I. THE CRYSTAL STRUCTURE OF POTASSIUM SILVER CYANIDE

II. AN X-RAY EXAMINATION OF THE 12-MOLYBDOPHOSPHATES AND RELATED COMPOUNDS

III. THE CRYSTAL STRUCTURE OF CADMIUM CHLORIDE

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I. THE CRYSTAL STRUCTURE OF POTASSIUM SILVER CYANIDE

INTRODUCTION

The crystal structure of potassium silver cyanide, $KAg(CN)_2$, is of particular interest on account of the presence of the chemically very stable complex anion, $Ag(CN)_2^-$. It is perhaps of some theoretical importance to know whether the angle between the bonds formed by the silver atom with the cyanide groups within the ion approaches more closely to the tetrahedral angle of 109°28' or to linearity, that is to 180°. The X-ray investigation of these crystals was undertaken at the suggestion of Professor Linus Pauling, with the hope of reaching a definite conclusion regarding the problem stated above in addition to determining the crystal structure.

The crystals of $KAg(CN)_2$ used in this investigation were obtained from Professor Pauling. They are described by Groth[1] as trigonal with α = 66°57', and as showing $\{100\}$ and $\{111\}$, often with a comparable degree of development so that the crystals resemble regular octahedra. As a matter of fact various stages of development of $\{111\}$ were found among the specimens here studied. Some crystals were rhombohedra, others closely resembled regular octahedra, while a few formed plates on $\{111\}$, in addition, of course, to intermediate habits. However, there was nothing in the external appearance to indicate the presence of a polar axis, that is the absence of a center of symmetry within the crystal, a fact of importance in later considerations. No appreciable cleavage is observed for crystals of $KAg(CN)_2$.

DETERMINATION OF THE UNIT CELL AND SPACE GROUP

Since the X-ray data show the underlying lattice of $KAg(CN)_2$ to be hexagonal, all indices used hereafter in this paper will be referred to a hexagonal unit, the axes of which coincide in direction with the projection upon the basal plane of the crystallographic rhombohedral axes. Laue photographs were prepared using general radiation from a tungsten anticathode tube with the X-ray beam inclined at various small angles to the basal plane, (00·1), and to a rhombohedral face, ($2\bar{1}$·2). Oscillation photographs were prepared by reflecting Mo Kα radiation filtered thru zirconia from (00·1) and from a ground face, (11·0).

The value of a, the edge of the smallest hexagonal unit, was determined from layer line reflections appearing on oscillation photographs for which the radiation was reflected from (00·1). With the projection on the basal plane of a crystallographic rhombohedral axis as the axis of oscillation, the identity distance in this direction as calculated by means of the Polanyi formula, $s\lambda = I \sin\mu$, is found to be 7.34 Å. With, however, a direction in the basal plane which made an angle of 30° with the preceding one as the axis of oscillation, the observed layer line spacings lead to an identity distance of $\sqrt{3} \cdot 7.34 = 12.71$ Å (see Table I). These results fix unambiguously the value of a, the edge of the smallest hexagonal unit, as 7.34 ± 0.1 Å.

TABLE I

Layer Line Data from Photograph I B

s	Distance from -s to +s	Sin μ	I	$I/\sqrt{3}$
1	1.119 cm	.05586	12.66 Å	7.31 Å
2	2.241	.11136	12.71	7.34
3	3.387	.16698	12.72	7.34
4	4.573	.22291	12.71	7.34
6	7.087	.33399	12.71	7.34

Calculations made by means of the Bragg equation, $n\lambda = 2d \sin\theta$ for the equatorial reflections on oscillation photographs from (00·1) lead to an observed spacing along c of $\frac{d(00·1)}{n_1} = 8.84 \pm 0.1$ Å (see Table II). However, the odd orders are apparently missing upon these photographs, indicating that the true unit translation along c is $(2)(8.84) = 17.68$ Å. This view is confirmed both by means of Laue photographs, and by the observation that the layer line spacings upon an oscillation photograph with c as the axis of oscillation lead to an identity distance in this direction of 17.7 Å.

TABLE II

Data from the Equator of Photograph I A

(h k·l)	Line (Mo K)	Sin θ	$\dfrac{d(00 \cdot 1)}{n_1}$
(00·n_1)	α	.0403	8.80 Å
(00·$2n_1$)	α	.0802	8.84
(00·$3n_1$)	α	.1201	8.85
(00·$4n_1$)	α	.1603	8.84
(00·$5n_1$)	α	.2001	8.86
(00·$6n_1$)	α_1	.2401	8.85
(00·$7n_1$)	α_1	.2807	8.83
(00·$8n_1$)	α_1	.3207	8.84

Average 8.84 Å

The hexagonal unit with a = 7.34 Å, c = 17.7 Å was used to calculate values of n λ for all of the observed reflections upon two completely indexed Laue photographs. The X-ray beam was slightly inclined to the normal to (00·1) for one of these, and to ($\bar{2}1$ 2) for the other. In both cases no calculated value of n λ was found to be less than 0.24 Å, the short wave length limit of the radiation employed, while a total for the two photographs of about 56 forms were observed to reflect in the first order. Selected data in the first order from the second of these photographs are given in Table III (with this crystal orientation only two planes, (h k·ℓ) and (k h·ℓ), of each form gave observed reflections).

TABLE III

Representative First-Order Laue Data from a $(2\bar{1}\cdot2)$ Photograph

Photograph II A

Form $\{hk\cdot\ell\}$	$n\lambda$ Å
$\bar{4}4\cdot\bar{5}$	0.35, 0.47
$\bar{5}5\cdot\bar{2}1$	.39, .42
$\bar{3}2\cdot\bar{2}0$	.35
$\bar{3}2\cdot\overline{15}$	.36, .40
$\bar{2}1\cdot\overline{14}$	.43, .46
$\bar{3}2\cdot\overline{11}$	.29, .35
$\bar{1}0\cdot\bar{8}$	.26, .30
$\bar{4}5\cdot2$	.27, .38
$6\bar{4}\cdot7$	.27
$11\cdot10$	.27
$\bar{3}6\cdot10$	.33
$\bar{3}8\cdot15$	.32, .36
$\bar{3}3.2$	.24, .42
$\bar{4}6\cdot5$	.35, .44
$5\cdot\overline{11}\cdot10$	.43, .40

If six molecules of $KAg(CN)_2$ be placed in a hexagonal unit with a = 7.34 Å, c = 17.7 Å, the calculated density is 2.36 g/ml, which is in satisfactory agreement with the experimental value of 2.32 ± 0.1 g/ml determined by the displacement method using benzene. This unit, therefore, contains 6 $KAg(CN)_2$.

If now the underlying lattice were rhombohedral, only planes with $\frac{2h + k + \ell}{3}$ integral could give any reflections except the third, sixth, ninth, etc. orders. Inspection of the Laue data contained in Table III, for instance, reveals many planes for which $\frac{2h + k + \ell}{3}$ is not integral, but which reflect for values of $n\lambda$ less than 0.72 Å, three times the short wave length limit. Also (00·1) reflects in the second, fourth, eighth, tenth, etc. orders, thus clearly demonstrating that the lattice is not rhombohedral. This means, therefore, that the unit hexagonal cell with a = 7.34 Å, c = 17.7 Å containing 6 $KAg(CN)_2$ is to be accepted as the true one.

Laue photographs taken with the X-ray beam normal to (00·1) show a three-fold axis and three planes of symmetry, so that the point-group is C_{3v}, D_3, or D_{3d}. The space groups based upon a hexagonal lattice which are isomorphous with these point-groups are:[2] C_{3v}^1, C_{3v}^2, C_{3v}^3, C_{3v}^4, D_3^1, D_3^2, D_3^3, D_3^4, D_3^5, D_3^6, D_{3d}^1, D_{3d}^2, D_{3d}^3, D_{3d}^4. Of the space-groups listed, all of those with special criteria except two may be eliminated by the presence of "forbidden" reflections. However, besides the space-groups without special criteria, there are left C_{3v}^4 and D_{3d}^2, which have $\{m\ m\ 2\bar{m}\cdot\ell\}$ halved[3] for ℓ odd. That is, for these two space-groups, reflections of this type may appear only in even orders. The procedure adopted was to look for reflections of this type on both Laue and oscillation photographs for which the corresponding planes were in favorable position to reflect. No reflection was found which would rule out C_{3v}^4 and D_{3d}^2, although planes of the type $\{m\ m\ 2\bar{m}\cdot\ell\}$ with ℓ even were observed to reflect in all orders, as well as planes with ℓ odd in even orders. Among the observed

absences required by these space-groups were the following:

1. The odd orders of (00·1) from (00·1) to (00·27) inclusive (even orders from (00·2) to (00·28) were present).

2. On photographs from (00·1) with a as the axis of oscillation, $(2\ \bar{1}\cdot7)$ to $(2\ \bar{1}\cdot19)$, $(4\ \bar{2}\cdot11)$ to $(4\ \bar{2}\cdot19)$, $(\bar{2}\ 1\cdot7)$ to $(\bar{2}\ 1\cdot19)$ and $(\bar{4}\ 2\cdot9)$ to $(\bar{4}\ 2\cdot19)$, all for ℓ odd.

3. On a photograph from (11·0) with c as the axis of oscillation, (11·1), (22·1), (33·1), (44·1), (11·3), (22·3), (33·3), (11·5), (22·5), (33·5), (22·7), (33·7), etc., together with corresponding planes of the negative forms, that is $(\bar{1}\ \bar{1}\cdot1)$ etc.

4. On Laue photographs, about 20 forms of the type $(m.m.2\bar{m}.\ell)$ with ℓ odd in the first order.

A total of about 60 absences of the kind required was observed for planes which were in favorable position to reflect, a number so large as to make it very difficult to account for them with any structure not based upon either C_{3v}^4 or D_{3d}^2. It seems highly probable, therefore, that an accepted structure for $KAg(CN)_2$ must be based upon one of these two space-groups.

A fundamental difference between D_{3d}^2 and C_{3v}^4 arises on account of the fact that the former possesses a center of symmetry while the latter has none. Because of this it is probable that a crystal with a structure based upon C_{3v}^4 will show the pyroelectric effect, while this is not possible in the case of D_{3d}^2. Hence an experiment demonstrating the presence of pyroelectricity would show definitely that the space-group is not D_{3d}^2, while a negative result

would make D_{3d}^2 seem more probable than C_{3v}^4. Such an experiment was actually performed upon a crystal of octahedral habit about 5-6 mm. long after the manner described by Groth.[4] No pyroelectricity was indicated for $KAg(CN)_2$, although tourmaline as a "blank" substance gave an entirely definite positive result. Since neither the preceding experiment nor anything in the face development indicated that the crystals lack a center of symmetry, it was attempted next to find a structure based upon D_{3d}^2.

DETERMINATION OF THE STRUCTURE

Six molecules of $KAg(CN)_2$ must be placed within the unit cell in positions given by the space-group D_{3d}^2. An examination of the possibilities[5] at once reveals that the structure must have many parameters, so that a "rigorous" determination is hardly possible. The procedure adopted was to make a minimum number of plausible assumptions regarding this compound, and to test their reasonableness wherever possible.

Since the silver atoms have approximately three times the scattering power for X-rays of the potassium ions, which in turn possess about three times the scattering power of carbon or nitrogen atoms, it is to be anticipated that the stronger reflections, particularly those appearing at wide angles of scattering, must be due in large part to silver. The relative unimportances of carbon and nitrogen for large angles of reflection will often be accentuated since it may be expected that these two kinds of atoms usually will not scatter in phase with each other. In fact it is only the presence of such a

relatively large number of carbon and nitrogen atoms which causes them ever to be of significance for large angles of reflection, since the scattering power of such light atoms decreases so rapidly with decreasing interplanar distance. In view of these considerations, the procedure has been to find reasonable approximate positions first for silver and then for potassium by making use of wide angle reflections which appeared upon a number of basal plane oscillation photographs.

The photographs used were of the two kinds previously mentioned. That is, both a, the hexagonal axis, and a direction in the basal plane making an angle of 30° with a, were used as axes of oscillation. A horizontal slit system and a crystal with a face 3-4 mm. across were used. Basal plane reflections as far as (00·28) were obtained by taking successive photographs with a 20° cam, the angle between the X-ray beam and (00·1) in the starting position being changed according to need.

The indices of all important layer line reflections were assigned without ambiguity by drawing the reciprocal lattice[6] for the orthohexagonal unit, that is for the corresponding orthorhombic unit with axes a, b = $\sqrt{3}$ a, c, a and c being the hexagonal axes. The orthohexagonal unit with twice the volume of the hexagonal unit, is end-centered, and therefore reflections with h+k odd cannot appear. With planes of this type eliminated, there is a one-to-one correspondence between those remaining in the orthohexagonal unit, and the possible planes of the hexagonal unit, the equations for transformation of indices being (primes refer to the orthohexagonal unit):

$$h = k'$$
$$k = \frac{k' - h'}{2}$$
$$\ell = \ell'$$

Besides the various orders of (00·1), two types of reflections appearing upon these oscillation photographs were used in the following considerations. Namely, those arising from planes with zero index referred either in the one case to a, or in the other case to b, the axis orthogonal to a. In Figures 1 - 4 are given reproductions of four oscillation photographs with indices indicated for those planes which are used in the considerations to follow.

D_{3d}^{2} furnishes four sets of two, two sets of four, two sets of six, and one set of twelve (general) equivalent positions.[7] Six silver atoms may be placed in one of the two sets of six, or in some combination of the sets of four and two equivalent positions. With silver in 6g, that is, at

1/2,1/2,1/4; 0,1/2,1/4; 1/2,0,1/4; 1/2,0,3/4; 1/2,1/2,3/4; 0,1/2,3/4,

the structure factor for silver alone is

$$S_{Ag} = 2 \ Ag \left[e^{\pi i (h+k)} + e^{\pi i h} + e^{\pi i k} \right] \cos \frac{\pi \ell}{2}$$

For ℓ odd, $\cos \frac{\pi \ell}{2} = 0$, and $S_{Ag} \equiv 0$. But it is observed that reflections of the type (20·ℓ) with ℓ odd are among the strongest appearing upon any of the photographs (see Figures 1 and 2). Furthermore all reflections of this type from $\ell = 3$ to $\ell = 21$ appear and each is much stronger than the adjacent reflections with ℓ even for which 6g would give $S_{Ag} = \pm 6Ag$, that is it would require all six silver atoms to be scattering in phase. A similar alternation of intensities is observed for planes of the type (40·ℓ) (see Figure 2). These data make 6g so highly improbable as positions for silver atoms that it is eliminated from further consideration.

