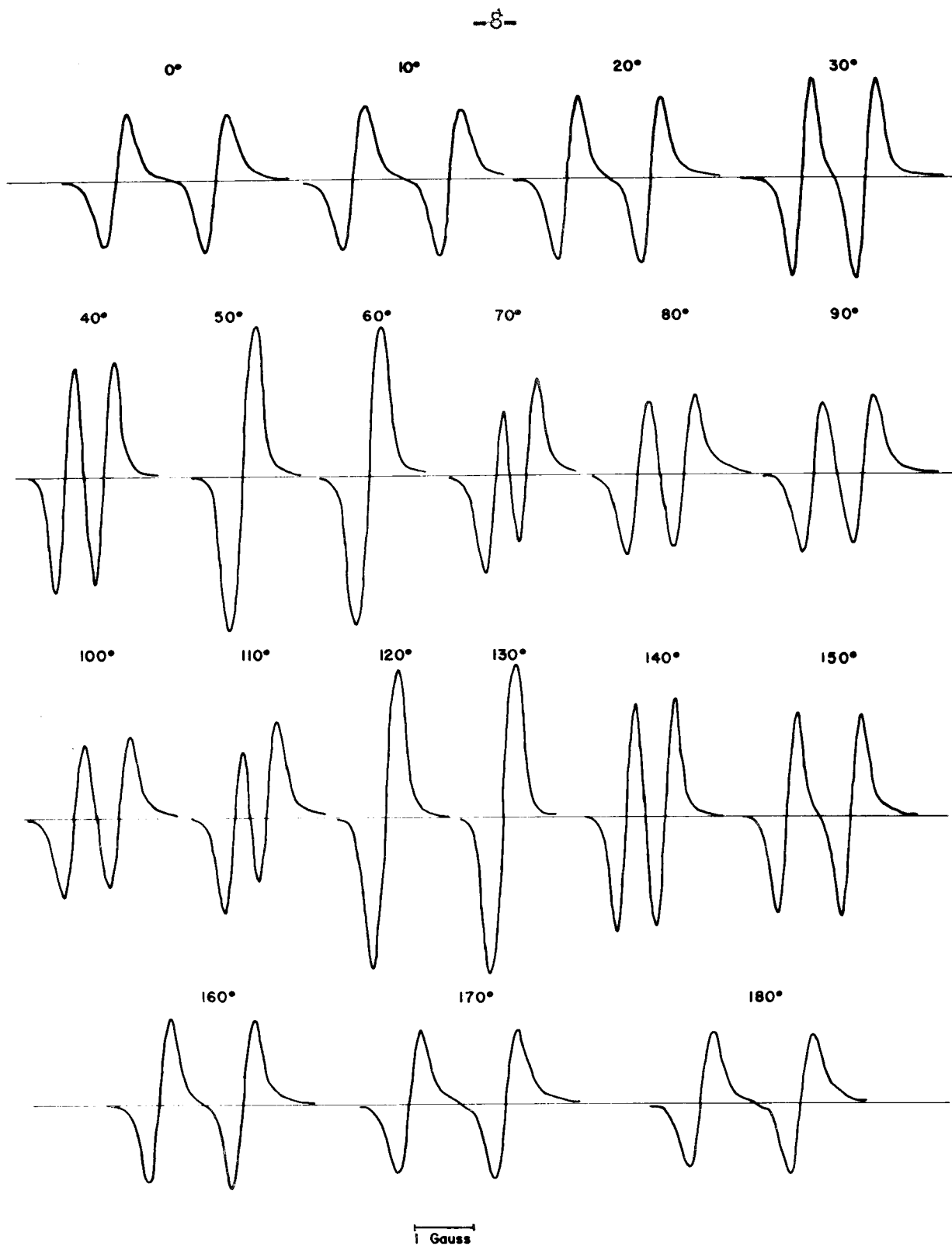


FIG. 2: Traces of a sequence of proton resonances in a single crystal of $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. The angle indicated is that between the c-axis and H_0 while the crystal is rotated about an a-axis.

actual resonance peaks from zero to 180 degrees. Figure 3 shows a plot of the dependence of separation upon angle. If the separation follows the theoretical $(3\cos^2\theta - 1)$ dependence the separation should theoretically go to zero at 55 degrees as indicated by the dotted line. The values of the separations are tabulated in table I. The central column in the table lists the absolute values of $(3\cos^2\theta - 1)$ multiplied by a constant factor of 0.845.

A determination of the proton splitting at 16 megacycles yielded a value of 1.65 gauss at zero degrees which is within the margin of error of the 1.67-69 gauss determined at 6.4 megacycles.

TABLE I

Separation of the two lines in the proton resonance spectrum of $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ at various orientations of the c-axis relative to H_0 .

