The Crystal Structure of Tetramminopalladous Chloride $Pd(NH_3)_4Cl_2 \cdot H_2O$.

By

B. N. Dickinson in Pasadena.

(With 3 figures.)

Introduction.

An investigation of the crystal structure of tetramminopalladous chloride has considerable interest because.of Werner's contention that compounds containing bivalent palladium (or platinum) possess a planar configuration consisting of four groups coordinated about the central palladium atom. The correctness of this assumption has been verified in the case of potassium chloroplatinite and palladite by the x-ray studies of Dickinson (1). Pauling (2) has shown theoretically that the bivalent transitional elements platinum, palladium, and nickel can form bonds directed toward the corners of a square. Recently Cox (3) has reported that tetramminoplatinous chloride, $Pt(NH_3)_4Cl_2 \cdot H_2O$, is in accord with Werner's viewpoint and has a structure closely similar to that of potassium chloroplatinite. The determination of the structure of tetramminopalladous chloride was undertaken to test Werner's assumption for a cation containing bivalent palladium. This palladium compound might reasonably be expected to have the same structure as $Pt(NH_3)_4Cl_2 \cdot H_2O$; it is shown in this paper that the structure is closely related to the potassium chloroplatinite structure, but is based on a unit containing two molecules instead of one as reported by Cox for the platinum com pound.

Tetramminopalladous chloride forms pale yellow tetragonal needles from a solution of diamminopalladous chloride in aqueous ammonia. In most cases the crystals we prepared developed prism faces belonging only to . {110}.

The Unit Cell and Space Group.

Oscillation photographs for determining the lattice constants were prepared by reflecting $MoK\alpha$ radiation filtered through zirconia from a developed prism face (110) and a ground face (001). As an aid in fixing the position of the central image the spectrum from a given crystal face was recorded on both sides of the photograph in a manner which gave a pattern symmetrical about the central image. The distance of the plate from the crystal was determined by simultaneously registering the spectrum from the cleavage face of calcite.

In Table I A are given the data obtained from an oscillation photograph from (001). The value of c_0 as determined from these data is 4.34 ± 0.05 Å. The identity distance along c as calculated by means of the Polanyi formula, $s\lambda = I \sin \mu$, was found to be 4.3 Å.

Table I A. Spectral Data from (001).

Reflection	Line	sin θ	d_{001}
001	α	0.08151	4.356 Å
002	α	0.16408	4.323
		Average	4.34

The data given in Table I B, obtained from an oscillation photograph from a developed prism face (110) with [1$\bar{1}$0] as the axis of oscillation (the indices referring to the true unit described below), lead to a spacing of 7.284 ± 0.02 Å. This might be taken as the value of d_{100}. It is found, however, that no unit with $a_0 = 7.284$ Å accounts for the presence of several reflections observed in the first and other layer lines of this photograph. The smallest value of a_0 which does account for these reflections is $\sqrt{2} \times 7.284 = 10.302$ Å. No reflections were observed on any oscillation or Laue photograph which could not be accounted for on the basis of a unit of structure with $a_0 = 10.302$ Å and $c_0 = 4.34$ Å, which may hence be confidently accepted as the true unit.

Table I B. Spectral Data from (110) with [1$\bar{1}$0] Vertical.

Reflection	Line	sin θ	Spacing
110	α	0.04866	7.288 Å
220	α	0.09761	7.266
330	α	0.14609	7.282
440	α_1	0.19432	7.285
440	α_2	0.19535	7.290
550	α_1	0.24286	7.287
660	α_1	0.29124	7.294
		Average	7.284

Using the radiation from a tube with a tungsten anticathode operated at a peak voltage of 52 kv., Laue photographs were made with the beam approximately normal to (110) and to (001).

Employing the values $a_0 = 10.302$ Å and $c_0 = 4.34$ Å, no value of $n\lambda$ calculated from a Laue photograph completely indexed with the aid of a gnomonic projection was found to be less than the short wave limit, 0.24 Å, although sixty-one forms were reflecting in the first order. Some of the first order reflections appearing on this photograph are given in Table II. Hence the values 10.302 ± 0.03 Å and 4.34 ± 0.05 Å for a_0 and c_0 respectively were accepted as correct.

