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THE CRYSTAL STRUCTURE OF MAGNESIUM PLATINOCYANIDE HEPTAHYDRATE

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ABSTRACT

Positions of the Mg and Pt atoms in crystals of $MgPt(CN)_4 \cdot 7H_2O$. These have been definitely determined by means of x-ray oscillating-crystal photographs and Laue photographs, using the theory of space-groups. Because the other atoms are too light in comparison with the metal atoms, especially Pt, their positions could not be determined. The Pt atoms are located at 0 0 0 and $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, the Mg atoms at $0\;0\;\frac{1}{2}$ and $\frac{1}{2}\,\frac{1}{2}\;0$, in a tetragonal unit of structure 14.6A×14.6A×3.13A. Two units of structure are shown in the figure. The peculiar *optical properties* are believed to be associated with the unusual arrangement of the heavier atoms in widely spaced rows parallel to the tetragonal axis. In these rows Mg atoms alternate with Pt atoms, and the distance between any two adjacent atom-centers is 1.57A. The shortest distance between rows, however, is 10.3A, 6.6 times the distance between atoms in the same row. The *atomic radii* of Mg and Pt as determined by Bragg from other crystal data do not agree with the observed distance between these atoms, the calculated value being 2.7A, the observed distance 1.57A. The observed distance, however, is consistent with that calculated by the method of Davey, who assumes that the radius of an ionized atom differs much from the radius of the same atom un-ionized, and that the radii of Cs^+ and I^- are substantially equal in crystals of CsI.

INTRODUCTION

TETRAGONAL crystals of $MgPt(CN)_4 \cdot 7H_2O$[1] are of special interest because of their peculiar optical properties[2] and resultant beautiful appearance. They are red by transmitted light, but by reflected light the prism faces are a brilliant metallic green and the ends of the prism, perpendicular to the tetragonal axis, have a violet

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[1] The water content is said to vary *continuously* from 8.1 H_2O to 6.8 H_2O, when exposed to dry air, the crystals being similar in this respect to the zeolites. See H. B. Buxhoevden and G. Tammann, Zeit. anorg. Chem., **15**, 319–327 (1897); and J. W. Mellor, Comprehensive Treatise of Inorganic and Theoretical Chemistry, Longmans Green and Co., **6**, 575–576 (1925).

[2] R. W. Wood, Physical Optics, 2nd Ed., The Macmillan Co., New York, 560–561 (1919). For a bibliography of this and other platinocyanides, and their crystallography, see Gmelin-Kraut, Handbuch der Chemie, Carl Winter, Heidelberg, **5** .3, 867–868 (1915).

tinge. They exhibit strong dichroic fluorescence; rays polarized in the direction of the tetragonal axis are yellow, those polarized perpendicular to the axis are red. Other hydrated salts containing the platinocyanide ion fluoresce when exposed to ultra-violet light or radium, but with these salts the fluorescence does not appear to be polarized as it is in the magnesium salt. None of these other salts is known to be tetragonal, being either orthorhombic or monoclinic.

The crystals have been examined crystallographically by Lang,[3] who observed the forms $\{100\}$, $\{001\}$ and $\{111\}$, and found the axial ratio $c/a=0.6103$.

The determination of the crystal structure was undertaken at the suggestion of H. E. Ives of these laboratories, in the hope that it might furnish some suggestion for an explanation of the optical behavior. The crystals were prepared by slow evaporation of an aqueous solution. X-ray data were obtained from oscillating-crystal photographs and Laue photographs.

THE UNIT OF STRUCTURE

Molybdenum K–radiation was reflected onto a photographic plate from (100)′ and (001)′ faces (primed crystallographic indices are those according to Lang[3]) of an oscillating crystal, using a calcite crystal for comparison. The sines of the grazing angles θ for reflection are given in Table I. The wave-length of the $K\alpha_1$ line is taken to be 0.7075A, and the grating space of calcite 3.029A.[4]

TABLE I

Oscillating-crystal data, using Mo $K\alpha_1$ radiation, $\lambda=0.7075A$

(*hkl*) Old	(*hkl*) New	sin θ	(*hkl*) Old	(*hkl*) New	sin θ
(100)′	(110)	0.034	(001)′	(001)	0.226
		0.0686			
		0.1028			
		0.1369			
		0.1711			
		0.2054			

If that reflection from each face which occurs at the smallest angle is considered to be in the first order, the dimensions of the corresponding unit of structure are $10.3A\times10.3A\times1.57A$. However, when the content of this unit is calculated from the density, directly measured as 2.39 g/cm^3, it is found to be only 1/2 molecule of $MgPt(CN)_4\cdot7H_2O$.