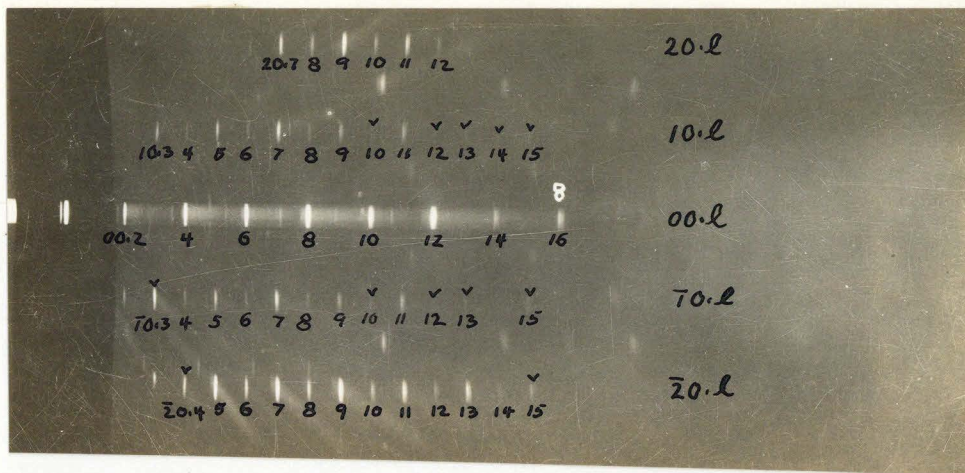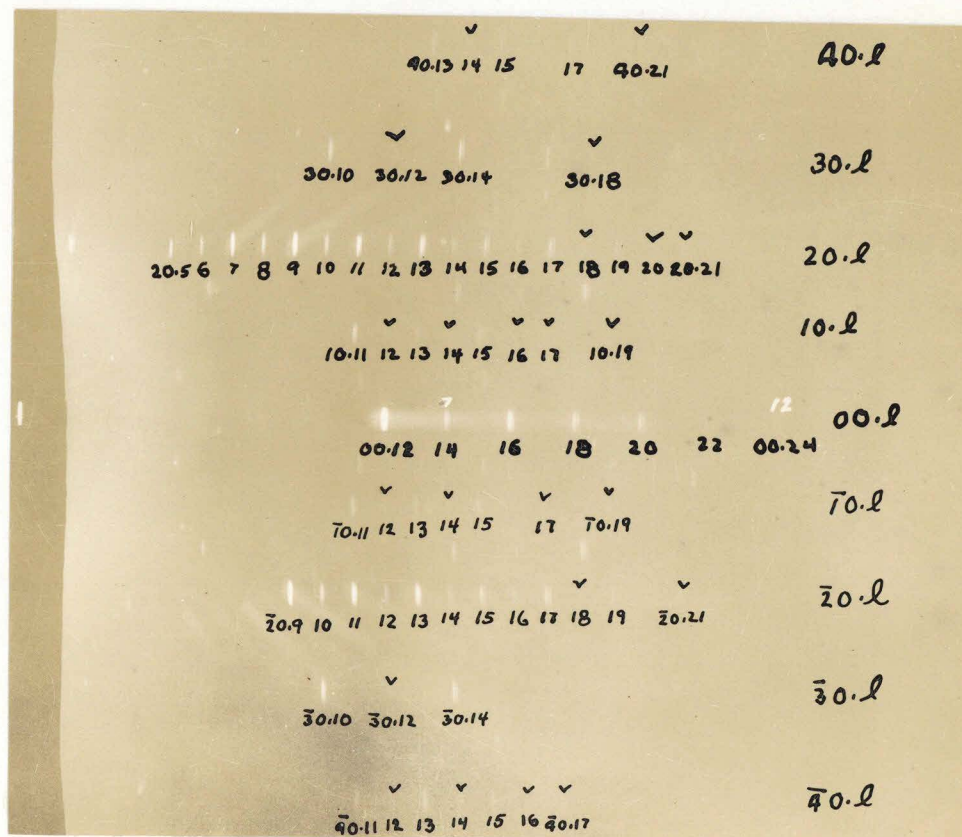Figure 1. Oscillation Photograph from (00·1) of KAg(CN)$_2$.
[10·0] Vertical. 0-20°.

Figure 2. Oscillation Photograph from (00·1) of KAg(CN)$_2$.
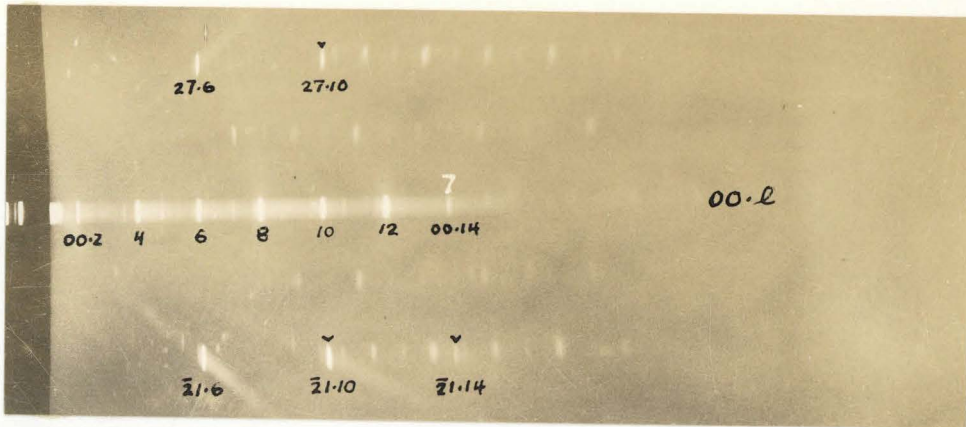[10·0] Vertical. 15-35°.

Figure 3. Oscillation Photograph from (00·1) of KAg(CN)$_2$.
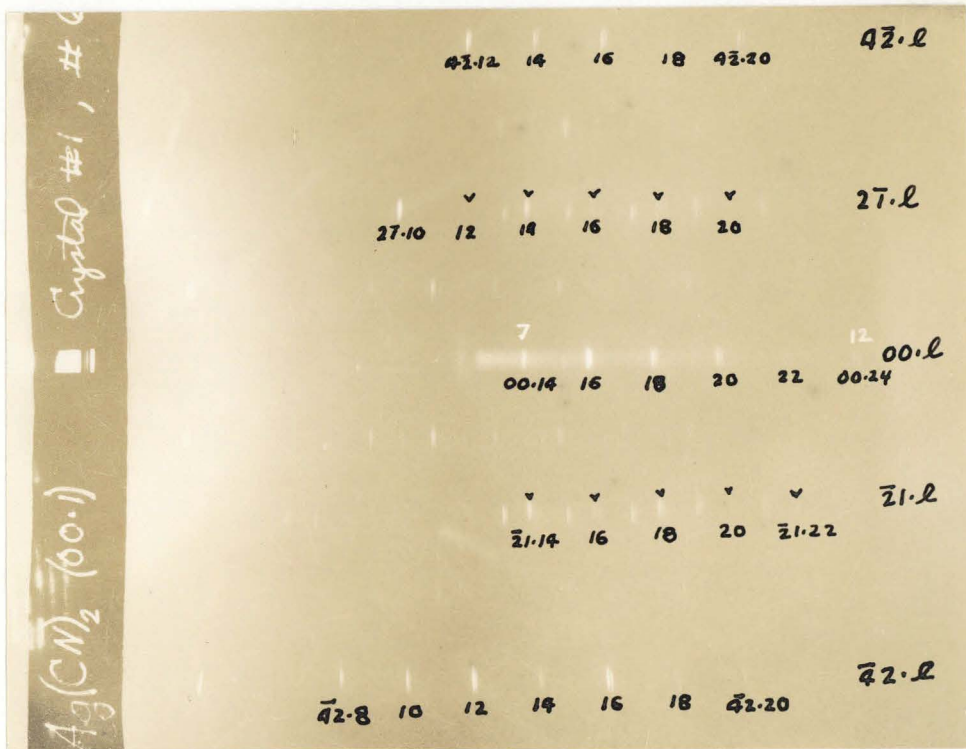
a Vertical. 0-20°.

Figure 4. Oscillation Photograph from (00·1) of KAg(CN)$_2$.

a Vertical. 15-35°.

The other possibility which would make the silver atoms crystallographically equivalent is 6h with positions at

$u,\bar{u},0;\quad 2\bar{u},\bar{u},0;\quad u,2u,0;\quad \bar{u},u,\frac{1}{2};\quad 2u,u,\frac{1}{2};\quad \bar{u},2\bar{u},\frac{1}{2},$

for which (angles are expressed in units of 2π)

$$S_{Ag} = 2iAg\left[\sin(hu-ku) + \sin(hu+2ku) - \sin(2hu+ku)\right]$$

for ℓ odd, and

$$S_{Ag} = 2\ Ag\left[\cos(hu-ku) + \cos(hu+2ku) + \cos(2hu+ku)\right]$$

for ℓ even.

The data indicate that S_{Ag} for $(20\cdot\ell)$ and $(40\cdot\ell)$ with ℓ odd should be nearly a maximum. For these reflections,

$$S_{Ag} = 2iAg\left[2\sin hu - \sin 2hu\right].$$

Differentiating and setting the result equal to zero, the condition for maxima and minima is found to be

$$\cos hu = \cos 2hu.$$

For $(20\cdot\ell)$, S_{Ag} is a maximum for $u = 1/6, 1/3, 2/3, 5/6$. For $(40\cdot\ell)$, S_{Ag} is a maximum for $u = 1/12, 1/6, 1/3, 5/12, 7/12, 2/3, 5/6, 11/12$. The values of u which are not included in both lists give only $|S_{Ag}| = \sqrt{3}\ Ag$ for $(20\cdot\ell)$, and this does not seem adequate in view of the intensity relations previously discussed. The values of 1/3 and 2/3 lead to the more specialized positions 2c and 2d, and are, of course, impossible. There remain 1/6 and 5/6 as approximate values for u, and the first of these may be selected arbitrarily without loss of generality. It may be pointed out that the value, u = 1/6 leads to an equal spacing of silver atoms about 3.67 Å apart in two planes parallel to $(00\cdot1)$, except that one atom per unit cell is missing from each layer (see Figure 6). As the interatomic distance in metallic silver is but 2.89 Å, the above spacing is entirely satisfactory.

For the possible combinations by which the silver atoms are put into two or more crystallographically non-equivalent positions, it may be said that qualitative considerations of the kind already used suffice to eliminate most of them. In any event, no arrangement remains which gives an approximately uniform distribution of silver atoms as in 6h.

There is apparently no reason to doubt that each silver is bonded to two carbons of cyanide groups, since these complex ions are extremely stable chemically. If both carbon and nitrogen were put into the general position, there would be four layers of each kind of atom parallel to (00·1) within the unit cell. By assigning proper values of the six parameters, the carbon and nitrogen atoms may be arranged so as to bear the correct relation to the silver atoms in 6h in order to have $Ag(CN)_2^-$ ions as a structural unit, and at the same time to have the cyanide groups in approximate closest packing within each layer (see Figure 6). It is then possible to put the six potassium atoms in regions of large negative potential, and in fact to arrange them so that each is surrounded by six nitrogens of six cyanide groups at the corners of an octahedron. In other words, $KAg(CN)_2$ is an ionic crystal made up of K^+ and $Ag(CN)_2^-$ ions, while $Ag(CN)_2^-$ is an electron pair bond complex, and it seems possible to find a structure which satisfies the exigencies of this mixed state of affairs.

The positions referred to for the potassium ions are given by 2b (0,0,1/4; 0,0,3/4) and 4f (1/3,2/3,u; 1/3,2/3,u; 2/3,1/3,$\frac{1}{2}$-u; 2/3, 1/3, u+$\frac{1}{2}$) with u in the neighborhood of 1/4. Returning to a consideration of various reflections appearing upon oscillation photographs (Figures 1-4), it now seems worth while to calculate the sum of the

structure factors of silver and potassium for the more complex planes, and to compare these with observation. For the present purpose, the silver and potassium parameters may be taken as 1/6 and 1/4 respectively. The results are summarized below:

1. For $(40 \cdot \ell)$ and $(\overline{4} \, 0 \cdot \ell)$, (Figure 2),

    a. ℓ odd,

$$S_{Ag} + S_K = -3\sqrt{3} \text{ i Ag.}$$

    b. ℓ even,

$$S_{Ag} + S_K = -3 \text{ Ag}$$

A quite regular alternation of intensities is observed for the ranges $(\overline{4} \, 0 \cdot 11)$ to $(\overline{4} \, 0 \cdot 17)$ and $(40 \cdot 13)$ to $(40 \cdot 19)$, with the reflections with ℓ odd considerably stronger than the adjacent ones for ℓ even.

2. For $(30 \cdot \ell)$ and $(\overline{3} \, 0 \cdot \ell)$, (Figure 2),

    a. ℓ odd,

$$S_{Ag} + S_K = 0.$$

    b. ℓ even,

$$S_{Ag} + S_K = -2Ag + 6K \text{ for } \ell/4 \text{ integral,}$$
$$S_{Ag} + S_K = -2Ag - 6K \text{ for } \ell/4 \text{ half-integral.}$$

The reflections with ℓ odd are not observed. Only two very weak reflections, $(30 \cdot 12)$ and $(\overline{3} \, 0 \cdot 12)$, are observed for $\ell/4$ integral (it may be recalled that the scattering power of silver is about three times that of potassium). Strong reflections are observed for $(3 \, 0 \cdot 10)$, $(\overline{3} \, 0 \cdot 10)$, $(3 \, 0 \cdot 14)$, and $(\overline{3} \, 0 \cdot 14)$, while $(3 \, 0 \cdot 18)$ and $(\overline{3} \, 0 \cdot 18)$ also appear. From the construction in the reciprocal lattice which was used

to assign these indices, it appears that other planes with $\ell/4$ half-integral were not in position to reflect.

    3. For $(2\ 0 \cdot \ell)$ and $(\bar{2}\ 0 \cdot \ell)$,   (Figures 1 and 2),

        a. ℓ odd,

$$S_{Ag} + S_K = 3\sqrt{3}\ i\ Ag.$$

        b. ℓ even,

$$S_{Ag} + S_K = -3\ Ag.$$

    Reflections in the ranges from $(20 \cdot 4)$ to $(20 \cdot 21)$ and $(\bar{2}\ 0 \cdot 3)$ to $(\bar{2}\ 0 \cdot 21)$ appear with those with ℓ odd considerable stronger than the adjacent ones with ℓ even. The intensities for both ℓ odd and ℓ even gradually fall off with increasing ℓ, of course.

    4. For $(1\ 0 \cdot \ell)$ and $(\bar{1}\ 0 \cdot \ell)$,   (Figures 1 and 2),

        a. ℓ odd,

$$S_{Ag} + S_K = \sqrt{3}\ i\ Ag.$$

        b. ℓ even,

$$S_{Ag} + S_K = Ag.$$

    Again an alternation of intensities is observed in the ranges from $(10 \cdot 3)$ to $(10 \cdot 19)$ and $(\bar{1}\ 0 \cdot 3)$ to $(\bar{1}\ 0 \cdot 19)$ with considerably greater intensities for ℓ odd.