Angle	$\Delta H(\text{gauss})$	$0.845(3\cos^2\theta - 1)$	Angle	$\Delta H(\text{gauss})$
0	1.67	1.69	180	1.69
10	1.61	1.61	190	1.63
20	1.40	1.40	200	1.42
30	1.06	1.06	210	1.08
40	0.63	0.64	220	0.65
50	0.00	0.20	230	0.00
60	0.00	0.21	240	0.00
70	0.51	0.55	250	0.52
80	0.77	0.77	260	0.78
90	0.86	0.85	270	0.84
100	0.75	0.77	280	0.75
110	0.53	0.55	290	0.52
120	0.00	0.21	300	0.00
130	0.00	0.20	310	0.00
140	0.66	0.64	320	0.65
150	1.10	1.06	330	1.08
160	1.38	1.40	340	1.41
170	1.62	1.61	350	1.62
180	1.69	1.69	360	1.69

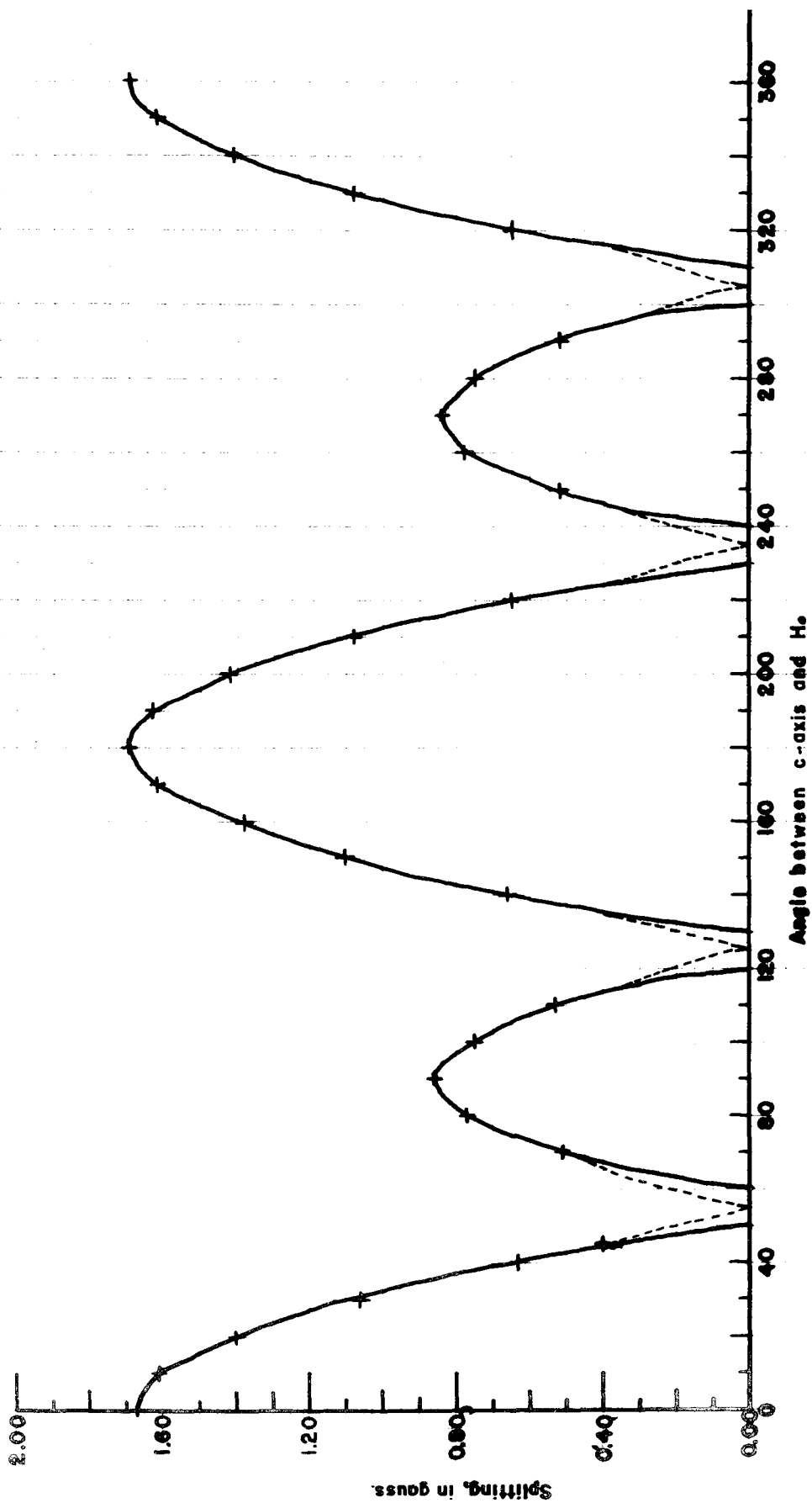


FIG.3: Plot of proton resonance splittings in a single crystal of C₆₀H₁₂Cl₂·3H₂O as a function of angular orientation.