Using the values of a_0 and c_0 just found, the density calculated with the assumption that the unit contains two molecules was found to be 1.89 g/cm³, which agrees satisfactorily with the experimental value of 1.93 ± 0.1 g/cm³ measured by the suspension method using a mixture of methylene iodide and benzene.

The reflections from planes with $h + k$ odd are the ones requiring us to choose a two-molecule unit with $a_0 = 10.302$ Å and $c_0 = 4.34$ Å rather than a one-molecule unit with $a_0 = 7.284$ Å and $c_0 = 4.34$ Å. Eleven reflections of this type are given in Table II which contains the data from a single Laue photograph.

Table II. Representative Planes Reflecting in the First Order on a Laue Photograph.

Plane	$n\lambda$	Plane	$n\lambda$	Plane	$n\lambda$	Plane	$n\lambda$
023	0.318 Å	$\bar{2}43$	0.301 Å	$\bar{3}75$	0.438 Å	$9\bar{5}2$	0.416 Å
$02\bar{5}$	0.355	$4\bar{2}5$	0.280	$\bar{4}4\bar{1}$	0.316	$\bar{5}93$	0.372
065	0.398	$6\bar{2}3$	0.408	$4\bar{5}1$	0.406	$11.\bar{5}.\bar{2}$	0.474
$1\bar{1}\bar{1}$	0.368	$33\bar{1}$	0.426	$6\bar{4}1$	0.266	$\bar{6}81$	0.352
$\bar{1}1\bar{2}$	0.430	$33\bar{2}$	0.356	$6\bar{4}3$	0.313	$\bar{6}8\bar{3}$	0.366
113	0.296	335	0.406	$\bar{4}83$	0.434	$10.\bar{6}.\bar{1}$	0.340
$11\bar{5}$	0.349	$4\bar{3}0$	0.315	$10.\bar{4}.3$	0.363	$\bar{6}.10.\bar{3}$	0.458
$\bar{1}22$	0.268	$4\bar{3}\bar{2}$	0.352	$\bar{5}60$	0.419	$\bar{7}90$	0.345
$2\bar{1}3$	0.440	$\bar{3}4\bar{3}$	0.448	$5\bar{6}2$	0.414	$\bar{7}9\bar{1}$	0.362
$\bar{1}33$	0.319	$5\bar{3}1$	0.436	$\bar{5}71$	0.460	$\bar{7}9\bar{2}$	0.349
314	0.380	$5\bar{3}\bar{3}$	0.401	$\bar{5}72$	0.329	$\bar{7}.11.1$	0.407
$4\bar{1}3$	0.374	$\bar{3}5\bar{4}$	0.423	$\bar{5}7\bar{3}$	0.425	$\bar{7}.11.\bar{2}$	0.434
$\bar{1}54$	0.395	$6\bar{3}2$	0.382	$\bar{5}7\bar{4}$	0.346	$\bar{7}.11.\bar{3}$	0.396
$51\bar{5}$	0.434	$7\bar{3}3$	0.322	$9\bar{5}0$	0.424	$\bar{8}.10.\bar{1}$	0.306
$3\bar{2}1$	0.268	$7\bar{3}\bar{4}$	0.422	$9\bar{5}1$	0.366	$\bar{8}.12.\bar{1}$	0.376

The appearance of reflections from planes with l even and $h + k$ odd in the odd orders eliminates the face-centered, end-centered, and body-

centered tetragonal lattices and six planes of this type were observed to reflect in the first order on a single Laue photograph (Table II). The planes are ($\bar{1}22$), ($4\bar{3}0$), ($56\bar{2}$), ($4\bar{3}\bar{2}$), ($6\bar{3}2$), and ($\bar{5}60$) reflecting at $n\lambda$ equal to 0.268 Å, 0.315 Å, 0.414 Å, 0.352 Å, 0.382 Å, and 0.419 Å respectively. Thus the structure must be based on a simple tetragonal lattice.