    5. For $(4\ \bar{2} \cdot \ell)$ and $(\bar{4}\ 2 \cdot \ell)$,   (Figure 4),

        a. ℓ odd,

$$S_{Ag} + S_K \equiv 0 \quad \text{(as required by } D_{3d}^2 \text{).}$$

        b. ℓ even,

$$S_{Ag} + S_K = 6\ Ag + 6\ K \quad \text{for } \ell/4 \text{ integral,}$$

$$S_{Ag} + S_K = 6\ Ag - 6\ K \quad \text{for } \ell/4 \text{ half-integral.}$$

Reflections with ℓ odd, of course, are not observed. Quite strong reflections are observed in the ranges from $(4\ \bar{2}\cdot 10)$ to $(4\ \bar{2}\cdot 20)$ and $(\bar{4}\ 2\cdot 10)$ to $(\bar{4}\ 2\cdot 20)$ with ℓ even. The intensities for $\ell/4$ integral are in every case stronger than the two adjacent ones for $\ell/4$ half-integral.

6. For $(2\ \bar{1}\cdot \ell)$ and $(\bar{2}\ 1\cdot \ell)$, (Figures 3 and 4),

    a. ℓ odd,

$$S_{Ag} + S_K \equiv 0 \quad \text{(as required by } D_{3d}^2\text{)}.$$

    b. ℓ even,

$$S_{Ag} + S_K = -2Ag + 6K \quad \text{for } \ell/4 \text{ integral,}$$
$$S_{Ag} + S_K = -2Ag - 6K \quad \text{for } \ell/4 \text{ half-integral.}$$

Reflections with ℓ odd, of course, are not observed. An alternation of intensities is observed in the ranges from $(2\ \bar{1}\cdot 6)$ to $(2\ \bar{1}\cdot 20)$ and $(\bar{2}\ 1\cdot 6)$ to $(\bar{2}\ 1\cdot 20)$, with the reflections for $\ell/4$ half-integral decidedly stronger than adjacent reflections for $\ell/4$ integral.

7. For $(00\cdot \ell)$, (Figures 1-4),

    a. ℓ odd,

$$S_{Ag} + S_K \equiv 0 \quad \text{(as required bu } D_{3d}^2\text{)}.$$

    b. ℓ even,

$$S_{Ag} + S_K = 6Ag + 6K \quad \text{for } \ell/4 \text{ integral,}$$
$$S_{Ag} + S_K = 6Ag - 6K \quad \text{for } \ell/4 \text{ half-integral.}$$

Reflections with ℓ odd, of course, are not observed. The details in the observed reflections are not accounted for by the above structure factors, but there is general qualitative agreement. As would be anticipated from the preceding calculations, and from a con-

sideration of other factors which influence the intensity of scattered X-rays, the (00·n) reflections are observed to be the most intense ones appearing upon these photographs.

The preceding comparisons reveal good qualitative egreement between calculated and observed intensities for each set of layer line reflections. Although of a somewhat less definite character, the intensity relations between layer lines seems to be satisfactory qualitatively. The structure in its rough outlines now appears to have a considerable probability of being correct, and it will be worth while to attempt to fix parameter values with some accuracy.

As previously mentioned, in this atomic arrangement the carbon and nitrogen atoms are to be placed in the general position. There are then three parameters along c, one for carbon, another for nitrogen, and a third for the potassium ions in 4 f. With the use of a simplifying assumption regarding the relative position of carbon and nitrogen atoms of the same cyanide group, it is found possible to evaluate these three parameters using the (00·n)reflections.

Hydrogen cyanide, HCN, is found[8] from band spectral data to be a linear molecule in the normal state with a carbon-nitrogen separation of 1.15 Å. It seems safe to assume that a similar state of affairs will be maintained in $Ag(CN)_2^-$, so that the carbon-nitrogen separation will be 1.15 Å, and both atoms of a cyanide group will lie in a straight line with the silver atom (this does not imply linearity for the complete $Ag(CN)_2^-$ ion). The separation of silver and carbon atoms is expected to be about 2.1 Å, so that the length of the $Ag(CN)_2^-$ ion, if it be linear, is expected to be about 6.5 Å. Now c/2 is observed to be 8.84 Å, so the possibility of nearly linear ions along c bound to-

gether by potassium ions is to be considered. Proceeding from this point, parameter values for carbon and nitrogen may be assigned so that the centers of gravity of the cyanide groups of each layer are in closest packing, and the potassium-nitrogen separation for $u_K = 1/4$ is of the right order of magnitude, that is about 2.85 Å. With this arrangement, the projection of the carbon-nitrogen separation, 1.15 Å, upon c is 1.02 Å, and will not be greatly different for reasonable variations in the x and y parameters of carbon and nitrogen. If z_N is the parameter along c for nitrogen, then in the following treatment $z_N - \dfrac{1.02}{17.7}$ will be used for z_C, the parameter along c for carbon. With this assumption, the number of parameters along c is reduced from three to two, that is to z_N and u_K.

It should be pointed out, perhaps, that having put silver in 6h, potassium in 2b and 4f, and carbon and nitrogen in the general position of D_{3d}^2, ~~that~~ the only new assumption made for the purpose of treating (00·n) reflections is that the cyanide groups are oriented approximately along c. In view of the magnitude of c, it is seen that a considerable departure from the orientation with respect to c assumed for CN⁻ would have only a small effect upon these considerations.

The structure factor for (00·n), n even, is

$$S = 6F_{Ag} + 2F_K(-1)^{n/4} + 4F_K \cos n\, u_K + 12F_N \cos nz_N + 12F_C \cos nz_C$$

in which the F's are the atomic scattering powers for X-rays for the particular interplanar distance, $d_{(00·n)}$. The F-values of Pauling and Sherman[9] are employed thruout this paper. After making the substitution $z_C = z_N - 0.058$ in S, the square roots of the relative intensities were calculated by

$$\sqrt{I} = \sqrt{n}\left(\frac{1 + \cos^2 2\theta}{2\sin^2 2\theta}\right)^{1/2} S.$$

$$\left(\frac{1 + \cos^2 2\theta}{2 \sin^2 2\theta}\right)^{1/2}$$ takes care of the Lorentz and polarization factors. Since a horizontal slit system was used, in the various positions for reflection the cross-section of the X-ray beam intercepted by the crystal was proportional to $\sin\theta$ and therefore to n, thus making necessary the inclusion of $\sqrt{n}$ as a factor. It is to be noted that the temperature factor, which as a matter of fact is large for $KAg(CN)_2$, has been omitted.

$\sqrt{I}$ for all even order reflections from (00·2) to (00·28) was plotted against z_N in the range from 0 to 1/4 for several values of u_K in the neighborhood of 1/4. One set of these, for $u_K = 0.260$, is shown in Figure 5. Now if a reflection of given order was observed to be more intense than another of lower order, only those values of z_N (and u_K) were considered as possible for which $\sqrt{I}$ for the higher order reflection was calculated to be the larger. It is clear that the omission of the temperature factor from the expression used in calculating $\sqrt{I}$ lends the desirable measure of safety in making comparisons of this type. The following intensity relations are observed for the (00·n)· reflections:

(00·4) > (00·2), (00·6) > (00·2), (00·8) > (00·2), (00·12) > (00·2);
(00·8) ≈ (00·4); (00·8) > (00·6), (00·12) ≈ (00·6); (00·12) > (00·10);
(00·16) > (00·14), (00·18) > (00·14), (00·20) > (00·14);
(00·24) > (00·22); (00·28) ≳ (00·26).

The comparison (00·8) nearly as strong as (00·4) limits z_N to values near 0.15 for all values of u_K in the neighborhood of 1/4. The effect of a small change of $\pm\epsilon$ from 0.250 in the potassium parameter is to make the structure factors and hence $\sqrt{I}$ larger for reflections
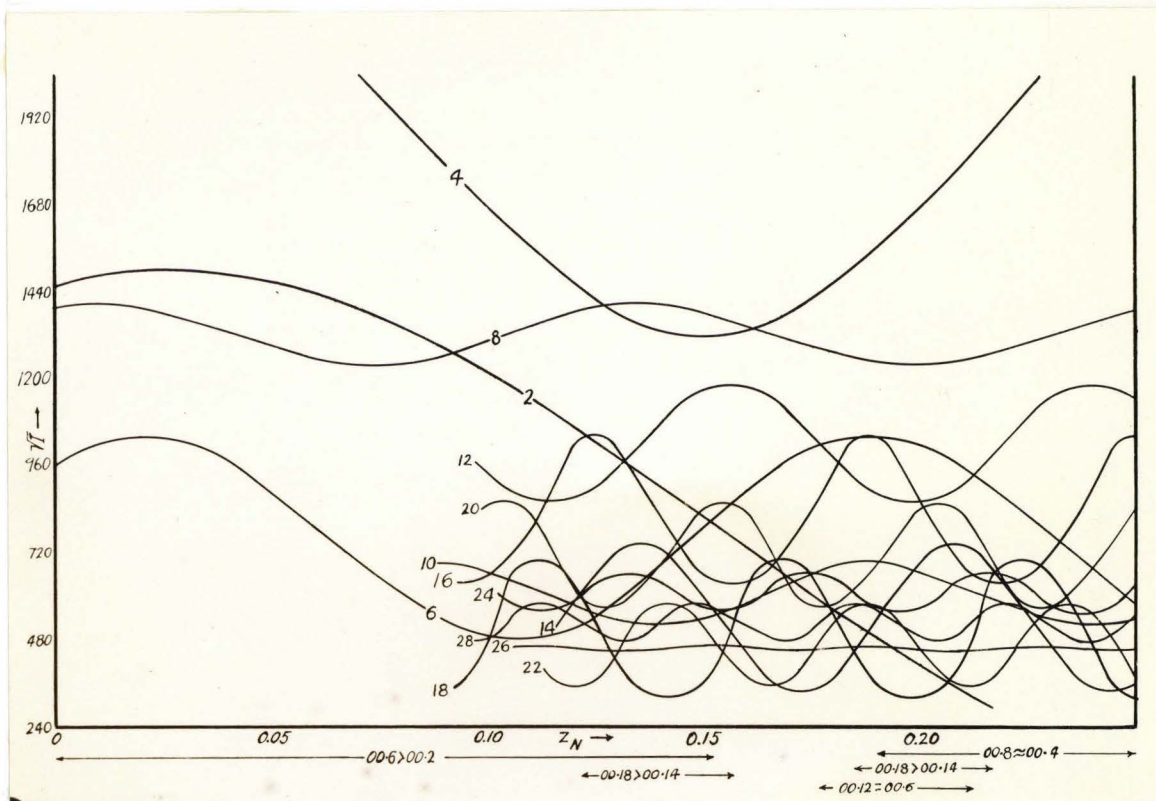
Figure 5. The calculated intensities of (00·n) reflections as a function of the nitrogen parameter, z_N, for the potassium parameter, u_K, equal to 0.240 or 0.260.

with n/4 half-integral, and smaller for those reflections with n/4 integral. The sign of the change is of no significance here, but it cannot be more than 0.020, since for such a change the inequalities (00·24) > (00·22) and (00·20) > (00·14) are no longer accounted for satisfactorily. Also the fact that with $u_K = 0.250$, $\sqrt{I}$ for (00·20) is calculated to be much larger than for the adjacent reflection (00·18), whereas (00·18) is observed to be somewhat the stronger of the two, indicates that the potassium parameter must be slightly different from 1/4. A general agreement between calculated and observed intensities which accounts for all of the observed inequalities listed above is obtained for $u_K = 0.260$ or 0.240; $z_N = 0.167$, $z_C = 0.109$. The ambiguity in the value of the potassium parameter will be considered later.

With the assumptions which have been made, it has been determined that $u_{Ag} \approx 1/6$, $u_K = 0.260$ or 0.240, $z_N = 0.167$, $z_C = 0.109$. It remains to assign values for the other four carbon and nitrogen parameters, to investigate possible variations in u_{Ag} from the value 1/6, and to decide which value is correct for u_K.

If it be further assumed that the cyanide groups are in close-packed layers parallel to (00·1), then their position may now be fixed by the values found for z_N and z_C. Putting $u_{Ag} = 1/6$ and assuming that the carbon and nitrogen atoms of a cyanide group lie in a straight line with the silver atom, the values for the other parameters are calculated to be

$$x_N = 0.365; \quad x_C = 0.295;$$
$$y_N = 1/3 ; \quad y_C = 1/3.$$

With the use of the foregoing complete assignment of parameter values, relative intensities were calculated for a particular class of

reflections appearing upon Laue photographs taken with the X-ray beam
almost exactly perpendicular to (00·1). Intensity comparisons were
made between those corresponding positive and negative forms, that is,
between $\{hk\cdot\ell\}$ and $\{\bar{h}\bar{k}\cdot\ell\}$, which reflected in the first order. This
is practicable since nearly the same values of $n\lambda$ were observed for
all planes of both forms, and hence all factors influencing the inten-
sity of the scattered radiation, with the single exception of the
structure factor, are nearly identical for both forms. Slight depar-
ture from an exactly symmetrical orientation of the crystal was taken
care of by the following averaging process used in determining relative
intensities. The intensities of all significant spots occurring upon
three nearly symmetrical photographs of considerably different exposure
times were obtained by visual comparison with a scale prepared for the
purpose of estimating Laue intensities. As the intensities of the re-
flections for different forms varied greatly, it was usually found ad-
visable in the case of a given pair of forms to employ the photograph
of photographs for which comparison could be made with greatest con-
fidence. The ratio of intensities for corresponding positive and
negative forms, $\frac{I\{\bar{h}\bar{k}\cdot\ell\}}{I\{hk\cdot\ell\}}$, was evaluated from the foregoing data by
comparing reflections on the same photograph for which the values of
$n\lambda$ differed by less than about 0.01 Å. Usually about three such com-
parisons were found for each pair of forms, and gave reasonably con-
sistent results. The mean values obtained together with the approximate
values of $n\lambda$ are given in Table IV.

These comparisons are especially significant for fixing car-
bon and nitrogen parameters, for only these atoms are responsible for
the differences in intensities observed between corresponding positive

and negative forms. That is,

$$(S_{Ag} + S_K)_{\{hk\cdot\ell\}} = (S_{Ag} + S_K)_{\{\bar{h}\bar{k}\cdot\ell\}} \ , \ \ell \text{ even;}$$

$$(S_{Ag} + S_K)_{\{hk\cdot\ell\}} = -(S_{Ag} + S_K)_{\{\bar{h}\bar{k}\cdot\ell\}} \ , \ \ell \text{ odd.}$$

The ratio $\dfrac{I_{\{\bar{h}\bar{k}\cdot\ell\}}}{I_{\{hk\cdot\ell\}}}$ was calculated using the F-values of

Pauling and Sherman, and the parameter values previously suggested.
Since it will be shown that 0.260 is the correct value to use for the
potassium parameter, the results given in Table IV are given for this
case only.