The cobalt resonances were measured at 11.976 megacycles, corresponding to a field of 11,854 gauss for the cobalt nucleus resonance. The spectrum covered a range of some 1300 gauss, and thus a rather wide scan was necessary. It was found that the scanning unit at this range was quite non-linear and a different technique was used to calibrate and measure the splittings from that used for the protons. In order to expedite matters a simple nomograph was constructed to eliminate the drudgery of carefully measuring each resonance peak with a ruler and interpolating. Marks are placed on the chart paper every revolution of the scan dial at each dial division ending in --95. Utilizing an aqueous cobaltic solution the magnetic field scanning dial was advanced to successive points corresponding to the markers on the chart paper. At each of these points the frequency was changed until the resonance peak was centered on the oscilloscope, and the frequency measured with a Signal Corps Frequency Meter model BC-221-N. Taking the value of 10.11 megacycles for the resonant frequency of cobalt at 10,000 gauss, the magnetic field was then calculated at each marker point on the chart paper by multiplying the measured frequency by $(10,000/10.11)$. A large piece of graph paper was then marked off at intervals exactly equal to the intervals on the chart paper, and the calculated field plotted at each point; a smooth curve was then drawn through these points. To measure the magnetic field at any resonance peak it was then only

necessary to align the chart paper interval markings with the corresponding markings on the abscissa of the nomograph and tape the chart to a T-square to permit rapid and easy measurements. The T-square was then moved up the nomograph until the center of the resonance peak coincided with the curve on the nomograph. It was then a simple matter to read the magnetic field at that point from the nomograph.

With the c-axis of the $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ crystal parallel to H_0 the cobalt spectrum consists of seven lines spread over a distance of some 1260 gauss with the central peak at about 11,850 gauss. The six outer peaks are symmetrically disposed about the central peak with equal spacing between peaks of 210 gauss. The central peak is some eight gauss wide. From this maximum the spacing decreases to zero at 55 degrees where only one peak is present. This is clearly visible in the series of traces in figures 4 and 5. The geometry of the crystal orientation is the same as for the proton resonances described on page 7. Once again the position of the a-axis in no way effects the spectra. Figure 6 contains a plot of splittings as a function of angular orientation. The results are tabulated in table II. The numbers at the heads of the columns in table II refer to the various peaks, 4 being the central peak; 1, 2, and 3 the low field peaks in that order; and 5, 6, and 7 the high field peaks. The reference point in the magnetic field has been shifted so that the zero point coincides with the central peak. Gaps in the table indicate