Since a Laue pattern with the beam normal to (001) shows a four-fold axis and four planes of symmetry and that with the beam normal to (110) shows a two-fold axis and two planes of symmetry, the point-group symmetry is V_d, C_{4v}, D_4, or D_{4h}. The space groups isomorphous with these point-groups and based on a simple tetragonal lattice are D_{4h}^1 to D_{4h}^{16} inclusive, C_{4v}^1 to C_{4v}^8 inclusive, D_4^1 to D_4^8 inclusive, and V_d^1 to V_d^8 inclusive.

The space groups which can be discarded by the consideration of special criteria are given in Table III.

Table III. Space Groups Eliminated by Special Criteria.

Space Groups	Representative Data	Conclusion
D_{4h}^2, D_{4h}^4, D_{4h}^6, D_{4h}^8, D_{4h}^9, D_{4h}^{11}, D_{4h}^{13}, D_{4h}^{15}, C_{4v}^5, C_{4v}^6, C_{4v}^7, C_{4v}^8, V_d^2, V_d^4	(113) reflects at $n\lambda = 0.296$ Å	Eliminated
D_{4h}^3, D_{4h}^4, D_{4h}^7, D_{4h}^8, D_{4h}^{11}, D_{4h}^{12}, D_{4h}^{15}, D_{4h}^{16}	($\bar{5}60$) reflects at $n\lambda = 0.419$ Å	Eliminated
D_{4h}^2, D_{4h}^4, D_{4h}^6, D_{4h}^8, D_{4h}^{10}, D_{4h}^{12}, D_{4h}^{14}, D_{4h}^{16}, C_{4v}^3, C_{4v}^4, C_{4v}^5, C_{4v}^6, V_d^6, V_d^8	(023) reflects at $n\lambda = 0.318$ Å	Eliminated
D_4^3, D_4^4, D_4^5, D_4^6, D_4^7, D_4^8	(001) and (002) appear on oscillation photographs	Eliminated

The remaining space groups are D_{4h}^1, D_4^1, C_{4v}^1, V_d^1, V_d^5, D_4^2, V_d^3, D_{4h}^5, C_{4v}^2 and V_d^7. The space groups D_{4h}^5, C_{4v}^2, and V_d^7 require that planes belonging to {0 k l} with k odd reflect only in the even orders and several absences of this type were observed on the Laue photographs. Further, no reflections from planes {0 k l} with k odd appeared on an oscillation photograph from (010) although from the construction of the sphere of reflection in the reciprocal lattice it was found that planes from twenty-eight forms of this type were in position to reflect. These planes are (0 k 0) where $k = 1, 3, 5, \ldots 13$; (0 k 1) where $k = 1, 3, 5 \ldots 13$; (0 k 2) where $k = 1, 3, 5 \ldots 13$; and (0 k 3) where $k = 1, 3, 5 \ldots 13$. Only planes

were counted which would reflect to a region of the film where other lines were present. Therefore, we are to consider that the correct space group is one of the set D_{4h}^5, C_{4v}^2, and V_d^7.

The absence of an observable pyroelectric effect[1] for $Pd(NH_3)_4Cl_2 \cdot H_2O$ indicates that D_{4h}^5 is the most probable space group, since it is the only one of the three possessing a center of symmetry; it was found possible to base a satisfactory structure on this space group.

The Atomic Arrangement.

With two molecules in the unit cell, there must be placed 2 Pd, 2 O, 4 Cl, and 8 N, and these atoms are to be distributed among the sets of equivalent positions as given in Wyckoff's tables for D_{4h}^5. The positions (a) were selected for the palladium and (i) for the nitrogen atoms since in this manner we obtain a planar configuration consisting of four ammonia molecules situated at the corners of a square surrounding the central palladium atom. Other possible arrangements for the palladium and nitrogen atoms either give rise to non-planar configurations for the cation or else planar configurations involving angles different from 90° between the Pd-N bonds and hence are not in accord with the considerations stated in the introduction. Also the positions (k) can probably be excluded for the nitrogen atoms because there is insufficient room for two ammonia groups along the c-axis. For the same reason we cannot use either the positions (e) or (f) in any combination for placing nitrogen.