TABLE IV

Intensity Relations for Certain Laue Reflections

X-Ray Beam Normal to (00·1)

Comparison	n λ	$\dfrac{I_{\{\bar{h}\bar{k}\cdot\ell\}}}{I_{\{hk\cdot\ell\}}}$	
		Calculated	Observed
$\{33\cdot2\}$ with $\{\bar{3}\bar{3}\cdot2\}$	0.35 Å	1.03	1.0
$\{14\cdot2\}$ with $\{\bar{1}\bar{4}\cdot2\}$	0.44	3.37	3.5
$\{24\cdot3\}$ with $\{\bar{2}\bar{4}\cdot3\}$	0.46	1.36	1.4
$\{13\cdot1\}$ with $\{\bar{1}\bar{3}\cdot1\}$	0.36	1.96	1.7

The foregoing results provide strong general justification
for the structure, and indicate that the selection of x and y parameters
which has been made is a fair approximation to the true values. Now if it
be assumed simply that the x and y values of the carbon and nitrogen par-
ameters lie in the general neighborhood of those just considered, it is
possible to fix the value of the silver parameter within narrow limits.

Upon an exceptionally clear photograph (Figure 2), (30·12) is
very faintly but unmistakably observed, while the adjacent reflections

(30·11) and (30·13) are absent. Now it may be verified that the struc-
ture factors for the two cases of (30·ℓ) reduce to the following after
putting $u_{Ag} = 1/6 + \delta$, and making use of the trigonometric addition for-
mulas (angles are expressed in units of 2π):

$$S = 2Ag\left[\cos 6\delta - 2\cos 3\delta\right] + 2K\left[(-1)^{\ell/4} + 2\cos \ell u\right]$$
$$+ 4C\left[2\cos 3/2(x_C + y_C)\ \cos 3/2(x_C - y_C) + \cos 3(y_C - x_C)\right]\cos \ell z_C$$
$$+ 4N\left[2\cos 3/2(x_N + y_N)\ \cos 3/2(x_N - y_N) + \cos 3(y_N - x_N)\right]\cos \ell z_N \text{ for } \ell \text{ even,}$$

$$S = -2\ i\ Ag\left[2\sin 3\delta + \sin 6\delta\right] + 4\ i\ C\left[2\sin 3/2(x_C - y_C)\cos 3/2(x_C + y_C)\right.$$
$$\left. + \sin 3(y_C - x_C)\right]\cos \ell\ z_C + 4\ i\ N\left[2\sin 3/2(x_N - y_N)\cos 3/2(x_N + y_N)\right.$$
$$\left. + \sin 3(y_N - x_N)\right]\cos \ell\ z_N \text{ for } \ell \text{ odd.}$$

To calculate S, it is assumed for both carbon and nitrogen
that $|x - y| \lesssim 0.05$, $2/3 - 0.05 \lesssim |x = y| \lesssim 2/3 + 0.05$.
This would seem to be well within the range of variations to be antici-
pated. In the calculation of the intensities which follows, all factors
except the temperature factor are included, and this will be but little
different for these neighboring reflections. Either 0.240 or 0.260 for
u_K leads to the same result in this case.

Considering the effect of carbon and nitrogen on the calculated
intensities for (30·11) and (30·13), it may be seen by actual calculation
that a number of factors in both cases tend to make their contributions
quite negligible. In the first place the quantities inside the square
brackets are not much different from zero thruout the range of values
that have been assumed for the x and y parameters, and in addition the
coefficients determined by $\cos \ell z$ are small for (30·11) and are of
opposite sign and nearly equal in magnitude for (30·13). It now may

be asserted with confidence that any substantial contribution to the
calculated intensities for these planes must be due to silver alone.
For $\delta = 0$, the contribution of silver to these structure factors is
also zero.

This is not the case for (30·12), however. There is obtained

$$S_{(30·12)} = 2 \text{ Ag}\left[\cos 6\delta - 2 \cos 3\delta\right] + 5.92 \text{ K} - 1.85 \text{ C} + 8.65 \text{ N}$$

using the limits of the range indicated for the x and y parameters of
carbon and nitrogen together with $u_K = 0.260$ or 0.240, $z_N = 1/6$,
$z_C = 0.109$. In order to account for the appearance of (30·12), it is
necessary to have a calculated intensity of fair magnitude, and the pre-
ceding equation shows that this may be obtained only by taking a dif-
ference of effective scattering by potassium and nitrogen working against
silver and carbon. Now the scattering due to silver is a minimum for
$\delta = 0$, and for this case there is obtained in a manner similar to that
employed for the (00·n) reflections (n $\approx$ 3.5 for this case),

$$\sqrt{I/n} \approx + 10.$$

This very small value for $\sqrt{I/n}$, representing as it does a preponderance
of effective scattering due to potassium and nitrogen over that of sil-
ver and carbon, may be made perhaps as much as +15 by taking more reason-
able values for the x and y parameters of carbon and nitrogen. Also as
the potassium parameter approaches nearer to or departs farther from 1/4,
I is increased or decreased respectively. But, as the silver parameter
departs from 1/6, the value of I only very slowly decreases to zero and
then increases, corresponding to a change in preponderance of effective
scattering from potassium and nitrogen to silver (and carbon). How-
ever, $S_{(30·13)}$ and $S_{(30·11)}$, which were shown to be substantially zero
for $\delta = 0$, will mount in value as $|\delta|$ increases relatively with

very great rapidity, even while $S_{(30 \cdot 12)}$ is still decreasing. In fact, for $|\delta| = 0.003$, $S_{(30 \cdot 11)}$ and $S_{(30 \cdot 13)}$ will be greater already than $S_{(30 \cdot 12)}$, and will remain so for further changes in the silver parameter of nearly $\pm 1/6$. It is therefore highly probable that $u_{Ag} = 1/6 \pm 0.002$, and virtually no deviation from the value 1/6 is to be anticipated.

The preceding argument applies in similar form to the comparison of $(\bar{3}0 \cdot 11)$ and $(\bar{3}0 \cdot 13)$ with $(\bar{3}0 \cdot 12)$, for which the observed intensity relations are as with the corresponding planes of the positive forms.

A comparison of relative intensities within the three sets of reflections $(40 \cdot \ell)$, $(20 \cdot \ell)$, $(10 \cdot \ell)$, all with ℓ odd, leads to the selection of 0.260 rather than 0.240 for the potassium parameter. It is observed that such a series of reflections, say $(20 \cdot \ell)$ with ℓ odd, may be divided into two sub-series each of which shows a "normal" decline in intensity with increasing angle of reflection, but differing from each other in average intensity. For $(20 \cdot \ell)$, the reflections with $\ell = 4n + 1$ are appreciably more intense on the average than those with $\ell = 4n - 1$, that is, the first sub-series is on the whole recognizably more intense than the second (Figures 1 and 2). An exactly analogous condition holds for $(40 \cdot \ell)$, but for $(10 \cdot \ell)$ the relation is reversed, that is, the sub-series with $\ell = 4n - 1$ is stronger than that with $\ell = 4n + 1$. Furthermore, the phenomenon is somewhat more marked for higher values of ℓ.

Since for $(20 \cdot \ell)$ and $(10 \cdot \ell)$, both with ℓ odd, there are about five reflections for each sub-series, it was considered justifiable to regard the contributions of carbon and nitrogen as averaging out, upon the whole (rough calculations show that these contributions are

small anyway). With this assumption it is easy to show that a small positive deviation from the value of 1/4 for the potassium parameter accounts for the observed relations. In the expressions which follow, u_K is put equal to $1/4 + \epsilon$.

For both $(20 \cdot \ell)$ and $(40 \cdot \ell)$ with ℓ odd,

    a. $\ell = 4n + 1$,

$$|S_{Ag} + S_K| = 3\sqrt{3}\, Ag + 2\sqrt{3}\, K \sin \ell \epsilon$$

    b. $\ell = 4n - 1$,

$$|S_{Ag} + S_K| = 3\sqrt{3}\, Ag - 2\sqrt{3}\, K \sin \ell \epsilon$$

For $(10 \cdot \ell)$ with ℓ odd,

    a. $\ell = 4n + 1$,

$$|S_{Ag} + S_K| = \sqrt{3}\, Ag - 2\sqrt{3}\, K \sin \ell \epsilon$$

    b. $\ell = 4n - 1$,

$$|S_{Ag} + S_K| = \sqrt{3}\, Ag + 2\sqrt{3}\, K \sin \ell \epsilon$$

A value of zero for ϵ means that the potassium ions contribute nothing to the reflections, while a small value for ϵ means that the main contribution due to silver will be changed somewhat in a regular manner. Since the argument of the sine is $\ell \epsilon$, the effect will become more marked with increasing ℓ so long as $\ell \epsilon < 0.25$ (in the present instance ℓ goes to 21 and $|\epsilon| = 0.01$). For a positive ϵ , the intensity relations between the sub-series for each of these three groups of reflections will be properly correlated, whereas for a negative ϵ , cell relations will be reversed. The conclusion is, therefore, that $u_K = 0.260$ rather than 0.240.

The same result may be deduced with the use of the planes of the corresponding negative forms, namely, $(\overline{4}\,0 \cdot \ell)$, $(\overline{2}\,0 \cdot \ell)$, and

$(\bar{1}\, 0 \cdot \ell)$, forwhich almost identical intensity relations are observed.

The values with an estimated accuracy of the eight parameters of this structure have been found to be as follows:

$u_{Ag} = 1/6 \pm 0.002;$ $u_K = 0.260 \pm 0.005;$

$z_N = 0.167 \pm 0.005;$ $z_C = 0.109 \pm 0.005;$

$x_N = 0.365;$ $x_C = 0.295;$

$y_N = 1/3;$ $y_C = 1/3.$

Higher values of x_N and x_C, and lower values of y_N and y_C than those just given are scarcely to be expected, as will be clear from the discussion of interatomic distances which will follow. It is difficult also to estimate the magnitude of possible variations in the opposite directions for these parameters, but in any event a better agreement between calculated and observed intensities for the Laue reflections which have been used may hardly be anticipated.

Definite information regarding the temperature factors for the individual atoms in this compound is not available. That it is very large may be seen by comparing the calculated values of $\sqrt{I}$ shown in Figure 5 with the $(00 \cdot n)$ reflections shown in Figures 1-4. It is probable also that the temperature factor will depend in a marked fashion on the angle which the X-ray beam makes with the crystal axes when in the reflecting position. Hence it may not be feasible or particularly significant to assume an overall temperature factor for the purpose of correlating quantitatively the observed intensity relatinns between $(00 \cdot n)$ and layer line reflections. If a constant overall temperature factor were assumed for this purpose, however, it would need to be of the order of magnitude of that found

for sylvine (KCl).[10] That is, a factor of about $\left(e^{-\frac{0.44}{\alpha^2}}\right)^2$ would need to be included in all calculated intensities. This is sufficient to make the new calculated intensity for (00·28) only about 1/9 of the former value, and even this reduction may not be entirely adequate.

DISCUSSION OF THE STRUCTURE

The structure as determined is shown graphically in Figure 6. The simplest "ideal" structure of this type is one with $u_{Ag} = 1/6$, $u_K = 1/4$, $x_N = y_N = 1/3$, and $z_N = 1/6$. Such an assignment of parameter values leads to interatomic distances as follows: Ag-N, 3.20 Å; K-N, 2.86 Å; Ag-Ag, 3.67 Å; N-N (same layer), 4.24 Å; N-N,(adjacent layers), 3.84 Å. The Ag-N separation may be expected from analogy[11] with $K_2Cd(CN)_4$, in which Cd-N = 3.28 Å, to lie between 3.15 and 3.35 Å. The K-N distance observed[12] in KN_3, in which potassium has a coordination number of eight is 2.96 ± 0.06 Å. In the foregoing "ideal" arrangement, each potassium is surrounded by six nitrogens at the vertices of a regular octahedron, and the separation of 2.86 Å is of the right order of magnitude. However, it is quite certain that the nitrogen atoms will not be even approximately spherically symmetrical, so that the "ideal" structure will be deformed thru displacement of potassium, nitrogen, and carbon atoms in a manner difficult to predict. There will then be three different K-N separations which will depend upon the angle between the line from potassium to nitrogen and the figure axis of the cyanide group.
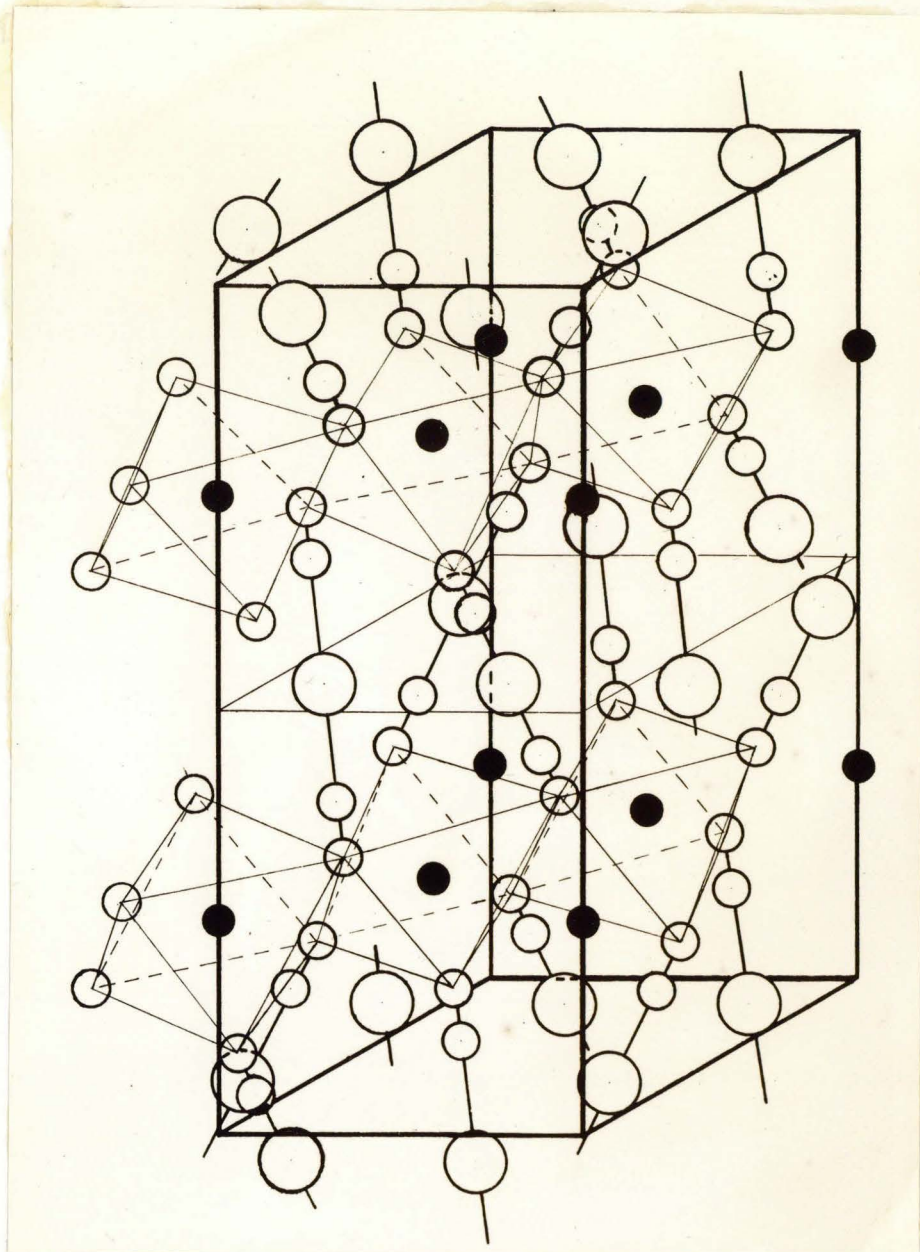
Figure 6. The structure of potassium silver cyanide. Large open circles represent silver atoms, small open circles carbon and nitrogen atoms, and small closed circles potassium ions. The Ag(CN)$_2$ ion is indicated as a structural unit by the lines joining carbon with silver and with nitrogen atoms. Heavy lines mark the hexagonal unit of structure, and light lines the coordinated octahedron formed by six nitrogen atoms about each potassium ion.