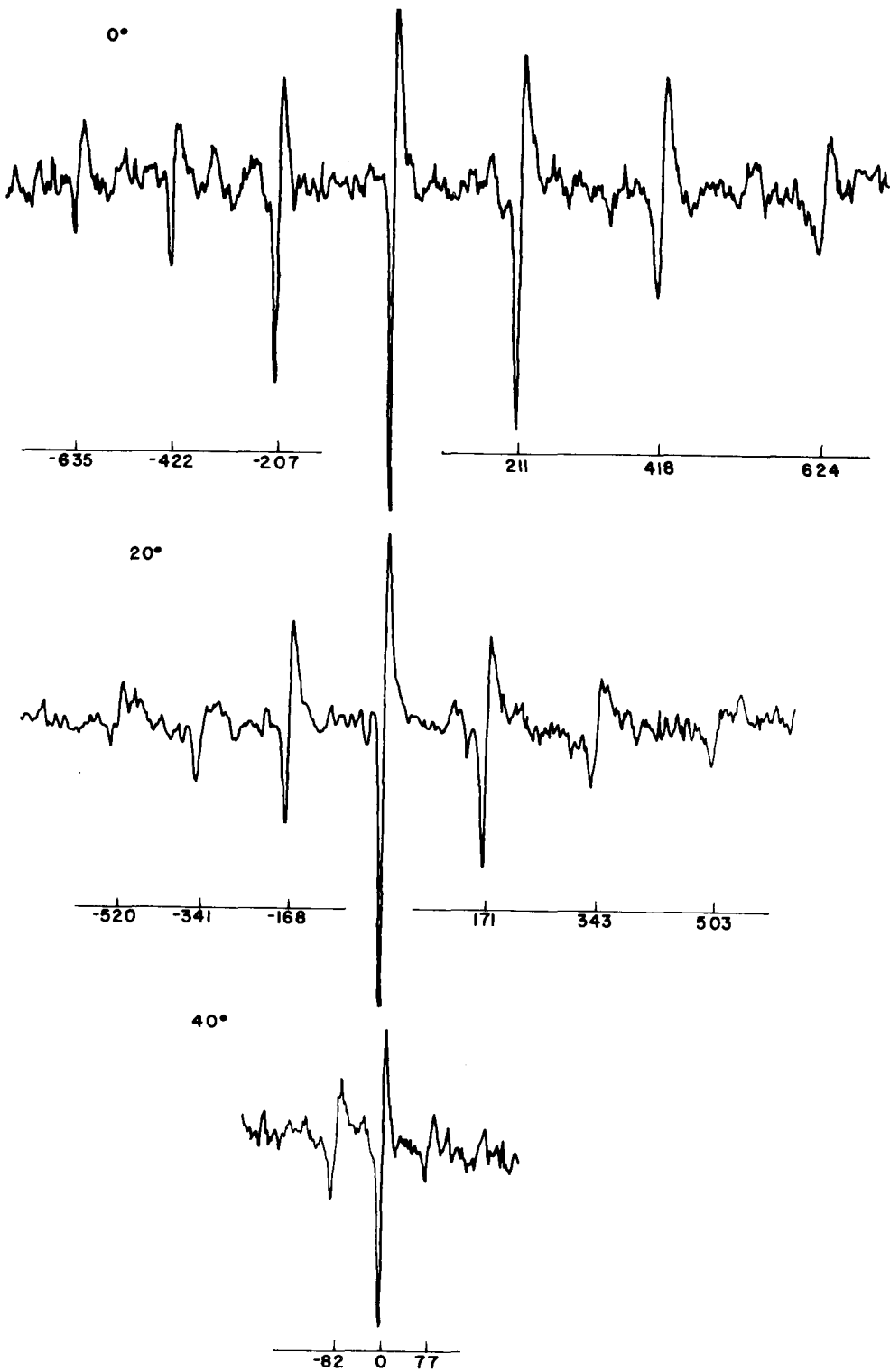


FIG.4: Traces of a sequence of cobalt resonances in a single crystal of $(\text{Co(en)}_3)_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ at various angular orientations. The field scan is non-linear. The scales below the traces denote distances in gauss from the central peak, which is taken as zero, to the outer peaks.

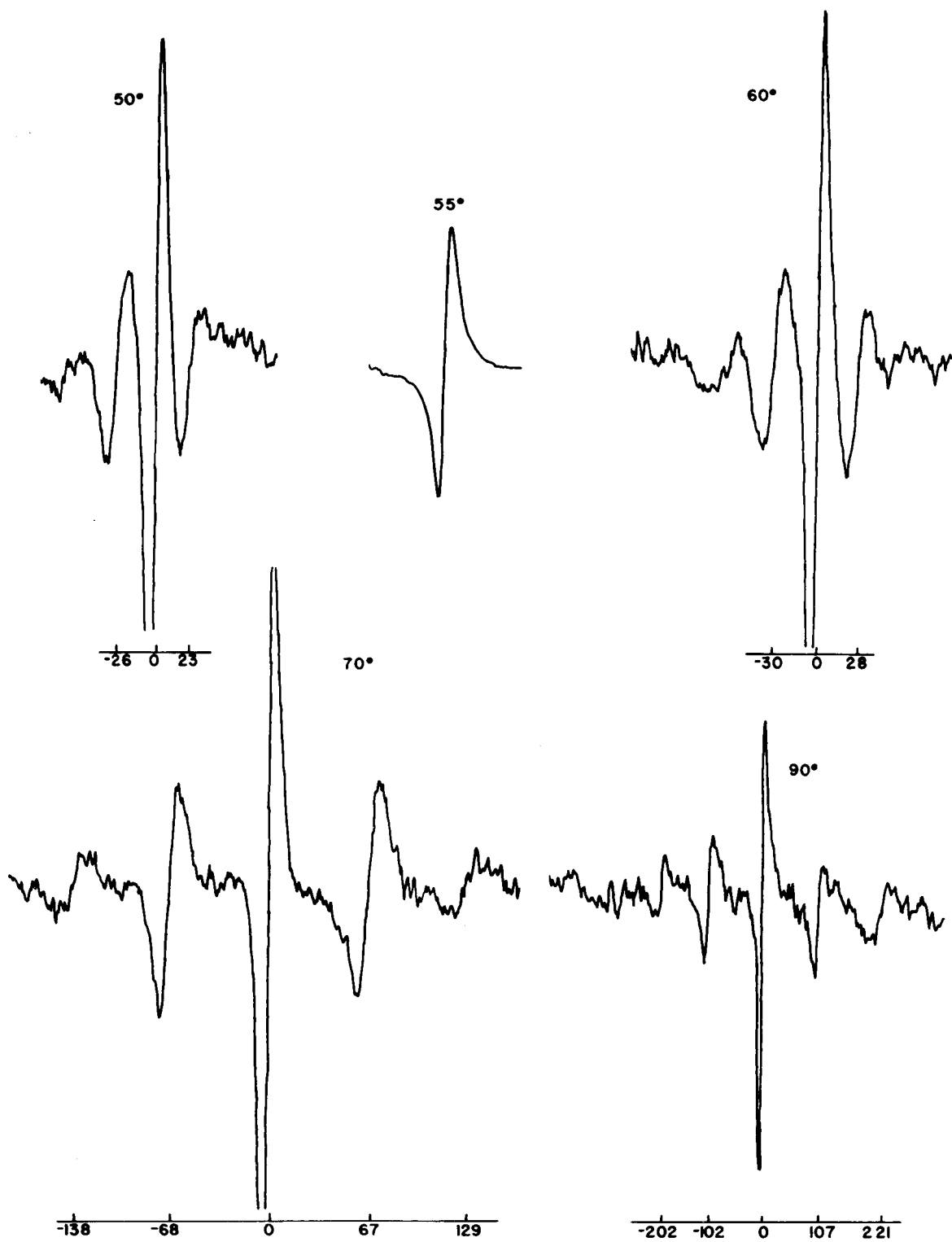


FIG. 5: Further traces from the sequence of Fig. 4. Except for the 90 degree trace the field scan rate is slower than that in fig. 4.

unresolved or absent peaks. The average separation value in the next to the last column was arrived at by averaging the figures in columns 1 and 7, each divided by three; figures in columns 2 and 6 each divided by two; and the figures in columns 3 and 5. The $(3\cos^2\theta - 1)$ column has again been indicated, this time multiplied by 105 to indicate the rather close agreement with the expected theoretical dependence.