The chlorine atoms are to be placed in one of the sets of four equivalent positions or in two of the three available sets of two equivalent positions (b), (c), and (d).

We can eliminate the positions (e) and (f) since the value $c_0 = 4.34$ Å is too small to accomodate two chloride ions in the unit along the c-axis.

It was observed that the lines from $(h\,k\,0)$ and $(h\,k\,2)$, although having approximately the same intensity, frequently differed greatly in intensity from $(h\,k\,1)$. These inequalities were noted both for planes with $h + k$ even and $h + k$ odd. Since the structure factors for the palladium and nitrogen atoms with the arrangement selected for them above do not depend on the index l, this effect can be accounted for only by placing the chlorine atoms in (h), in which case the structure factor contains the factor $e^{\pi i l}$. The scattering power of the two oxygen atoms is too small to

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1) No pyroelectricity was indicated for $Pd(NH_3)_4Cl_2 \cdot H_2O$ by an experiment performed according to the method described by Martin (4), although tourmaline and $K_3Cu(CN)_4$ gave positive results.

account for these phenomena. With the chlorine atoms in (g) the chlorine structure factor would be independent of l and hence could not affect the relative intensities of $(h\,k\,0)$, $(h\,k\,1)$, and $(h\,k\,2)$. Also these atoms cannot be in any two of the sets (b), (c), and (d), since in this case they would not contribute to the structure factor for planes with $h + k$ odd.

Of the sets of two equivalent positions (b), (c), and (d) available for the oxygen, the possibility (b) may be ruled out because it does not provide sufficient space for a water molecule. It was more difficult to decide between (c) and (d); however, the latter positions gave somewhat better agreement with the intensity data and accordingly were chosen.

The hydrogen atoms cannot of course be located by the use of x-ray data.

Evaluation of the Parameters[1].

Using the atomic arrangement selected in the preceding section, the individual structure factors are as follows:

$$S_{Pd} = f_{Pd}\,\{1 + e^{\pi i(h+k)}\},$$
$$S_{Cl} = 2f_{Cl}\,e^{\pi il}\{e^{\pi ik}\cos{(h+k)}\,u_{Cl} + e^{\pi ih}\cos{(h-k)}\,u_{Cl}\},$$
$$S_N = 2f_N\,[\cos{(hu_N + kv_N)} + \cos{(hv_N - ku_N)} + e^{\pi i(h+k)}\,\{\cos{(hu_N - kv_N)} + \cos{(hv_N + ku_N)}\}],$$

and $S_O = f_O\,(e^{\pi ih} + e^{\pi ik})$.

The atomic scattering factors of Pauling and Sherman (5) are used throughout this paper.

We can employ the intensity data from oscillation photographs prepared from any prism face with the c-axis vertical to determine the value of the single chlorine parameter. Due to the factor $e^{\pi il}$ entering in S_{Cl} the chlorine atoms will contribute in the same sense to all reflections lying in the same zone line (planes $(h\,k\,l)$ with $l = 1, 2, 3, \ldots$) with l even, and in an opposite sense to the planes in this zone line with l odd while the signs of the other atomic structure factors will remain unchanged for all these reflections. Further, S_{Pd} is equal to $2f_{Pd}$ for planes with $h + k$ even; therefore, in this case $S_{Pd} + S_N + S_O$ will be positive, since $2f_{Pd} > 8f_N + 2f_O$ for all values of $(\sin\theta)/\lambda$.

The following types of inequalities which apply to reflections with $h + k$ even lying in the same zone line were observed.

(1) $(h\,k\,2) > (h\,k\,1)$

(2) $(h\,k\,1) > (h\,k\,0)$ and $(h\,k\,3) > (h\,k\,2)$

(3) $(h\,k\,0) > (h\,k\,1) > (h\,k\,2) > (h\,k\,3)$

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1) A more detailed account of the material of this section is contained in the author's dissertation.