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[3] V.v. Lang. Sitz. Ber. Akad. Wiss. Wien, **111** .2a, 1161 (1902).

[4] A. H. Compton, H. N. Beets and O. K. De Foe, Phys. Rev. (2) **25,** 625–629 (1925).

Analysis of Laue photographs (tungsten target x-ray tube) taken with the beam perpendicular to the (001)′ face and perpendicular to the (100)′ face showed that the unit of structure must be enlarged to 14.6A×14.6A×3.13A, containing two molecules. The faces originally designated (100)′, (001)′ and (111)′ by the crystallographers now become (110), (001) and (041), respectively. Hereafter, all indices will be referred to the new unit just described, containing two molecules.

In analyzing the Laue photographs, spots were projected onto a gnomonic net, and the wave-lengths calculated according to the equation

$$n\lambda = 2d_{100}\,(h^2 + k^2 + l^2a^2/c^2)^{-1/2}\sin\theta$$

where λ is the wave-length of the x-rays, $d_{100} = 14.6$A, $c/a = d_{001}/d_{100}$, $d_{001} = 3.13$A, and h, k and l are the indices of the reflecting plane. The smallest value of $n\lambda$ calculated for any spot was found to be 0.25A, a value consistent with the voltage across the tube, therefore reflections for which the value of $n\lambda$ lay between 0.25 and 0.50A were considered to be first order reflections only. For all planes which reflected in the first order, $h+k+l$ was an even number, consequently the structure is built on a body-centered lattice. Planes for which $h+k+l$ was odd were considered to reflect only in the second order when $n\lambda$ lay between 0.50 and 1.00A.

THE SPACE-GROUP AND THE ARRANGEMENT OF THE ATOMS

All types of forms, that is, forms whose indices represented all combinations of odd and even indices (including forms $\{001\}$, $\{0kl\}$, $\{hk0\}$, $\{h \cdot h \cdot 2p+1\}$ and $\{h \cdot h \cdot 4p\}$, where p is any integer) reflected in either the first or second order depending *only* on whether $h+k+l$ was an even or an odd number. Furthermore, the Laue photograph taken with the x-ray beam perpendicular to the (001) planes showed a tetragonal axis of symmetry and four reflection planes; and the photograph for which the beam was perpendicular to the (110) planes showed a digonal axis of symmetry and two reflecting planes. The only space-groups[5] with which these data are consistent are D_{4h}^{17}, D_4^9, C_{4v}^9 and $D_{2d}^{11} = V_d^{11}$. Since there is no evidence that the crystals do not possess all the symmetry which it is possible for a tetragonal crystal to possess, the correct space-group is probably D_{4h}^{17}.

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[5] W. T. Astbury and Kathleen Yardley, Phil. Trans. Roy. Soc. Lond., **224A** 221–257 (1924).

The arrangements[6] predicted by all of these space-groups except C_{4v}^9 for two equivalent atoms in a unit of structure, are the same, namely:

$$(1)\ 0\,0\,0,\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2} \qquad (2)\ 0\,0\,\tfrac{1}{2},\ \tfrac{1}{2}\,\tfrac{1}{2}\,0.$$