TABLE II

Positions of the peaks in the cobalt resonance spectrum of $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ as a function of angular orientation

Angle	1	2	3	4	5	6	7	Average*	$(3\cos^2\theta-1)$ X105
0°	635	422	207	0	211	418	624	210	210
10	598	398	194	0	200	399	596	198	200
20	520	341	168	0	171	343	503	171	173
30		260	126	0	127	256		128	131
40			82	0	77			80	80
50			26	0	23			25	25
55				0				0	0
60			30	0	28			29	26
70		138	68	0	67	129		68	68
80	296	191	93	0	97	203		97	96
90		202	102	0	107	221		105	105

*See text

An earlier cobalt measurement at 6.4 megacycles yielded a value of approximately 1350 gauss for the total spread at zero degrees. This value of 1350 was arrived at by a very rough approximation from the ammeter readings on the magnet power supply and is taken as an indication that the splittings in the cobalt resonance are not changed at different frequencies of observation.

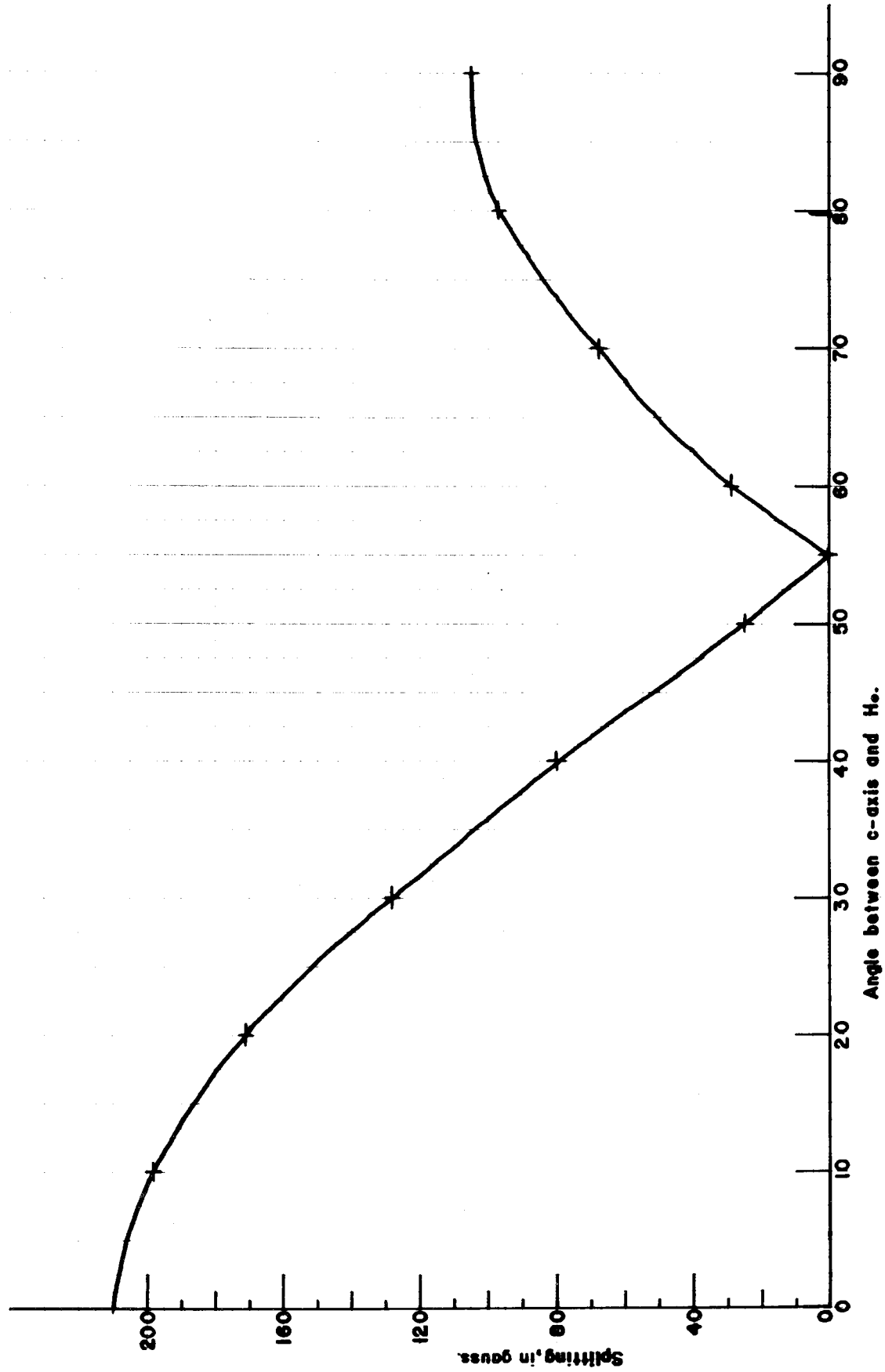


FIG. 6. Plot of splittings of the cobalt resonance in a single crystal of $\text{Co(en)}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$.