Variations in the temperature correction, atomic scattering factors, specific times of illumination of planes, etc. will affect the relative intensities of these lines, however, since the inequalities $(h\,k\,0) > (h\,k\,2)$ and $(h\,k\,1) > (h\,k\,3)$ which were observed in all cases can result only from such variations, it was assumed that the resultant effect of all these factors would act to diminish the intensity as the index l increases. Therefore, the inequalities of cases (1) and (2) can arise only because the sign of S_{Cl} for planes with l even differs from the sign of S_{Cl} for planes with l odd.

We infer in case (1) that S_{Cl} is positive for $(h\,k\,0)$ and $(h\,k\,2)$, because only if this assumption is correct can $|S_{hk2}|$ exceed $|S_{hk1}|$ since $S_{Pd} + S_N + S_O$ is positive for all the lines $(h\,k\,0)$, $(h\,k\,1)$, $(h\,k\,2)$, and $(h\,k\,3)$. If the inequalities (2) hold, we conclude that S_{Cl} for $(h\,k\,0)$ and $(h\,k\,2)$ is negative. Case (3) arises when the chlorine contribution is small.

The palladium and oxygen atoms do not contribute to the lines for which $h + k$ is odd, and since the sign of S_N is uncertain, no assumption as to the sign of S_{Cl} can be made for such reflections.

The chlorine parameter is evaluated by finding which values of u_{Cl} will give S_{Cl} the proper sign in all cases.

Fig. 1 is a device for representing the results of the procedure we have just given. Each arrow marks the region eliminated by the inequality
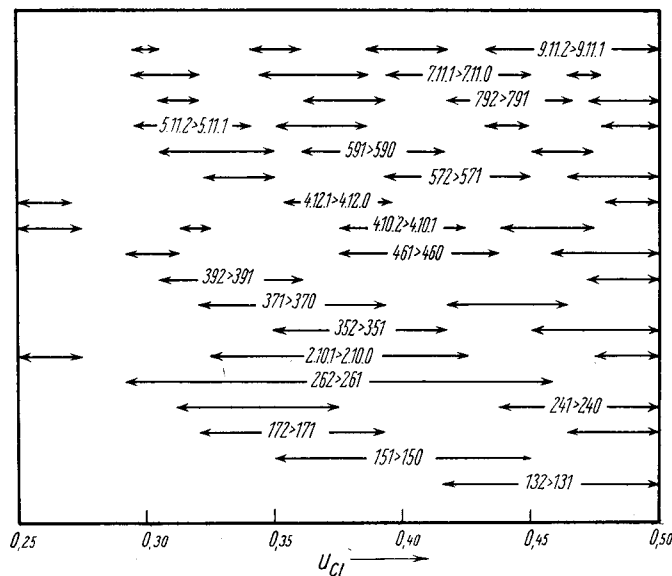

Fig. 1. Regions eliminated for u_{Cl} by considering the sign of S_{Cl} for $(hk0)$.

with which the arrow is labeled. As a result u_{Cl} is limited to the range of values between 0.275 and 0.292 when only the values between 0.25 and 0.50 are considered. However, the chlorine structure factor for planes with $h + k$ even is symmetrical about the point $u_{Cl} = 0.25$ and, therefore, the values between 0.208 and 0.225 also form a possible range for the chlorine parameter. Equivalent structures arise from the choice of either range.

It was not possible to find a single value of the parameter lying in the range 0.275 to 0.292 for which the calculated values of S_{Cl} for both (680) and (8.10.0) are in agreement with the experimental observations that these quantities are small negative numbers. In the range 0.275 to 0.292 only values less than 0.28125 give rise to negative calculated values of S_{Cl} for (680) while S_{Cl} for (8.10.0) is negative only for values of u_{Cl} greater than 0.28125. However, there is some justification for supposing that this discrepancy arises from small inaccuracies in the experimental data, since it was observed that (681) > (680) while (682) > (683), and in all other sequences where the inequality $(h\,k\,1) > (h\,k\,0)$ appeared the inequality $(h\,k\,3) > (h\,k\,2)$ was also found even when it was judged from the first inequality that $|S_{Cl}|$ is small.