The atom-positions predicted by C_{4v}^9 are:

$$(3)\ 0\,0\,\mathrm{u}\,;\ \tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2}+u\,;$$

where u may have values between zero and unity. In either case the Mg and Pt atoms are placed in lines parallel to the tetragonal axis, and each line is composed of both kinds of atoms arranged alternately. If the values of u are put equal to 0 and $\frac{1}{2}$, the positions of the atoms according to (3) are those specified in (1) and (2). Although the x-ray diffraction data do not rule out arrangement (3) for values of u which do not differ by $\frac{1}{2}$, physical considerations make it very probable that the atoms lie in the unique positions. If they were not so placed these atoms would be grouped in pairs, each Mg atom, for example, being nearer to one of its neighboring Pt atoms than to any other Pt atom, and the shortest distance between the centers of a Mg and a Pt atom would be less than 1.57A, a distance already considerably smaller than that to be expected on the basis of Bragg's values of atomic radii,[7] or of Wyckoff's more recent tabulation,[8] although not surprisingly small according to Davey's hypothesis.[9]

The x-ray data are of course quite powerless to place the C, N, O or H atoms, since the reflecting powers of these atoms are much less than those of the Mg and Pt atoms. Possible arrangements for C and N atoms include those placing them at the corners of squares of undetermined sizes which lie in planes parallel to (001) planes and which have Pt atoms at their centers. Such an arrangement is similar to that of the Cl atoms around the Pt atoms in K_2PtCl_4.[10]

Seven molecules of H_2O cannot be placed in a manner consistent with the apparent high symmetry. It is suggested as probable that the

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[6] R. W. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space-Groups, Carnegie Institution of Washington Publication No. 318, 78–99 (1922).

[7] W. L. Bragg, Phil. Mag. (6) **40**, 169–189 (1920). The radius assigned to Mg is 1.42A. The radius of Pt is not given in this article but may be calculated from more recent data [Pt to Cl, 2.33A in K_2PtCl_4, R. G. Dickinson, J. Am. Chem. Soc. **44**, 2409 (1922)] using Bragg's radius for Cl, 1.05A. This gives for Pt the radius 1.28A. The distance Mg–Pt from these data is 2.7A, a value to be compared with 1.6A, the distance Mg–Pt here found by experiment in $MgPt(CN)_4 \cdot 7H_2O$.

[8] R. W. G. Wyckoff, Proc. Nat. Acad. Sci., **9**, 33–38 (1923).

[9] W. P. Davey, Gen. Elect. Rev., **29**, 274–287 (1926).

[10] R. G. Dickinson, loc. cit. 7.

highest observed water content,[1] corresponding to $MgPt(CN)_4 \cdot 8H_2O$, is that characteristic of perfect crystals. The 16 oxygen atoms, and also the 32 hydrogen atoms, can then be placed in equivalent positions according to arrangements derived from the space-group D_{4h}^{17}, the only one of the possible space-groups listed above which will permit 32 atoms to be arranged in equivalent positions.

Data from one of the Laue photographs are given in Table II, where d/n and λ are expressed in A, and I is the estimated photographic intensity of the spot. In this table are included all planes having $d/n > 1.00$A which were inclined to the x-ray beam so that they could have reflected any wave-lengths between 0.25 and 0.50A.

TABLE II

Laue photographic data for $MgPt(CN)_4 \cdot 7H_2O$. *W radiation incident normally upon (110) planes*

$n^*(hkl)$	d/n	I	λ	$n(hkl)$	d/n	I	λ
$(\bar{3}41)$	2.13A	5	0.44A	$(\bar{7}.12.1)$	0.99A	0.4	0.47A
$(\bar{4}51)$	1.83	2	.33	(053)	.99	.5	.47
$(\bar{5}61)$	1.60	0.3	.25	$2(\bar{3}51)$	.97	.3	.37
(112)	1.56	4	.46	$(\bar{1}63)$	.96	.5	.45
$(\bar{1}32)$	1.49	3	.42	$(\bar{2}73)$	.93	.4	.42
$2(\bar{3}40)$	1.45	1	.42	$(\bar{8}.13.1)$	.91	.3	.40
$(\bar{3}52)$	1.33	0.7	.34	$(\bar{7}.11.2)$	.91	.2	.32
$(\bar{7}90)$	1.27	.6	.32	$2(\bar{4}70)$	.90	.2	.47
$(\bar{6}91)$	1.23	.8	.44	$(\bar{3}83)$	.89	.3	.38
$(\bar{5}72)$	1.15	.1	.25	$(\bar{4}93)$	.85	.2	.35
$2(\bar{4}50)$	1.13	.1	.25	$2(\bar{4}61)$	.85	.1	.28
$2(\bar{2}41)$	1.13	.3	.49	$(\bar{9}.14.1)$	.84	.2	.34
$(\bar{7}.11.0)$	1.11	.4	.48	$(\bar{7}.13.2)$	.83	.3	.40
$(\bar{7}.10.1)$	1.11	.4	.36	(334)	.77	.1	.34
$(\bar{5}92)$	1.05	.5	.42	(354)	.75	.1	.44
(123)	1.04	.3	.31	(174)	.73	.1	.42
(233)	1.01	.3	.50	$(15.\bar{9}.2)$	.73	.05	.32
$(\bar{8}.11.1)$	1.01	.3	.30	$(\bar{1}94)$	.71	.1	.39
(143)	1.00	.3	.50	$(\bar{3}.11.4)$	.67	.1	.35