Proton resonances were also observed in $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ and dextro- $\text{Co}(\text{en})_3\text{Br}_3 \cdot \text{H}_2\text{O}$. The spectrum for the hexamine chloride consists of one single line of the order of two gauss wide. The dextro-ethylenediamine bromide is somewhat anomolous. As in the racemized chloride two types of lines are visible, a narrow central line superimposed upon a much broader line. However, the narrow central peak is rapidly saturated, and it is impossible to get a complete line on the chart paper even with the gain of the radio-frequency current turned to its minimum level. The broader peak is easily visible, and is approximately 5 gauss wide.

THEORY, DISCUSSION, AND CONCLUSIONS

A. Proton resonances in $\text{Co}(\text{en})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$: In the course of his study of the proton resonance of the waters of hydration in gypsum single crystals Pake showed (11) that for systems of two identical nuclei one should find two resonance peaks at magnetic field values given by

$$H = H_0 \pm \frac{3}{2} ur^{-3}(3\cos^2\theta - 1) \quad (1)$$

where H_0 is the magnetic resonance field strength, u is the nuclear magnetic moment, and θ the angle between the vector joining the two identical nuclei and H_0 .

Disregarding possible structural differences there are three chemically distinct proton species in the molecule, the CH and NH protons on the ethylenediamine groups, and

the protons in the waters of crystallization. The spectrum indicates two distinct types of proton lines. It is not possible to make any definite conclusions at this stage of the research, however, we might indicate certain possibilities.

J. ter Berg (12) has studied the structure of $\text{Co(en)}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and has determined the space group, unit cell, and positions of the cobalt atoms. The crystal belongs to the trigonal system and has space group $\overline{\text{P}}3\text{c1}$ with four molecules per unit cell. The four cobalt atoms lie at four-fold equivalent lattice positions given by: $1/3, 2/3, z$; $1/3, 2/3, (\frac{1}{2} + z)$; $2/3, 1/3, z$; and $2/3, 1/3, (\frac{1}{2} - z)$. In other words, the cobalt atoms lie along two chains each parallel to the c-axis, and situated one third and two thirds the distance along the vector $(\underline{a} + \underline{b})$ respectively. The chains consist of alternate dextro- and levo- groups, and are completely out of phase with each other. Unfortunately this structural determination did not include the positioning of the ethylenediamine groups nor the hydrated waters.

The unusual narrowness of the central proton peaks is, no doubt, due to internal rotation of one type of proton, and could be easily verified by examining the spectra at different temperatures. Since Waugh's work (13) indicated no internal rotation of the chelating groups, it is perhaps most logical to assume that these narrow peaks are due to the water molecules which are rotating. Insofar as this portion of the research is concerned the next logical step

is to grow crystals from the anhydrous salt in heavy water. The H_2O molecules would all be replaced by D_2O , and it seems highly likely that the protons on NH_2 groups would be replaced by deuterium atoms, the CH_2 protons remaining unchanged. The proton resonance would then be due solely to the CH_2 protons and an unambiguous assignment of the resonance peaks could be made.

The possibility that the central sharp peaks is due to rotating ethylenediamine groups is not, however, to be completely negated. Richter's work (14) indicated a great uncertainty as to the validity of Waugh's conclusions regarding the rigidity of the chelating groups. Furthermore, the situation existing in the anhydrous salt might not be duplicated in the hydrated single crystal. Figure 7 indicates a $\text{Co}(\text{en})_3^{+3}$

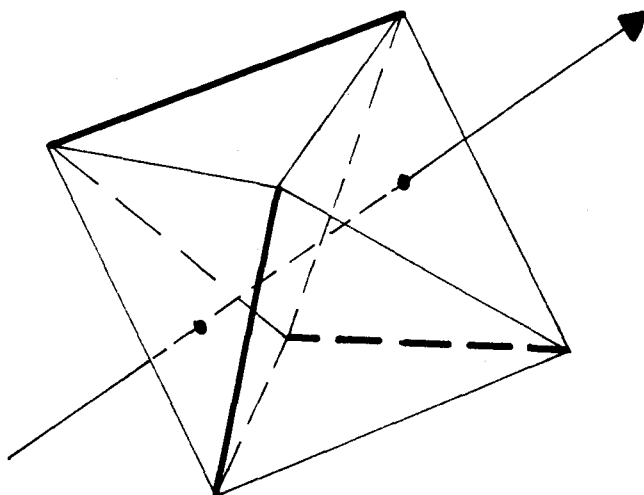


Fig. 7: $\text{Co}(\text{en})_3^{+3}$ ion showing 3-fold rotation axis. Heavy lines are the en bridging groups

ion group as it is usually pictured in its simple octahedral structure. It has a three-fold rotation axis as indicated in the diagram, and this could well be an axis of rigid rotation. It would still not be clear whether the sharp lines are due to the CH or NH protons, but this too could be determined by crystallization from heavy water.