In a manner similar to the one given above u_{Cl} was evaluated assuming that the oxygen atoms occupied positions (c) rather than (d). This process gave the values between 0.277 and 0.284 as the best parameter range. Throughout this range, however, serious discrepancies arose for the planes (130), (170), (680), and (8.10.0) and for these reasons the oxygen atoms were placed in positions (d).

By comparing for several planes the observed sizes of S_{Cl} as estimated from the relative intensities of the lines $(h\,k\,l)$ where $l = 0, 1, 2, 3$ with the corresponding values of S_{Cl} calculated at various points in the range 0.275 to 0.292, the best value of u_{Cl} was found to be about 0.285 ± 0.01.

Using the Pd-N separation[1]) of 2.02 Å we can reduce the number of independent nitrogen parameters to one by writing

$$\text{(I)} \quad u_N^2 + v_N^2 = (2.02/10.302)^2.$$

Using equation (I) and giving u_{Cl} a certain value the structure factor for all the atoms in the unit becomes a function of u_N. Therefore, we can evaluate the nitrogen parameter as follows. It was observed that (410) > (210), whereas for any value of u_{Cl} lying in the range 0.275 to 0.292 it

was calculated that $|S_{210}| > |S_{410}|$ when u_N is in the range between 0.139 ($u_N = v_N$) and 0.000 ($v_N = 0.196$). When $u_{Cl} = 0.285$ the inequality (660) > (330) restricts u_N to the values between 0.184 and 0.196 while the inequality (550) > (330) limits u_N to the range 0.191 to 0.196. Using equation (I) the corresponding ranges permitted for v_N are found to be 0.00 to 0.068 and 0.00 to 0.044. Only these three comparisons were found to be useful for evaluating the nitrogen parameter.

An arrangement equivalent to the one just discussed is obtained if u_{Cl} is given a value in the other possible range for u_{Cl}, 0.208 to 0.225.

All three inequalities used above are taken from Table IV, containing data obtained from an oscillation photograph prepared from (110) with [1̄10] vertical. As a factor of safety a temperature correction was omitted in computing the values of the structure factors, but the Lorentz and polarization factors are included. S_{410} and S_{210} contain the factor $\sqrt{\omega}$ which is a correction for the varying specific times of illumination of planes inclined to the axis of rotation. ω is defined by the equation (8).

$$\omega = [1 - (u\lambda/d \; \sin \; 2\theta)^2]^{-\frac{1}{2}}$$

where u is the order of the layer line and d is the unit translation along the axis of rotation. Since [1̄10] was the axis of rotation, d is $\sqrt{2}a_0$.

We expect that the $Cl\text{-}NH_3$ separation will not be less than the ammonium-chlorine separation of 3.35 Å found in NH_4Cl (9). If the nitrogen parameters are given in turn the limiting values of the ranges just established we find the following chlorine-ammonia separations when $u_{Cl} = 0.285$. If u_N and v_N have the values 0.196 and 0.000 respectively, four of the surrounding eight ammonia groups will be at a distance of 3.23 Å from the chlorine atom and the other four at a distance of 3.66 Å. On the other hand, if $u_N = 0.191$ and $v_N = 0.044$ the $Cl\text{-}NH_3$ separation for the four groups first mentioned will be 3.57 Å and for the other four 3.31 Å. In the latter case four of the ammonia groups are separated from the chloride ion by a distance smaller than the $NH_4\text{-}Cl$ separation and since these four ammonia molecules approach the chloride ion as u_N decreases and v_N increases it appears that safe limits have been selected for u_N and v_N. It is probable that v_N has a value in the center portion of the range 0.000 to 0.044 and as a result all eight of the ammonia molecules surrounding a chloride ion will be approximately equidistant from it. When this condition is exactly satisfied we find that $u_N = 0.194$ and $v_N = 0.027$ and that the $Cl\text{-}NH_3$ separation is 3.44 Å.