For the structure as actually determined, that is, for $u_K = 0.260$, $x_N = 0.365$, $y_N = 1/3$, $z_N = 1/6$, $u_{Ag} = 1/6$, there are obtained: Ag-N, 3.29 Å; $(K-N)_1$ (K in a no parameter position), 2.97 Å; $(K-N)_2$, 3.05 Å; $(K-N)_3$, 2.56 Å. The angles between the lines joining potassium and nitrogen, and the extension of the figure axis of the cyanide group are calculated to be 76.7°, 73.5°, and 32.6°, respectively.

The results indicate that the relations of potassium with nitrogen are closely similar in two of the three cases, but are quite different for the third. The value of 2.56 Å found for the one K-N separation is certainly lower than would have been anticipated. It is to be noted, however, that if the potassium parameter were somewhat less than 0.260, this value would be increased. The fact that (00·18) is observed to be definitely stronger than (00·20) indicates that u_K is not less than 0.260, but deviations from the true atomic scattering powers in the F-values which were employed may more than make up the difference. It is quite possible and even probable that the concentration of six electrons in the bond eigenfunctions used in forming the triple bond may result in an effective center of scattering for X-rays lying between carbon and nitrogen. The "anomalous" (222) reflection observed for diamond is a case in point. It is to be noted also that with $u_K = 0.260$, the very weak but clear and definite reflection (30·12), used in fixing the silver parameter, hardly gives a calculated value for the intensity large enough to be in quantitative agreement with the (00·n) reflections of high order, even after the introduction of a

rather large temperature factor. The attribution of somewhat greater scattering powers to nitrogen and carbon would give improved agreement between calculated and observed intensities both for the comparison of (30·12) against the high orders of (00·n), and for (00·18) with (00·20).

It is rather probable also that variations in the four parameters x_C, y_C, x_N, and y_N could enter in such a way that the K-N separation of 2.56 Å would be appreciably increased, while retaining equally significant agreement between calculation and observation for the Laue reflections previously used. Such variations have not been found after a fair number of trials, however. It should be emphasized, moreover, that the correct answer to the problem is not known, that is, it is not possible from any independent considerations to say just what the minimum value for this K-N separation as a function of the angle ought to be. A value greater than 2.56 Å would be anticipated, however.

The assignment of parameter values which has given generally good agreement between calculated and observed intensities leads to an exactly linear configuration for the complex ion, $Ag(CN)_2^-$. Furthermore, the deviation from linearity will not be of importance for reasonably large variations in the x, y, and z parameters of carbon and nitrogen. It is true that alternative structures for which the complex ion would be appreciably kinked have not been considered in detail, but the evidence which has been presented in support of the proposed structure is quite convincing. It seems, therefore, that the essential linearity of the $Ag(CN)_2^-$ ion may be accepted with some confidence.

SUMMARY

Trigonal crystals of potassium silver cyanide, $KAg(CN)_2$, were subjected to an X-ray study using Laue and oscillation photographs. The underlying lattice was found to be hexagonal with a unit cell of dimensions $a = 7.34 \pm 0.1$ Å, $c = 17.7 \pm 0.2$ Å. Complete absence of reflections of the type $\{m\ m\ 2\bar{m}\ \ell\}$ render one of the two space groups D_{3d}^2 and C_{3v}^4 highly probable. The face development and the apparent absence of a pyroelectric effect make D_{3d}^2 (with a center of symmetry) somewhat more probable than C_{3v}^4, and it was found possible to base a satisfactory structure upon the former space-group.

Silver was placed in 6 h, potassium in 2 b and 4 f, and carbon and nitrogen in the general position according to Wyckhoff's tabulation (Reference 5). The approximate positions of first silver and then of silver and potassium (each with one parameter) were fixed by qualitative comparison with a number of observed regularities among numerous layer line reflections appearing upon oscillation photographs from the basal plane. With an assumption regarding the C-N separation in CN^- and the approximate orientation of a cyanide group with respect to c, the parameters along c (potassium, carbon, and nitrogen) were fixed by considering $(00 \cdot n)$ intensity inequalities. The x and y parameters of carbon and nitrogen were assigned values with the aid of observed intensity inequalities between reflections $\{hk \cdot \ell\}$ and $\{\bar{h}\bar{k} \cdot \ell\}$ appearing in the first order and at the same values of $n\lambda$ upon symmetric $(00 \cdot 1)$ Laue photographs. To fix accurately the value of the silver parameter at 1/6, and to remove an ambiguity in

the value of the potassium parameter, recourse was had to specialized arguments. The derived structure accounts at least qualitatively for observed intensity relations among all pertinent reflections appearing upon a number of photographs.

The structural units of $KAg(CN)_2$ are K^+ ions, and linear or nearly linear $Ag(CN)_2^-$ ions oriented at an angle of about 27° with c (see Figure 6). The cyanide groups are in approximately closest-packed layers parallel to (00·1), and each potassium ion is surrounded by six nitrogen atoms at the vertices of a distorted octahedron. The complete assignment of parameter values with an estimated accuracy in feasible cases is:

$u_{Ag} = 1/6 \pm 0.002$; $u_K = 0.260 \pm 0.005$; $z_N = 0.167 \pm 0.005$;

$z_N = 0.109 \pm 0.005$; $x_N = 0.365$; $x_C = 0.295$; $y_N = y_C = 1/3$.

Probably x_N and x_C have maximum values while y_N and y_C have minimum values. Interatomic distances are found as follows:

Ag-N, 3.29 Å; $(K-N)_1$, 2.97 Å; $(K-N)_2$, 3.05 Å; $(K-N)_3$, 2.56 Å.

The last interatomic distance is smaller than might be anticipated, and certain possible variations of parameter values which would make it somewhat larger are discussed.

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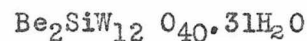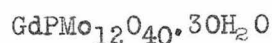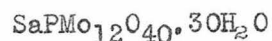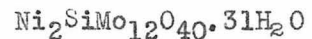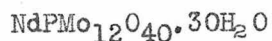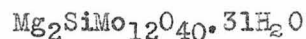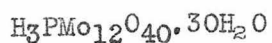
12. Same as Reference 11.

II. AN X-RAY INVESTIGATION OF THE 12-MOLYBDOPHOSPHATES
AND RELATED COMPOUNDS

INTRODUCTION

This X-ray investigation of the crystal structure of some
of the heteropolyacids and their salts represents an attempt to de-
termine the true molecular structure of these compounds. On account
of their exceedingly complex nature, however, the work described in
the following paragraphs has yielded only a quite limited class of
information.

The heteropolyacids such as 12-molybdophosphoric acid,
$H_3PMo_{12}O_{40} \cdot 30H_2O$, are treated at some length in various comprehen-
sive works on inorganic chemistry.[1] All of the considerations
here presented have to do with representatives of the so-called
12 class in which the number of molybdenum or tungsten atoms per
central atom (silicon, phosphorus, boron, etc.) is 12. Many other
compounds are known in which this ratio is less than 12, but this
figure is believed to represent the upper limit for stability.

Of this so-called saturated 12-class, the following com-
pounds have been subjected to an X-ray examination:

$H_3PMo_{12}O_{40} \cdot 30H_2O$ $Mg_2SiMo_{12}O_{40} \cdot 31H_2O$

$NdPMo_{12}O_{40} \cdot 30H_2O$ $Ni_2SiMo_{12}O_{40} \cdot 31H_2O$

$SaPMo_{12}O_{40} \cdot 30H_2O$

$GdPMo_{12}O_{40} \cdot 30H_2O$ $Be_2SiW_{12}O_{40} \cdot 31H_2O$

The above compounds have either been previously reported[2] or have
been shown during the course of this investigation to possess cubic
symmetry.

PREPARATION OF COMPOUNDS FOR STUDY

12-Molybdosilicic acid was prepared according to the directions of Rosenheim and Jaenicke,[3] and the other acids, obtained commercially, were Baker's CP grade. The various salts listed above were prepared by dissolving the calculated quantities of $(Mg, Ni, Be)CO_3$, $(Gd, Sa)Cl_3.6H_2O$, and Nd_2O_3 in solutions of the proper acid. The rare earth compounds were obtained thru the courtesy of Dr. Simon Freed of the University of California. All of the compounds investigated with X-rays crystallize as apparently regular octahedra, all sizes up to about 8 or 10 mm. on an edge being obtained in some cases. The compounds containing molybdenum possessed a characteristic yellow color.

Inasmuch as none of the crystals studied are at all stable in air, but upon exposure soon become covered with a layer of powdered material thru loss of water, and in addition are mostly unstable above 50°C, some difficulty was experienced in connection with the collection of the necessary data for this study. The three rare earth salts of molybdophosphoric acid had not been previously reported in the literature. They were identified as normal salts, and as crystallizing in the cubic system as outlined below.

For the identification of these compounds as the normal salts of the acids, the following rough partial analysis was performed. Crystals of the compound were removed from the saturated solution, and were dried more or less thoroly but as quickly as possible by pressing them between filter papers. A sample was weighed out quickly, and was then dissolved in distilled water. The rare earth ion was pre-

cipitated as oxalate by the addition of concentrated oxalic acid, and the mixture was warmed until the precipitate was coagulated. The solid was filtered off and washed first with warm oxalic acid solution, and finally with distilled water. After ignition in a porcelain crucible, the residue was weighed as M_2O_3. It was necessary to use small quantities of the compound, from 16-25 mg. of the oxide being obtained in each case. However, the final residue had the appearance characteristic of the pure rare earth oxide in each case. The percentages of rare earth calculated from experiment and from the formula $MPMo_{12}O_{40} \cdot 30H_2O$ are given in Table I.

TABLE I

The Rare Earth Content of Certain Salts of

Molybdophosphoric Acid

	Rare Earth Content		
	Nd	Sa	Gd
Experimental	5.35%	4.98%	5.73%
		5.13	
Theoretical	5.77	5.98	6.24

The experimental values are uniformly somewhat low, but the normal salt is indicated for each compound. The loss of from 1-3 mg. of the oxide as unprecipitated oxalate would account for the discrepancy in each case. Any solution adhering to the sample would cause an error in this direction also.

Upon heating a sample of the neodymium compound to constant weight in an oven at 105°, a loss of weight equivalent to about 20 H_2O per molecule was found. After further gentle heating to constant weight over a small open flame, a loss in weight equivalent

to 29.9 H_2O per molecule was obtained. It was assumed, therefore, that the correct formula for this and the two other closely related rare earth compounds is $MPMo_{12}O_{40} \cdot 3OH_2O$. In any event, two of three molecules of water in the formulas as written do not affect materially the considerations of this paper.

CRYSTALLOGRAPHIC EXAMINATION

Crystals of these rare earth compounds were mounted upon a goniometer used as a one-circle instrument with the edge, $[0\ 1\ \bar{1}]$, of an octahedral face vertical, and four measurements were taken from octahedral faces during rotation thru 360°. On account of the rapid deterioration of the crystal faces, signals were good only for about five minutes at most. During this period, however, repeated measurements from the same face usually gave values differing among themselves by less than three minutes. Three observations were taken for each face, and from the mean values the interfacial angles listed in Table II were obtained. The values for $GdPMo_{12}O_{40} \cdot 3OH_2O$ are for two different crystals, for each of which only three faces gave usable signals.

The data of Table II provide strong evidence that these compounds crystallize in the cubic system. This is further affirmed by the fact that the crystals appeared to be isotropic when examined with a polarizing microscope. Molybdophosphoric acid, reported as cubic, and crystallizing in small, quite perfect octahedra, was perhaps very weakly birefringent under a polarizing microscope, but the phenomenon was not at all marked.

TABLE II

Goniometric Data from Crystals of $MPMo_{12}O_{40} \cdot 30H_2O$
$[0\,1\,\bar{1}]$ Vertical

	Calculated for Cubic System	Observed for $NdPMo_{12}O_{40} \cdot 30H_2O$	Observed for $SaPMo_{12}O_{40} \cdot 30H_2O$	Observed for $GdPMo_{12}O_{40} \cdot 30H_2O$
$(111):(\bar{1}11)$	109°28'	109°25.5'	109°28'	109°27'
$(\bar{1}11):(\bar{1}\bar{1}1)$	70°32'	70°32'	70°31'	70°28.5'
$(1\bar{1}\bar{1}):(\bar{1}1\bar{1})$	109°28'	109°27.5'	109°29.5'	109°27.5'
$(1\bar{1}\bar{1}):(111)$	70°32'	70°35'	70°31.5'	70°29.5'

DETERMINATION OF THE UNIT CELL AND SPACE-GROUP

Laue photographs were prepared with the X-ray beam inclined at various small angles to the normal to (111) using general radiation from a tungsten anticathode tube operated at a peak voltage of about 55 kv. Oscillation photographs were prepared by reflecting MoK α radiation filtered thru zirconia from (111). On account of the instability of these crystals in air, it was necessary to protect them in some manner. Covering the specimen with a layer of paraffin or wax by dropping the molten material upon it almost completely spoiled the crystal. A coating of paraffin or Canada balsam could be left on a specimen by drenching it with a solution of one of these materials in benzene or xylene and allowing the solvent to evaporate (the heteropolyacids and their salts are generally very soluble in water, alcohol, ether, etc., so that the choice of solvents and protective material was quite limited), but the results were not good. It was found most satisfactory to stick the crystal to a cover glass with a film of optical wax, and then to cover it with vaseline. A crystal thus treated could be preserved in good condition for at least a week.