B. Cobalt resonances in $\text{Co}(\text{en})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$: The seven lines in the cobalt spectrum are easily explainable on the basis of quadrupole splitting. Co^{59} has a spin of $7/2$, thus a quadrupole moment for the cobalt nucleus is expected. For an isolated nucleus of magnetic moment μ , spin I , in a magnetic field H_0 along the z -axis, the magnetic energy levels are given by

$$E_m = -\mu H_0 / I \quad (2)$$

where m is the magnetic quantum number. In perfectly symmetrical environments this gives rise to $2I + 1$ equally spaced levels, and hence only one resonance peak. For nuclei of spin greater than $\frac{1}{2}$, if an electric quadrupole moment exists, the nucleus interacts with the electric environment if it has less than cubic symmetry. Using first order perturbation theory Pound (15) has shown that the energy levels now become

$$E_m = -\frac{\mu H_0}{I} + \frac{eQ}{4I(2I-1)} (3m^2 - I(I+1)) \delta V_{zz}^2 \quad (3)$$

the second term representing the displacement of the levels

of eq. (2) by the quadrupole interaction. The $2I$ intervals between the $(2I + 1)$ levels are now no longer equal. Thus in a single crystal containing nuclei disposed at equivalent lattice sites the resonance spectrum is split into $2I$ component lines, symmetrically placed on either side of the position the line would take in the absence of a quadrupole interaction.

Pound's treatment predicts an angular dependence given by

$$\frac{\partial^2 V}{\partial z^2} = \frac{1}{2}eq(3\cos^2\theta - 1) \quad (4)$$

where θ is the angle between the symmetry axis and H_0 (taken as the z-direction), and eq is a scalar description of the electric environment given by

$$eq = \int \rho(3\cos^2\theta - 1)r^{-3}dV \quad (5)$$

where the integral is taken over all charges outside the nucleus, r is the vector joining the nucleus to volume element dV , and θ is the angle between r and the symmetry axis. As is quite evident from figure 6 and the last columns of table II, the cobalt resonance splittings follow a $(3\cos^2\theta - 1)$ dependence quite closely. In view of the rather large splittings involved one would not have been at all surprised to find appreciable deviation from this law derived from first order perturbation theory.

Only one cobalt compound has been examined to any degree

of thoroughness. It would be especially interesting to continue this project with a study of the single crystals of such compounds as $\text{Co}(\text{NH}_3)_6\text{X}_3$ where X is one of many groups. Compounds of this type are assumed to have the ammonia groups octahedrally bonded to the central cobalt atom; if this were true the cobalt resonance could show no quadrupole interaction since the cobalts would lie at the centers of a cubically symmetric field. The existence of splittings would then give an indication of the degree of departure from the idealized octahedral bonding originally envisioned by Werner.

II. HIGH RESOLUTION NMR SPECTRA OF VARIOUS PHOSPHORUS COMPOUNDS

High resolution nuclear magnetic resonance spectra of a number of phosphorus compounds related to phosphine have been taken. The samples were all supplied by Dr. Walter Mahler of USC. A Varian high resolution NMR spectrometer operating at 40 megacycles was used. The splittings and chemical shifts were measured by inducing side bands with an audio oscillator. Fluorine shifts were referred to trifluoroacetic acid, proton shifts to benzene. All splittings are given in cycles per second; chemical shifts are measured in dimensionless units of $(\Delta H/H_0) \times 10^6$, where ΔH is the distance from the reference peak and H_0 the steady magnetic field. The results are tabulated below in table III. Figure 8 indicates traces of some actual spectra.

The results are all quite straightforward except for the cases of $(CH_3)_4P_2$ and $(CF_3)_4P_2$. These can be explained by postulating a coupling mechanism between the two central phosphorus atoms. One may envision two extreme cases of this mechanism for compounds of the form $(CX_3)_4P_2$. At one extreme is the case of no coupling in which event we would expect each half of the molecule to act independently giving rise to a doublet for the X resonance. At the other extreme is the case of complete coupling in which event the two central phosphorus atoms would act as a single nucleus with

Table III

Splitting and chemical shift data for various phosphorus compounds:

$(CF_3)_3P:$	CF_3 res:	pair of doublets; chem. shift of -9.8 P-F splitting: 89.5 cps F-F splitting: 3.0 cps
	PF res:	pair of quintets; chem. shift of 141. P-F splitting: 996 cps F-F splitting: 3.2 cps
$(CF_3)PF_2:$	CF_3 res:	pair of triplets; chem. shift of 5.8. P-F splitting: 86.9 cps F-F splitting: 5.8 cps
	PF_2 res:	pair of quartets; chem. shift of 28.4. P-F splitting: 1250 cps F-F splitting: 5.8 cps
$(CF_3)_2PH:$	CF_3 res:	pair of doublets; chem. shift of -29. P-F splitting: 68.8 cps F-H splitting: 9.7 cps
	PH_2 res:	pair of quartets; chem. shift of 3.6. P-H splitting: 203 cps F-H splitting: 12.2 cps
$(CF_3)PH_2:$	CF_3 res:	pair of triplets; chem. shift of -34. P-F splitting: 48.3 cps F-H splitting: 12.0 cps
	PH_2 res:	pair of quartets; chem. shift of 3.6. P-H splitting: 203 cps F-H splitting: 12.2 cps
$(CF_3)_2PCl:$	CF_3 res:	one doublet; chem. shift of -15.5. P-F splitting: 85.3 cps
	PCl_2 res:	one doublet; chem. shift of -5.9. P-F splitting: 79.8 cps
$(CF_3)PCl_4:$	CF_3 res:	one doublet; chem. shift of 0.88. P-F splitting: 153 cps
	CH_3 res:	one triplet; chem. shift of 5.5. P-H splitting: 7.1 cps
$(CF_3)_4P_2:$	CF_3 res:	one doublet with an anomolous peak in the center; chem. shift of -31. Doublet splitting: 84.9 cps
	$(CH_3)_2NP(CH_3)_2:$	H res: Two doublets separated by shift of 59.6 cps. P(CH ₃) ₂ res: chem. shift of 4.3. P-H splitting: 9.9 cps N(CH ₃) ₂ res: chem. shift of 5.8. P-H splitting: 5.4 cps