* $n=1$ unless otherwise stated.

DISCUSSION OF THE RESULTS

(a) *Optical properties.* As mentioned in the introduction, the fluorescent light is different in character depending on whether the plane of the analyzer is set parallel to or perpendicular to the tetragonal axis. Although some such difference would be expected for any fluorescent tetragonal crystal, a difference as large as that found for $MgPt(CN)_4 \cdot 7H_2O$ is not ordinarily observed. The reason for the peculiar optical properties of this crystal appear to be closely associated with the relative positions of the Mg and Pt atoms in it. These atoms are arranged in rows parallel to the tetragonal axis, the distance between atom-centers in any one row being 1.57A. The shortest distance between any two rows, however, is 10.3A, 6.6 times the distance between two atom-centers in the same row. This arrangement is illustrated, to scale, in Fig. 1. Vibrations of the metal atoms must therefore encounter much greater resistances in the axial direction than in directions perpendicular thereto. Even in the regions between the rows of Mg and Pt atoms where the fluorescent light may possibly originate, the components of the electric field parallel and perpendicular to the axis may be expected to differ greatly in magnitude, producing much different effects upon light polarized in these directions.

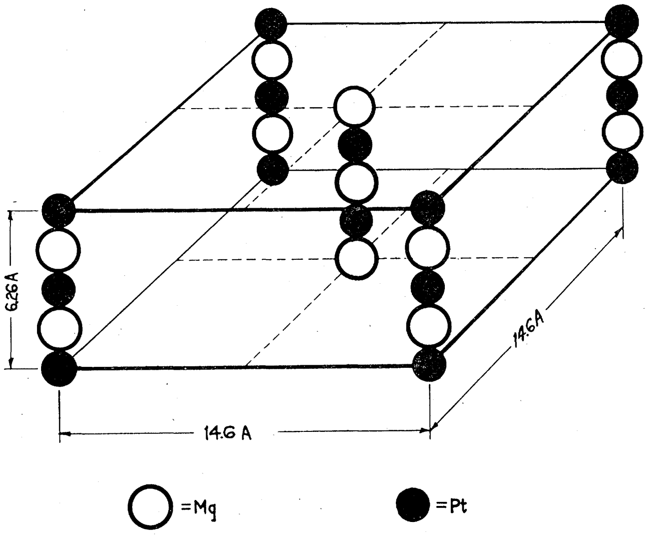

Fig. 1. Arrangement of magnesium platinum atoms in platinocyanide heptahydrate.