An additional difficulty arose because of the large absorption for X-rays of the tungsten and molybdenum atoms. Due to their ease of decomposition and softness, the crystals would not be ground conveniently to very thin plates, so that it was necessary to use very long exposures. This was especially true for compounds containing tungsten, for which only two or three really satisfactory photographs were obtained. Crystals of $Be_2SiW_{12}O_{40} \cdot 31H_2O$ seemed to be somewhat more imperfect in structure than were the crystals containing molybdenum.

In the considerations which follow, $NdPMo_{12}O_{40} \cdot 30H_2O$ will serve as the prototype for all of the compounds containing molybdenum, since the Laue and oscillation photographs obtained for any two members of this class were apparently indistinguishable. An example of such a Laue photograph is reproduced in Figure 1. It should be mentioned also that a crystal to plate distance of 7.5 cm. for the Laue photographs was demanded by the complexities of the pattern.

Making use of the Bragg equation, $n\lambda = 2d \sin\theta$, equatorial reflections on a (111) oscillation photograph of $NdPMo_{12}O_{40} \cdot 30H_2O$ lead to an observed spacing of $d(111)/n_1 = 13.3$ Å (see Table III). The smallest possible cubic unit is one with $a = 3 \cdot d(111)/n_1$, in which $n_1 = 1$, that is, $a = 23.1$ Å. All values of $n\lambda$ calculated on the basis of this unit for the reflections appearing upon two completely indexed Laue photographs were found to be above the short wave length limit, 0.24 Å, of the radiation employed. Data which include all reflections in the first-order for one of these photographs are given in Table IV, the extreme values of $\sin\theta$ and $n\lambda$ being listed for each form. For the two photographs, a total of more than 50 distinct forms reflected in the first order, with rather complex indices in most cases. Only those reflections for values of $n\lambda$ less than 0.48 Å need be purely first-order, of course.

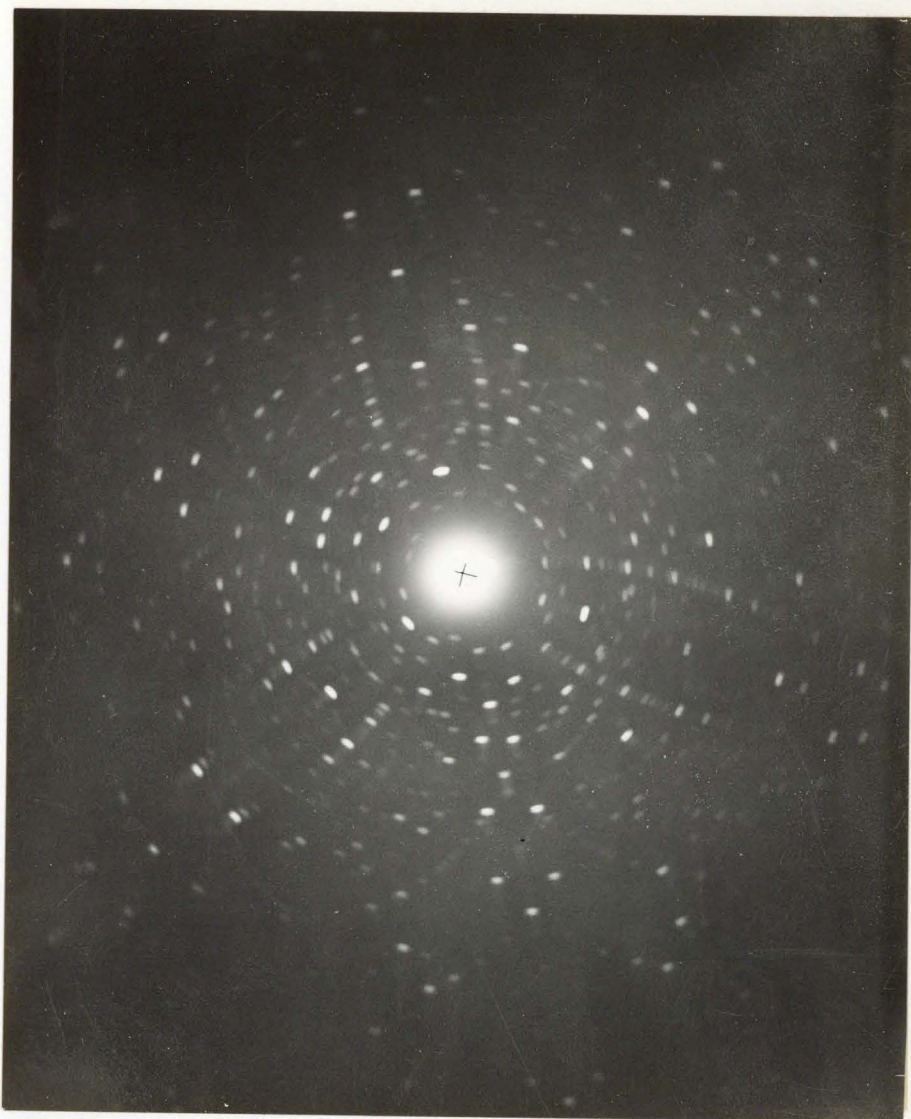Figure 1. Laue photograph of $NdPMo_{12}O_{40} \cdot 30H_2O$ taken with the X-ray beam nearly normal to an octahedral face.
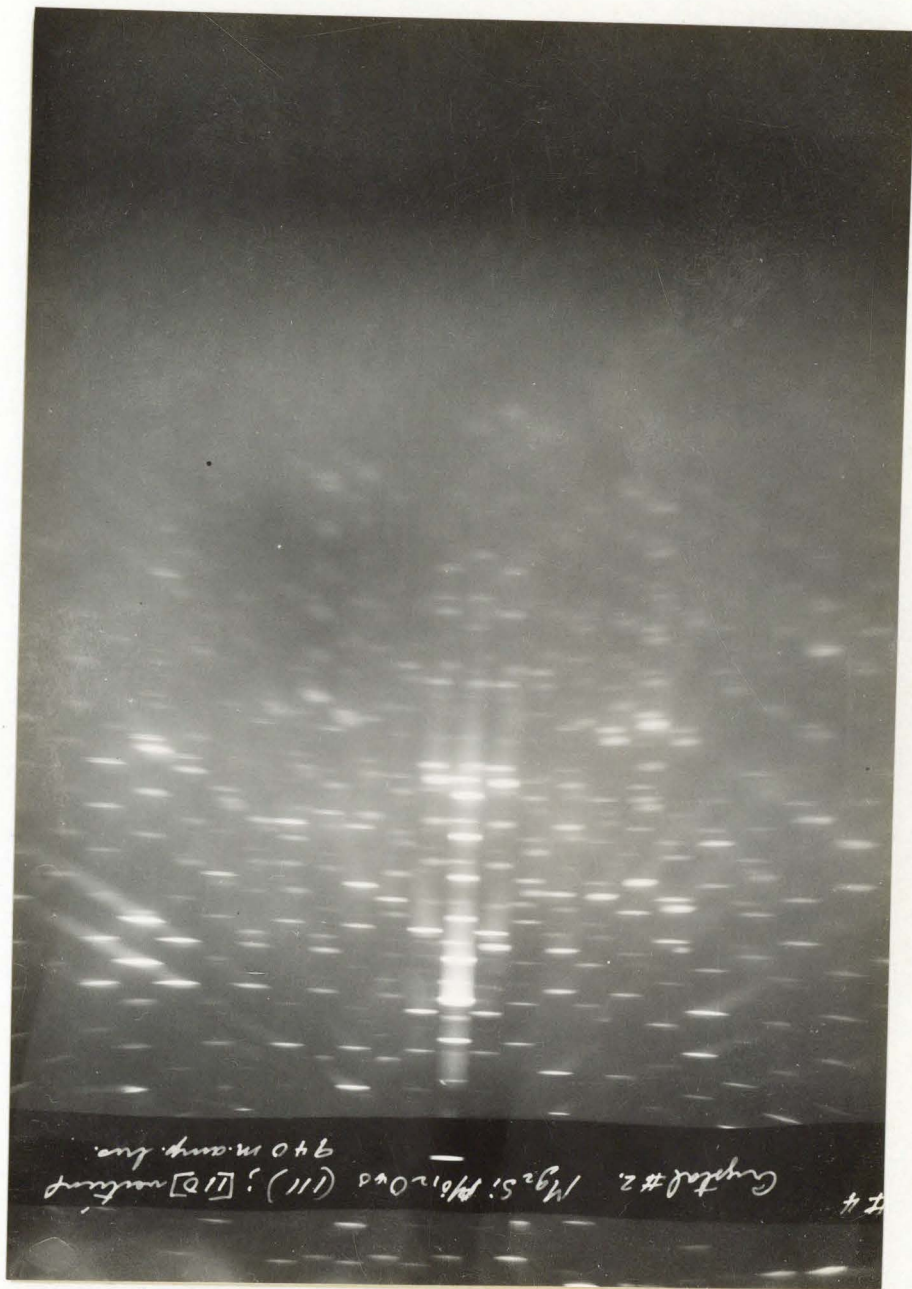
Figure 2. Oscillation photograph of $Mg_2SiMo_{12}O_{40} \cdot 30H_2O$ from (111) with 110 vertical.

TABLE III

Data from the Equator of a (111) Oscillation Photograph

of $NdPMo_{12}O_{40} \cdot 30H_2O$

Order from (111)	Line (Mo K)	Sin θ	d/n_1
$3n_1$	α	.07962	13.35 Å
$4n_1$	α_1	.10610	13.34
$5n_1$	α_1	.13298	13.31
$6n_1$	α_1	.15959	13.29
$7n_1$	α_1	.18638	13.29
$8n_1$	α_1	.21290	13.30
$9n_1$	α_1	.23930	13.31
		Average	13.31

TABLE IV

Data in the First-Order from a (111) Laue Photograph

of $NdPMo_{12}O_{40} \cdot 30H_2O$

(Pure first-order reflections for 0.24 Å $< n\lambda < 0.48$ Å)

Form $\{hk\ell\}$	Sin θ Min.	Max.	$n\lambda$ Min.	Max.
$7\bar{3}\bar{3}$	.051	.094	.29 Å	.53 Å
$51\bar{5}$	.056	.106	.36	.68
$13\cdot\bar{5}\cdot\bar{5}$	.097	.141	.30	.44
$13\cdot\bar{3}\cdot\bar{7}$	.094	.141	.29	.44
$13\cdot\bar{9}\cdot\bar{1}$	.097	.118	.28	.34
$\bar{9}55$	.072		.29	
$\bar{9}37$	.073		.28	
$\bar{9}19$	.072		.26	
$\bar{7}\bar{1}9$	.069	.076	.28	.31
$\bar{7}17$	.084		.39	
$\bar{7}35$	.062	.086	.31	.43
$\bar{3}59$	.076	.079	.29	.31
$\bar{5}\bar{1}7$	.073	.092	.39	.49
$3\cdot\bar{13}\cdot\bar{13}$	.106	.118	.26	.29
$33\bar{5}$	.066	.108	.46	.76
$9\cdot\bar{11}\cdot5$	.091	.132	.28	.40
$11\cdot\bar{11}\cdot3$	.105	.133	.31	.39
$11\cdot1\cdot\bar{9}$	.096	.146	.31	.47
$11\cdot\bar{1}\cdot\bar{7}$	.108	.158	.38	.55
$\bar{13}\cdot7\cdot9$	.118	.122	.31	.32
$759\bar{}$	.115	.140	.42	.52
$\bar{1}\cdot17\cdot\bar{11}$	.131	.169	.30	.38
$13\cdot5\cdot\bar{13}$	.126	.174	.31	.42
$11\cdot5\cdot\bar{11}$	.152	.157	.43	.44
$19\cdot\bar{19}\cdot9$	.180	.206	.29	.33
$9\cdot9\cdot\bar{13}$	.136	.178	.34	.45
$11\cdot11\cdot\bar{15}$	.164		.35	
$9\cdot7\cdot\bar{11}$	.158	.160	.46	.46
$13\cdot9\cdot\bar{15}$	.162	.206	.34	.43
$15\cdot3\cdot\bar{13}$	.119	.168	.27	.38
$13\cdot3\cdot\bar{11}$	.141	.181	.37	.48
$11\cdot9\cdot\bar{13}$	.185	.186	.44	.44
$13\cdot7\cdot\bar{13}$	.179		.42	
$17\cdot7\cdot\bar{15}$	.194	.200	.38	.39
$19\cdot9\cdot\bar{17}$	.204	.209	.35	.35
$15\cdot5\cdot\bar{13}$	.172	.221	.39	.50
$19\cdot5\cdot\bar{15}$	.184	.192	.34	.36
$19\cdot3\cdot\bar{13}$	.199	.215	.39	.43
$17\cdot1\cdot\bar{11}$	.174	.207	.39	.47
$\bar{11}\cdot11\cdot7$	.196	.220	.39	.44
$17\cdot\bar{1}\cdot9$	.196	.215	.47	.51
$13\cdot1\cdot\bar{9}$	.156	.171	.45	.50
$15\cdot\bar{1}\cdot9$	.139	.189	.36	.49
$\bar{1}\cdot19\cdot\bar{11}$	.173	.188	.36	.39

If 8 molecules of $NdPMo_{12}O_{40} \cdot 30H_2O$ be placed in a cubic unit with a = 23.1 Å, the calculated density is 2.68 g/ml, to be compared with the experimental value 2.62 $\pm$ 0.2 g/ml determined by the displacement method using benzene. In determining these densities, the crystals were dried in the manner previously described so that very accurate values are not to be anticipated. However, this cubic unit with a = 23.1 Å containing 8 molecules of the compound would seem to be well established.

In Table V, data are given for all of the compounds for which the size of the unit cell was determined in the manner already described. The unit is well established for the three rare earth salts of molybdophosphoric acid, and for $Mg_2SiMo_{12}O_{40} \cdot 31H_2O$. Only a photograph of rather small intensity was indexed for $H_3PMo_{12}O_{40} \cdot 30H_2O$ and none at all for $Ni_2SiMo_{12}O_{40} \cdot 31H_2O$, but a rather careful comparison of both Laue and oscillation photographs with those of the rare earth salts reveals nothing different. Hence the conclusions regarding size of unit and space-group may be expected to apply equally to all of the compounds just enumerated.

$Be_2SiW_{12}O_{40} \cdot 31H_2O$ is also included in Table V. The single Laue photograph of this compound which was indexed had about 36 forms reflecting in the first order with no value of $n\lambda$ falling below the short wave-length limit of 0.24 Å when calculated upon the basis of a unit with a = 23.3 Å. No particular accuracy can be claimed for the lattice constants given, so that it is possible and even probable that in the case of the three rare earth compounds, for instance, the indicated variation is not real.