As a check of the previous evaluation of u_{Cl} we can employ the following method. It will be assumed that for any value of u_{Cl} each

ammonia molecule of the surrounding eight is equidistant from the chlorine atom and hence we write

$$(\text{II}) \quad 4u_{Cl}u_N = u_N + v_N.$$

It has been shown that this condition must be at least approximately true if $u_{Cl} = 0.285$. Since in general the contribution of the nitrogen atoms to the intensities of lines is small and changes slowly as u_N and v_N are varied, a slight departure from the condition expressed by equation (II) should not introduce appreciable errors. Equations (I) and (II) allow us to express the structure factor for all the atoms in the unit as a function of u_{Cl}. Thus we can make use of intensity inequalities in the same manner as would be employed in a single parameter problem.
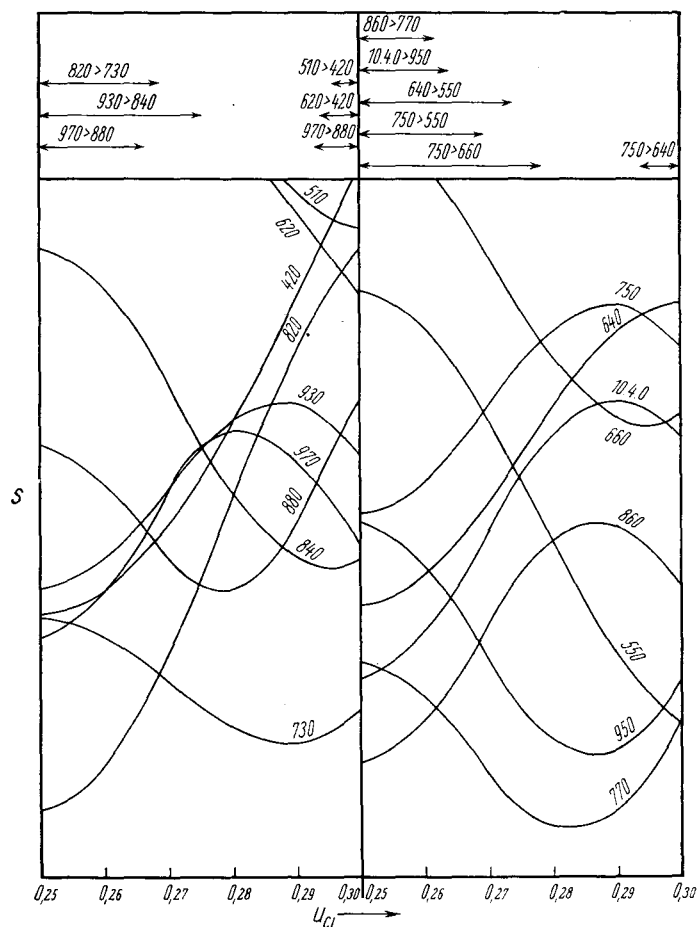

Fig. 2. Calculated structure factors for planes $(hk0)$ as functions of the parameter u_{Cl}.

Table IV*. Intensity Data for an Oscillation Photograph from (110) with [1̄10] Vertical; Oscillation 0-30°.