(b) *Atomic radii.* Since the original table of atomic radii in crystals proposed by Bragg[7] and based upon the inter-atomic distances observed in FeS$_2$, Fe, CaCO$_3$, C (diamond), etc., other values have been suggested, based on different methods of allotting to each atom its proper fraction of the total distance between its center and that of its neighbor, the quantity directly determined by means of x-rays. Wyckoff[8] has used the distances in CsCl$_2$I as a starting point, while Davey has assumed that the radii of Cs$^+$ and I$^-$ are equal in CsI, and has argued that ionized and un-ionized atoms have very different radii. Although it is to be expected that the radius of an atom will depend both upon the kind and upon the arrangement of the surrounding atoms, it nevertheless appears that when an atom has a fixed charge it behaves as if it had a "sphere of influence" which does not vary more than 10 percent if the surrounding atoms are not too different in the crystals compared. The radii proposed by Bragg and by Davey, however, differ from each other by much more than this amount, their values for the radius of the Cl^- ion being 1.05 and 1.59 A, and for the K^+ ion 2.07 and 1.55A, respectively. The nature of this difference causes great discrepancies in the predicted distances between ions of like sign such as I^- to I^-, or Mg^{++} to Pt^{++}. Bragg's predicted distance between I^- ions is 2.80A, while the observed distance is 4.21A in CdI_2 [11] and in SnI_4.[12] The predicted distance between S^{--} ions in MoS_2 [13] is 2.05A, the observed distance 3.49A.

It may be argued that the radii of negative ions "in contact" with each other will be greater than their radii in contact with positive ions, for the similar charges might be expected to keep them farther apart. This same argument, however, would tend to increase the distance between Mg^{++} and Pt^{++} ions to a value much greater than 2.70A, the sum of the Bragg radii, while the distance here observed is only 1.57A. All these discrepancies noted above may be removed by assigning to Mg^{++} a radius 0.87A, consistent with Davey's ideas, and to Pt^{++} a radius 0.70A, consistent with the distance between Pt^{++} and Cl^- in K_2PtCl_4 [10] and with Davey's value for the radius of the Cl^- ion. The structure of $MgPt(CN)_4 \cdot 7H_2O$ accordingly lends support to Davey's method of calculating atomic radii and to the results already obtained by this method.

Since writing the above, the authors have read the paper by W. L. Bragg on "Interatomic Distances in Crystals,"[14] in which he states that the radii given in his 1920 paper should be corrected by about 0.7A, the radii of the anions being increased and those of the cations decreased by this amount. This brings the radii into agreement with the values proposed by Wasastjerna[15] in 1923, but they still differ by about 0.2A from those proposed by Davey. A set of values which is intermediate between these two, and therefore not very different from either of them, may be obtained from the four relations:

$Mg^{++}+Pt^{++}=1.57$ (obs. in $MgPt(CN)_4 \cdot 7H_2O$), $Pt^{++}+Cl^-=2.33$

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[11] R. M. Bozorth, J. Am. Chem. Soc., **44,** 2232–2236 (1922).

[12] R. G. Dickinson, J. Am. Chem. Soc., **45,** 958–962 (1923).

[13] R. G. Dickinson and L. Pauling, J. Am. Chem. Soc. **45,** 1466–1471 (1923).

[14] W. L. Bragg, Phil. Mag. (7) **2,** 258–266 (1926).

[15] J. A. Wasastjerna, Soc. Sci. Fennica Comm. Phys.-Nat. **1,** No. 38, 1-25 (1923).

(obs. in K_2PtCl_4)[10], $Mg^{++} + O^{--} = 2.10$ (obs. in MgO),[16] and $Cl^{-} - O^{--} = 0.40$ (commonly accepted difference). Values so obtained are given in Table III.

TABLE III

Ion	Bragg (1920)	Wasastjerna (1923) Bragg (1926)	Davey (1926)	Calculated
Cl^{-}	1.05A	1.72A	1.59A	1.63A
O^{--}	0.65	1.32	>1.05	1.23
Mg^{++}	1.42	0.75	<1.05	0.87
Pt^{++}	(1.28)	——	——	0.70

Both Wasastjerna's values, and Davey's values as far as they go, are consistent with the observed distance between Mg^{++} and Pt^{++} in $MgPt(CN)_4 \cdot 7H_2O$, and the agreement with each seems good considering that the radius of the "sphere of influence" may be expected to change with the kind and arrangement of the surrounding atoms, and indeed the "radius" may be different in different directions especially in the case of atoms surrounded as are the Mg^{++} and Pt^{++} in $MgPt(CN)_4 \cdot 7H_2O$.

BELL TELEPHONE LABORATORIES, INC.,
September 15, 1926.

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[16] R. W. G. Wyckoff, Am. J. Sci. **10,** 107 (1925).