TABLE V

Data Establishing the Size of the Unit Cell

Compound	Edge of Unit Å	Density, g/ml Calculated	Experimental
$NdPMo_{12}O_{40} \cdot 3OH_2O$	23.1	2.68	2.62
$GdPMo_{12}O_{40} \cdot 3OH_2O$	23.0	2.72	-
$SaPMo_{12}O_{40} \cdot 3OH_2O$	22.9	2.76	2.60
$H_3PMo_{12}O_{40} \cdot 3OH_2O$	23.3	2.45	2.52
$Mg_2SiMo_{12}O_{40} \cdot 31H_2O$	23.4	2.50	2.56
$Ni_2SiMo_{12}O_{40} \cdot 31H_2O$	23.2	2.63	-
$Be_2SiW_{12}O_{40} \cdot 31H_2O$	23.3	3.60	3.66

A unit with a $\approx$ 23 Å containing 8 molecules appears from Table V to be highly probable for these compounds. It should be mentioned, however, that some difficulty was encountered in connection with the appearance upon Laue photographs of quite a number of "anomalous" spots. Usually these were poorly shaped and never did their analogues in other zones appear even with entirely favorable conditions for reflection. Furthermore, spots in the same relative position did not appear upon photographs taken from other specimens of the same compound. In one case ($SaPMo_{12}O_{40} \cdot 3OH_2O$) a well-shaped but very weak spot appeared upon an otherwise excellent photograph. If it represented a real reflection, this spot would have eliminated the three-fold axis normal to (111). Upon taking a series of photographs with another crystal for which the planes of each of the three zones in turn were in favorable position to reflect, no such spot appeared, however. Because of the great complexity of the Laue pattern

and the presence of so many very weak reflections, it was more difficult than usual to arrive at a definite decision regarding the true nature of these spots, but it can now be asserted with confidence that they are to be disregarded as bogus. That is, the previous conclusions regarding the crystal symmetry and the size of the unit cell may be accepted as highly probable.

Laue photographs taken with the X-ray beam normal to (111) show a three-fold axis and three planes of symmetry for all of these compounds, so that the point-group symmetry is T_d, O, or O_h. Now reference to Table IV reveals no first-order reflections appearing except for h k ℓ all odd, as is required by a face-centered lattice. This was found to be the case for every Laue photograph which was indexed. Assuming, therefore, a face-centered lattice, the following space-groups are to be considered:[4]

T_d^2, T_d^5, O^3, O^4, O_h^5, O_h^6, O_h^7, O_h^8.

T_d^5, O_h^6, and O_h^8, with the same special criteria,[4] are eliminated by the presence of reflections with h = $\pm$ k in odd orders, for instance (111), (333), etc. on oscillation photographs, and many reflections in the first-order on Laue photographs (see Table IV). Of the five remaining space-groups, T_d^2, O^3, and O_h^5 are without special criteria, and that for O^4 was not investigated. However, O_h^7 does not permit reflection in the second-order for planes of the type $\{ok\ell\}$ with k even and ℓ odd.[4] Because of this fact, and since the face-centered lattice does not permit odd-order reflections except for hkℓ all odd, no Laue reflections for planes of this kind can occur at a value of nλ less than 0.96 Å, i.e., four times the short wave-length limit of 0.24 Å, if the structure be based upon O_h^7.

The absence of all reflections for $\{ok\ell\}$ with k even and ℓ odd in the range $0.48 \text{ Å} < n\lambda < 0.96 \text{ Å}$ is therefore strong evidence that O_h^7 is the correct space-group. The procedure adopted was to look for all reflections of this sort upon Laue photographs for which the X-ray beam was inclined at various angles to the normal to (111).

No reflection which would eliminate O_h^7 was found for any of the compounds listed in Table V, but the evidence for this space-group is not overwhelming. The data obtained for $NdPMo_{12}O_{40}.30H_2O$ are discussed in detail in the following paragraphs.

Table VI contains a partial list of observed absences in the second order for forms of the type $\{ok\ell\}$ with k even, ℓ odd in the case of $NdPMo_{12}O_{40}.30H_2O$. if two or more planes of a form were in position to reflect for values of $n\lambda$ between 0.48 and 0.96 Å, the maximum and minimum values for $\sin\theta$ and $n\lambda$ within this range are indicated in the table.

TABLE VI

Observed Absences on Laue Photographs of $NdPMo_{12}O_{40} \cdot 30H_2O$

as Required by O_h^7

Form $\{ok\ell\}$	Sin θ		$n\lambda$ Å	
$0\bar{2}3$	.068		.87	
$04\bar{3}$	.103	.065	.95	.60
$0\bar{4}5$	.116	.079	.83	.57
$06\bar{5}$	.130	.099	.81	.58
$0\bar{6}7$	.155	.100	.78	.50
$08\bar{7}$	.148		.64	
$0\bar{8}9$	.142		.54	
$0\bar{4}7$	.162	.123	.93	.71
$08\bar{5}$	.185	.130	.91	.64
$0 \cdot 10 \cdot \bar{7}$	.233	.166	.88	.62
$0 \cdot \bar{8} \cdot 11$	.215	.160	.73	.54
$0 \cdot \bar{6} \cdot 11$	.255	.130	.94	.48

With regard to the data of Table VI, it may be said that only $\{0\bar{2}3\}$ gave discernible reflections in the fourth-order, that is for a value of $n\lambda$ greater than 0.96 Å. However, the fourth-order of $\{0\bar{4}5\}$, that is $\{0\cdot\bar{16}\cdot20\}$, is already of greater complexity than any form observed to reflect in the first-order (see Table IV) excepting only $\{\bar{19}\cdot19\cdot\bar{9}\}$. It is not surprising, therefore, that only $\{0\bar{2}3\}$ from the list given in Table VI was observed to give any reflections at all. On a quite asymmetric (111) photograph, five of the six normally appearing planes of $\{0\bar{2}3\}$ were observed to reflect with rather strong intensity for values of $n\lambda$ equal to or greater than 1.4 Å. However, $(\bar{2}30)$ with $n\lambda = 0.87$ Å was definitely absent, although $0.87/2 = 0.435$ Å was an entirely favorable value of the wave length, both on account of high intensity in the incident beam, and because of large absorption of the scattered radiation by the photographic plate. The value of $\sin\theta$, 0.068, was also favorable, and the reflection was expected in a clear region of the plate (the plate to crystal distance was 7.5 cm, so that reflections at values of $\sin\theta$ greater than 0.04 were well beyond the blackened region around the central image). However, it is entirely possible that the structure factor for $\{0\bar{2}3\}$ is nearly zero for second-order reflections. It may be mentioned also that on all photographs $\{0\bar{9}5\}$ and $\{0\bar{7}5\}$, which are of comparable complexity with the forms of Table VI, were observed to reflect in the second-order with medium to fairly strong intensities at values of $n\lambda$ greater than about 0.6 Å.

The material of the preceding paragraphs represents quite convincing evidence for selecting O_h^7 as the space-group of $NdPMo_{12}O_{40} \cdot 30H_2O$. For the other compounds containing molybdenum of Table V, the evidence for O_h^7 is quite similar except that no other photograph was sufficiently asymmetric to require a plane of $\{0\bar{2}3\}$ to reflect either in the second-order or not at all. As previously remarked, no photograph was indexed for $Ni_2SiMo_{12}O_{40} \cdot 31H_2O$ and a rather weak one for $H_3PMo_{12}O_{40} \cdot 30H_2O$, but for the three other compounds at least half a dozen and usually more absences of the type required by O_h^7 were observed. The apparent identity of the patterns observed on photographs taken under analogous circumstances of different compounds of this group supports strongly the view that O_h^7 is the common space-group for all of them.

The data for the single Laue photograph of $Be_2SiW_{12}O_{40} \cdot 31H_2O$ which was indexed indicates that O_h^7 is also the space-group in this case. As the photograph was not markedly asymmetric, only four forms of the type $\{ok\ell\}$ with k even, ℓ odd were in position to reflect in the second-order, and these, of course, did not appear. It may be mentioned, however, that $\{\bar{5}90\}$, $\{\bar{7}11\bar{0}\}$, and $\{\bar{5}70\}$ were all observed in the second-order on this photograph.

DISCUSSION OF POSSIBLE STRUCTURES

Not much progress was made toward finding the actual structure of these compounds, but a brief discussion of some of the possibilities may be of interest. O_h^7 furnishes sets of 8, 16, 32, 48, 96, and 192 equivalent positions.[5] The unit cell of $NdPMo_{12}O_{40} \cdot 30H_2O$, for instance, contains 8 molecules, so that there must be placed: 8 Nd, 8 P, 96 Mo, and at least 320 O and probably more as O and as OH. The properties of these compounds make it highly probable that a large part of the water content is present as water of constitution, so that OH groups may be expected to occupy definite positions in the structure. In any event not all of the oxygen can be in crystallographically equivalent positions. Unless the molybdenum in this compound is of three kinds crystallographically, it must occupy either 96 f with one or 96 e with two parameters. It would be possible, perhaps, to put molybdenum into one of the two sets of equivalent positions, and fix the parameter value or values with the use of reflections appearing at large values of $\sin \theta$. Such reflections, at least if they were strong, probably could be regarded as being due largely to molybdenum, although with these compounds the relatively large number of light atoms might still cause complications. Wide-angle reflections of appreciable intensity did not appear, however, even upon oscillation photographs with exposures of more than 1000 m. amp. hrs. For instance, (999) with $\sin \theta = 0.24$ was the last order of (111) to appear with fair intensity. The alternative to this procedure is to compare a complete set of intensities calculated for a predicted structure with those actually observed.

Pauling[6] has predicted a molecular structure for the members of the saturated 12-class of compounds which in itself is able to correlate satisfactorily a considerable mass of chemical and crystallographic data. Hence, it was considered worth while to endeavor to account for observed X-ray intensity relations by putting these complex ions into the unit cell in a manner determined by O_h^7. The point-group symmetry of the predicted structure for these complex ions is T_d. Now this is just the minimum molecular symmetry required by O_h^7 for 8 molecules in the unit cell. It is, therefore, possible to place 8 such ions within a unit cell in accordance with the requirements of O_h^7.

The predicted complex ion has a formula $\left[PO_4 \cdot Mo_{12}O_{18}(OH)_{36}\right]^{\equiv}$, and is of the general form of a regular tetrahedron with the vertices lopped off by planes perpendicular to the three-fold axes. The parameter values in Ångstrom units for a single complex ion with P or Si at the origin are given by Pauling.[6] Hence it is merely necessary to divide these by a, 23.1 Å, in order to obtain the parameter values to be used in calculating intensities for the unit cell. If this is done, there is obtained:[5] 8 P in 8 f; 32 O_I in 32 b with u = 0.040; 96 O_{II} in 96 e with v = 0.125, w = 0.032; 48 O_{III} in 48 c with t = 0.146; 96 O_{IV} in 96 e with v = 0.110, w = 0.208; 192 O_{IV} in the general position with x = 0.001, y = 0.229, z = 0.082; 96 Mo in 96 e with v = 0.584, w = 0.173 (the notation is that of Pauling.[6]). The oxygen marked O_{IV} have hydrogen associated with them to give hydroxyl groups. For a complete description of the predicted structures for these complex ions, including a number of illuminating sketches, the reader is referred to the original paper by Pauling.[6]

Using the values of the parameters just given means that
the tetrahedral complex ions with centers at 0 0 0 and 1/4 1/4 1/4
point toward each other, whereas a change thruout to negative values
means that these tetrahedra are base to base. Both of these possi-
bilities must be considered. In making actual intensity calculations
also, it was convenient to transform the origin to the center of sym-
metry at 1/8 1/8 1/8. It was found that with either positive or
negative values of the parameters, the calculated intensities for
(nnn) did not agree with observation. For instance, although (444)
reflected much more strongly than (333) or (222), it had the smallest
calculated structure factor of the three. This structure, therefore,
cannot be correct with the assigned parameter values.

However the predicted structure has ten parameters including
two for the relatively heavy and therefore strongly scattering molyb-
denum atoms. Hence it is evident that the calculated structure factors
may be considerably changed by introducing rather small variations in
the parameter values. The manner in which this should be done is not
at all obvious, however. For this reason, it was considered advisable
to try to fit the complex ions into the unit cell, and to see what
changes in parameter values would be necessary in order to obtain
generally satisfactory interatomic distances.

If the positive values of the parameters be used, the smallest
interatomic distance between atoms of two different ions is the O-O
separation of two oxygen atoms in the 96 O_{IV} positions. The distance
between O in uvu or vuu and O in 1/4 - u, 1/4 - u, 1/4 - v, for which
u and v have the values previously given, is calculated to be 2.27 Å.

If the negative values of the parameters be used, the smallest separation between two ions is that for two oxygen atoms in the 192 O_{IV} positions. The distance between O in $yz\bar{x}$ and O in $x + 1/4$, $1/4 - y$, $1/4 - z$ is calculated to be 2.18 Å. Now the minimum O-O separation for such a case as this should be about 2.70 Å, so that the values found are definitely unsatisfactory. All other interatomic distances are, however, fully as large as they need to be, and it seems quite probable that the complex ions could be distorted in a way that would remove the difficulty just mentioned. Some attempts to do this resulted in an improvement of only a little more than 0.1 Å for the second case, that is, with the tetrahedral ions at 000 and 1/4 1/4 1/4 base to base. It is again very difficult to decide which of the many factors should be varied, and for each such change the calculations are quite laborious. It is quite probable too that the molybdenum-oxygen bond is not purely ionic, so that it is possible that a smaller separation should be assumed in this case. In any event, it still seems not improbable that these complex ions could be fitted satisfactorily into the unit cell, especially in view of the large number of variable factors and the fact that in the one case but one and in the other case only two contacts between ions are unsatisfactory. It would still be necessary to test the structure for agreement between calculated and observed intensities, of course, if the results were to be given any great significance.

SUMMARY

Cubic crystals of some of the 12-molybdophosphates and related compounds, for instance, $NdPMo_{12}O_{40} \cdot 30H_2O$, were subjected to an X-ray examination. The normal neodymium, samarium, and gadolinium salts of 12-molybdophosphoric acid, not previously reported in the literature, were prepared and shown by goniometric measurements to crystallize in the cubic system. Laue and oscillation photographs lead to unit cells containing 8 molecules with a $\approx$ 23 Å. The space-group is probably O_h^7 for all of the compounds studied.

The possibility of fitting 8 complex ions with the molecular structure predicted by Pauling[6] within the unit cell is discussed. With the parameter values as assigned by Pauling, not even rough agreement was found between calculated and observed intensities for reflections appearing upon oscillation photographs. It was found also that either one or two ϕ to O distances between adjacent ions, depending upon whether positive or negative parameter values were used, would be too small. However, it is not improbable that variations in the 10 parameters (2 of which belong to molybdenum) may enter in such a way as to account for both of these discrepancies. The point-group symmetry of the predicted structure for the complex ions is T_d, and this is just the minimum molecular symmetry permitted by O_h^7 with 8 molecules in the unit cell.