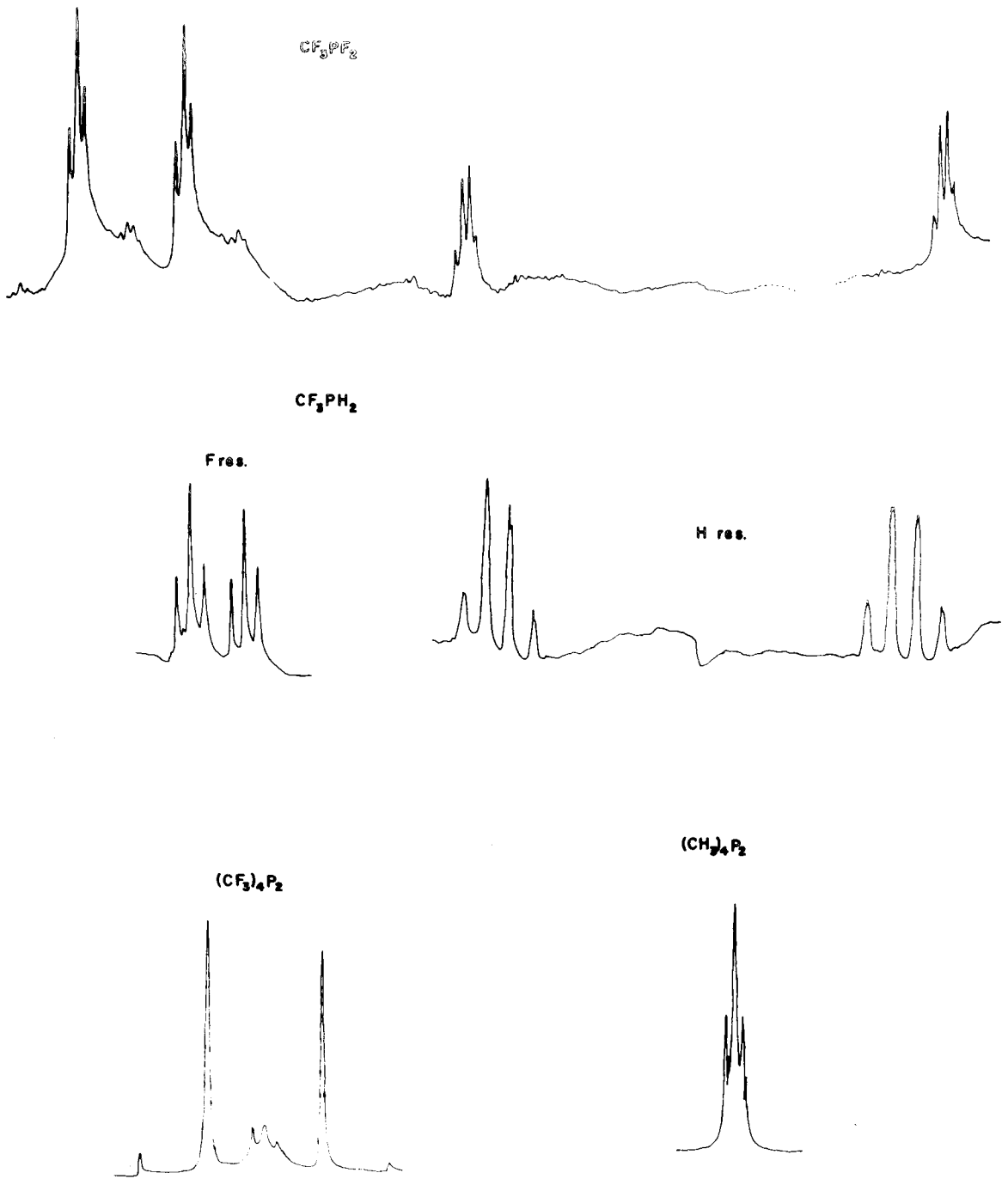


FIG. 8: Traces of some typical high resolution NMR spectra. See table I for splitting magnitudes.

a spin of unity giving rise to a triplet in the X resonance. For the compounds under discussion $(\text{CH}_3)_4\text{P}_2$ acts as the second extreme case giving rise to a triplet in the proton resonance as is evident from figure 8. The $(\text{CF}_3)_4\text{P}_2$ acts as an intermediate case with a clearly defined doublet and a vestigial triplet line between the two main outer peaks.

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