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III. The Crystal Structure of Cadmium Chloride

Introduction.

With the aid of data obtained from a reproduction of a Laue photograph published by Bruni and Ferrari[1] it was shown by Pauling[2] that the unit of structure of $CdCl_2$ and some other bivalent chlorides is a rhombohedron with $\alpha = 36°40'$ and $a = 6.35$ Å, about, containing $1\ CdCl_2$, Cd at 000, $2\ Cl$ at $u\,u\,u$, $\bar{u}\,\bar{u}\,\bar{u}$. The parameter value was not determined from the intensities of the reflections; it was pointed out, however, that the value $u = \frac{1}{4}$ leads to a reasonable structure. We have now made a study of crystals of $CdCl_2$ with the use of Laue and oscillation photographs, leading to the unambiguous deduction of the structure previously suggested and evaluation of the parameter as $u = 0.25 \pm 0.04$.

The Determination of the Atomic Arrangement.

Crystals of $CdCl_2$ were cleaved out of a mass obtained by heating NH_4CdCl_3 in a current of dry HCl in a porcelain crucible. Data from oscillation photographs of molybdenum K-radiation filtered through zirconia, given in Tables I and II, lead to a hexagonal unit with $a = 2.22$ Å and $c = 5.82$ Å. On assigning indices to the spots on a Laue photograph taken with the radiation from a tungsten tube operated at a peak voltage of 54 kv. on the basis of this unit, it was found that many spots led to values of $n\lambda$ as low as 0.09 Å, nearly one-third of the short wave-length limit $(0.24$ Å$)$ of X-rays present in the spectrum. For example, the spot assigned indices $(\bar{5}1.1)$ was found to have $n\lambda = 0.09$ Å. This unit is accordingly ruled out. The smallest hexagonal unit accounting for the observed reflections is obtained by tripling c and rotating through 30°. This unit, with $a = 3.85$ Å and $c = 17.46$ Å, contains $3\ CdCl_2$, corresponding to a calculated diensity of 4.05 g/cm³, in good agreement with the directly determined value[3] 4.047 g/cm³.

1) G. Bruni and A. Ferrari, Atti Lincei Rend. **2**, 457. 1925; **4**, 10. 1926.

2) Linus Pauling, Pr. Nat. Acad. Washington **15**, 709. 1929.

3) International Critical Tables, **1**, 120.

Table I.

Spectral Data from (111) of Cadmium Chloride. [101] Vertical
Photograph No. 1.

Distance between layer lines,

$s=1$ to $s=\overline{1}$	μ	$\sin \mu$	d_{001}	$d/\sqrt{3}$
3.75 cm.	$10°37'$	0.1842	3.85 Å	2.22

The observed reflections are all accounted for by the corresponding
rhombohedral unit, which has

$$a = 6.23 \text{ Å}, \qquad \alpha = 36°02',$$

and contains 1 $CdCl_2$. All indices used in this paper are referred to
the axes of this unit.

A Laue photograph taken with the incident beam normal to (111)
showed a three-fold axis and three symmetry planes, requiring that
the point group of the crystal be C_{3v}, D_3, or D_{3d}. The only space
groups isomorphous with one of these and based on a rhombohedral
lattice are C_{3v}^5, C_{3v}^6, D_3^7, D_{3d}^5 and D_{3d}^6. Of these C_{3v}^6 and D_{3d}^6 provide
no position for 1 Cd. The non-identical atomic arrangements given by
the others are

I. Cd at $u\,u\,u$, Cl at $v\,v\,v$, Cl at $w\,w\,w$, C_{3v}^5;

II. Cd at 0 0 0, 2 Cl at $u\,u\,u$, $\bar{u}\,\bar{u}\,\bar{u}$, D_3^7 and D_{3d}^5.

We shall not consider I., as the discussion of two parameters would be
very laborious, and II. is found to lead to a satisfactory structure.

The value of the parameter u in II. can be determined with the
use of only qualitative assumptions regarding relative reflecting powers.
The structure factor for reflection in the nth order from a plane (hkl) is

$$S_{hkl,n} = \overline{Cd} + 2\,\overline{Cl} \cos 2\pi n\,(h + k + l)\,u. \qquad (1)$$

The relative reflecting powers of Cd und Cl can be taken as roughly
proportional to the atomic numbers, 48 and 17, so that Equation 1
leads to a set of cosine curves which do not cut the u-axis. The factors
influencing the intensities of reflection, aside from the structure factor,
are such as to cause the intensity to fall off as the effective interplanar
distance d/n decreases, so that if a plane is observed to reflect more
strongly than another with larger d/n, its structure factor S must be
the larger. The observed intensities of reflection in five orders from
(111) are given in Table II, and curves of S as a function of u are
shown in Fig. 1. It is seen that the intensity inequalities $(444) > (222)$,
$(333) > (222)$ and $(555) > (222)$ limit $3u$ to the regions 0.20—0.29,

0.71—0.80 and 1.20—1.29, or u to 0.067—0.097, 0.237—0.267 and 0.40—0.43. The observed intensity relation $(23\bar{1}) > (1\bar{1}3)$ for reflections on the Laue photograph (Table III) rules out the region 0.40—0.43, and that $(2\bar{1}2) \gg (2\bar{1}1)$ rules out the region 0.067—0.097, so that u can be given the value 0.25 ± 0.01. A comparison of the observed intensities and the structure factors calculated for this value of u is made in Tables II and III.
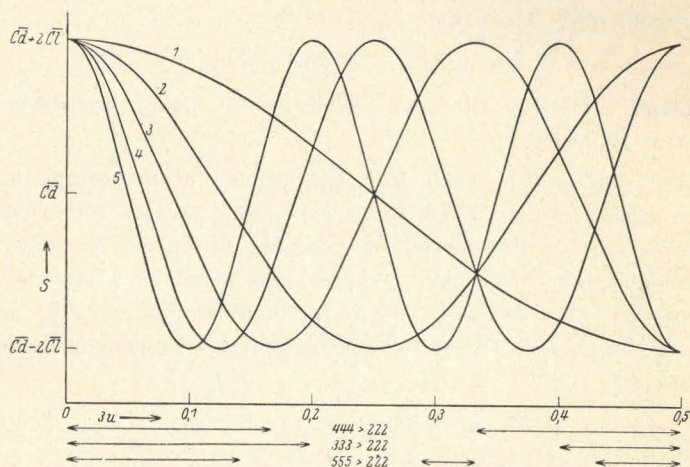

Fig. 1. Structure factor curves for cadmium chloride. The curves are symmetrical about $3\,u = 0.5$ so that the part shown is sufficient to obtain all possible ranges for u. Also, if u is substituted for $3\,u$ in the figure, the curves shown may be used to eliminate the regions 0.40—0.43 and 0.067—0.097 as possible values for u.

Table II.

Spectral Data from (111) of Cadmium Chloride.
Photograph No. 2.

Order	Line	Measured Distance	2θ	d_{111}	Estimated Intensity	S for $u = 0.25$
1	$MoK\alpha$	1.222 cm.	7.04	5.81	strong	$\overline{Cd}$
2	α	2.444	14.00	5.81	weak	$\overline{Cd} - 2\,\overline{Cl}$
3	α_1	3.670	21.05	5.82	medium	$\overline{Cd}$
3	α_2	3.701	21.20	5.80		
4	α_1	4.911	28.15	5.84	strong	$\overline{Cd} + 2\,\overline{Cl}$
4	α_2	4.948	28.40	5.82		
5	α_1	6.170	35.40	5.83	medium	$\overline{Cd}$
5	α_2	6.213	35.60	5.82	weak	

Table III.

Data for Intensity Comparisons from Laue Photograph No. 1.

$\{hkl\}$	$h+k+l$	d_{hkl}	$n\lambda$	Estimated Intensity	S for $u=0.25$
$1\bar{1}3$	3	0.948 Å	0.36 Å	0.3	$\overline{Cd}$
$23\bar{1}$	4	0.905	0.36	1.0	$\overline{Cd} + 2\,\overline{Cl}$
$2\bar{1}1$	2	1.245	0.41	0.3	$\overline{Cd} - 2\,\overline{Cl}$
$2\bar{1}2$	3	1.09	0.41	1.2	$\overline{Cd}$

Description of the Structure.

The structure found for cadmium chloride is represented in Fig. 2. It is a layer structure closely related to that of cadmium iodide. Each cation is surrounded by six chloride ions at the corners of a nearly regular octahedron, six edges of which are shared with other octahedra to form a complete octahedral layer. In the cadmium iodide structure[1] these layers are superimposed in such a way that each cation is directly above a cation in the layer below, whereas in the cadmium chloride structure each cation is directly above an anion in the layer below, and below an anion in the layer above. These two structures can be formally represented in the following way. Let A represent a layer of atoms with $X=0$, $Y=0$, X and Y being coordinates relative to axes 120° apart, B a layer with $X=\frac{1}{3}$, $Y=\frac{2}{3}$, and C a layer with $X=\frac{2}{3}$, $Y=\frac{1}{3}$. A, B, and C then represent close-packed spheres in a plane. The cadmium chloride and cadmium iodide structures then correspond to the following sequences of layers along [0001]:
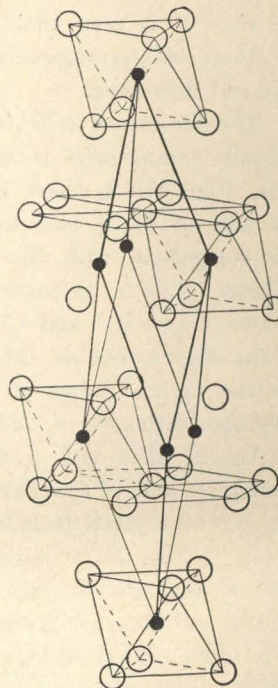

Fig. 2.

Fig. 2. The structures of cadmium chloride and other bivalent chlorides. Large open circles represent chloride ions, small closed circles cadmium ions. Heavy lines mark the rhombohedral unit of structure, and light lines the coordinated octahedron formed by six chloride ions about each cadmium ion.

1) Richard M. Bozorth, J. Am. chem. Soc. **44**, 2232. 1922.

Cadmium Chloride Structure			Cadmium Iodide Structure		
Cl at	A		I at	A	
Cd at	B		Cd at	B	
Cl at	C		I at	C	
Cl at	B		I at	A	
Cd at	C		Cd at	B	
Cl at	A		I at	C	
Cl at	C		I at	A	
Cd at	A		Cd at	B	
Cl at	B		I at	C	
Cl at	A		I at	A	
Cl at	B		Cd at	B	
Cl at	C		I at	C	

Thus it is seen that the difference in lattice and unit of structure for these two arrangements does not signify the existence of an essential physical difference.

The succession ACB ACB for Cl layers alone shows that the cadmium chloride arrangement is based on cubic close-packing of the large chlorine ions, from which there is indeed little distortion. The dimensions of the unit of $CdCl_2$ lead to Cl—Cl distances of 3.85 and 3.76 Å, which are compatible with the crystal radius of Cl^-, 1.81 Å. The Cd—Cl distance, 2.66 Å, is somewhat smaller than the sum of the radii calculated[1]) for Cd^{++} and Cl^-, 2.78 Å. This decrease is to be attributed to the deformation of the polarizable anion by the eighteen-shell cation; for the crystal radius of Cd^{++} leads to good agreement with observed interionic distances in CdF_2 and CdO.

Values of a and α calculated from published date of Bruni and Ferrari[2]) and of Ferrari, Celeri, and Giorgi[3]) may be given for a number of crystals isomorphous with $CdCl_2$. There are included $MgCl_2$, $CoCl_2$, $NiCl_2$, $FeCl_2$ with $\alpha = 33°33'$ and $a = 6.22$, 6.14, 6.13, and 6.20 Å, respectively; also $MnCl_2$ with $\alpha = 34°35'$ and $a = 6.20$ Å. Bruni and Ferrari have reported that $ZnCl_2$ shows the $MgCl_2$ structure, and Ferrari and Giorgi[4]) have reported a similar conclusion for $CdBr_2$. Finally Goldschmidt[5]) has reported that unpublished powder

1) Linus Pauling, J. Am. chem. Soc. 49, 765. 1927.
2) G. Bruni and A. Ferrari, Atti Lincei Rend. 2, 457. 1925; 4, 10. 1926.
3) Ferrari, Celeri, and Giorgi, Atti Lincei Rend. 9, 782. 1929.
4) Ferrari and Giorgi, Atti Lincei Rend. 9, 1134. 1929; 10, 522. 1929.
5) V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente VIII, p. 147.

photographic data obtained by Oftedal show that $RuCl_2$, $RhCl_2$, $IrCl_2$, $PtCl_2$, and $PdCl_2$ have a structure similar to that of $NiCl_2$.

A number of examples of crystals having the cadmium iodide structure may also be cited. Ferrari and Giorgi[1] place CoI_2, FeI_2, MnI_2, PbI_2, $CoBr_2$, $FeBr_2$, $MgBr_2$ and $MnBr_2$ in this category. Aminoff[2] found a similar structure for pyrochroite, $Mn(OH)_2$, and other hydroxides of this type are also known to crystallize similarly.

In general it is to be anticipated that the CdI_2 structure will be stable for compounds of the type MX_2 in which M has a coordination number of six and X has a large dipole moment, either permanent, as with the OH^- ion, or induced, as with the highly polarizable ions I^- and Br^-. The $CdCl_2$ structure is to be anticipated for compounds of this type in which M fulfills the same requirements as above, but in which X has a relatively small dipole moment, as with the Cl^- ion.

Summary.

With the aid of data obtained from Laue and oscillation photographs, it is shown that the unit of structure for $CdCl_2$ is a rhombohedron with $\alpha = 36°02'$ and $a = 6.23$ Å, containing 1 $CdCl_2$, Cd at 000, 2 Cl at $u\,u\,u$, $\bar{u}\,\bar{u}\,\bar{u}$, with $u = 0.25 \pm 0.01$. A layer structure along $[0001]$, closely related to that of CdI_2, is found for $CdCl_2$, the Cl^- ions being in approximate cubic close packing. $MgCl_2$, $CoCl_2$, $NiCl_2$, $FeCl_2$, $MnCl_2$, $RuCl_2$, $RbCl_2$, $IrCl_2$, $PtCl_2$, $PdCl_2$, and $CdBr_2$ are representatives of the $CdCl_2$ structure; CoI_2, FeI_2, MnI_2, PbI_2, $CoBr_2$, $FeBr_2$, $MgBr_2$, $MnBr_2$, and $Mn(OH)_2$ of the CdI_2 structure.

1) Ferrari and Giorgi, Atti Lincei Rend. 9, 1134. 1929; 10, 522. 1929.
2) Aminoff, Z. Krist. 56, 127. 1921.