Layer Line

Layer Line															
8th									910		10.2.0		11.3.0		12.4.0	
									2.9	3.2	2.0	2.9	1.15	1.94	0.70	1.38
7th							810		920		10.3.0		11.4.0			
							1.9	1.8	A	0.005	A	0.14	A	0.23		
6th						710		820		930		10.4.0		11.5.0		
						4.8	6.0	3.8	5.0	3.8	4.7	2.8	4.2	1.10	2.77
5th					610		720		830		940		10.5.0			
					2.1	1.3	A	0.01	0.65	0.61	A	0.02	A	0.04		
4th				510		620		730		840		950		10.6.0		
				15.0	13.1	12.0	11.6	2.2	1.2	3.1	3.2	1.0	1.0	1.10	2.2
3rd			410		520		630		740		850		960			
			10.0	8.9	0.80	0.50	0.55	0.40	0.50	0.13	A	0.12	A	0.00		
2nd		310*		420		530		640		750		860		970		
		20.0	26.9	8.5	7.2	14.0	12.3	5.5	6.2	5.7	6.5	2.0	3.0	2.1	3.5
1st	210*		320		430		540		650		760		870			
	3.3	4.2	A	0.20	1.85	1.14	1.2	0.55	0.60	0.44	A	0.00	A	0.02		
Equator		220*		330		440		550		660		770		880		
		>30.0	86.2	2.2	1.0	16.0	16.5	4.0	2.7	5.0	5.2	0.75	0.66	1.8	2.3

* The reflections consisting of an unresolved α-doublet are marked with asterisks and their calculated intensities have been multiplied by 1.5 to render them comparable with other lines consisting of α_1 alone. The data for (110) was omitted because the crystal did not intercept all of the beam when this plane reflected, while the crystal did intercept all of the beam when the other planes were in positions to reflect. Reflections not observed are designated by the letter A.

Table V. Intensity Data for an Oscillation Photograph from (110) with [1Ī0] Vertical; Oscillation 15—45°.

Layer Line

Layer Line											
8th	10.2.0		11.3.0		12.4.0		13.5.0		14.6.0		
	3.2	2.9	2.55	1.94	1.20	1.38	0.85	0.97	0.70	0.98	
7th		10.3.0		11.4.0		12.5.0		13.6.0			
		0.30	0.14	0.60	0.23	A	0.005	A	0.03		
6th	930		10.4.0		11.5.0		12.6.0		13.7.0		
	5.8	4.7	4.5	4.2	2.5	2.8	1.10	1.79	0.90	1.23	
5th		940		10.5.0		11.6.0		12.7.0			
		A	0.02	A	0.04	A	0.12	A	0.00		
4th	840		950		10.6.0		11.7.0		12.8.0		
	5.0	3.2	1.8	1.0	2.5	2.2	0.90	1.04	0.95	1.45	
3rd		850		960		10.7.0		11.8.0			
		0.40	0.12	A	0.00	A	0.05	A	0.17		
2nd	750		860		970		10.8.0		11.9.0		
	7.0	6.5	3.2	3.0	3.5	3.5	1.20	1.74	1.10	1.61	
1st		760		870		980		10.9.0			
		A	0.00	A	0.02	A	0.05	A	0.00		
Equator	660		770		880		990		10.10.0		
	6.4	5.2	1.25	0.66	2.6	2.3	0.90	0.80	1.05	1.55	

The comparisons used were taken from the data of Tables IV and V and are given in figure 2 in which the arrows designate the regions eliminated by these inequalities. The values permitted for u_{Cl} by this process lie in the range 0.278 to 0.293 which is in satisfactory agreement with the range 0.275 to 0.292 that was previously obtained in an independent manner and leads again to the value 0.285 ± 0.01 for u_{Cl}. Only inequalities were used in which a plane with a certain value of d_{hk0} was reflecting more strongly than another plane with a larger value of d_{hk0}. In all the comparisons employed except (750) > (640) it seemed fairly certain that the stronger line was absorbed to the greater extent in the crystal. The calulated structure factors contain the Lorentz and polarization factors and are corrected for the varying specific exposure times of lines by including the factor $\sqrt{\omega}$, but a temperature correction was omitted as a measure of safety.

In Tables IV and V we have listed the data obtained from two oscillation photographs from (110) with [1Ī0] as the axis of oscillation. In the right half of the space under each plane is given the value of the calculated

intensity of that plane divided by one thousand and in the other half is the observed intensity which was visually estimated by comparison with a scale having eighteen lines of darkenings for which the product x-ray intensity × time varies from 0.25 to 30. The values of the parameters used are $u_{Cl} = 0.285$, $u_N = 0.194$, and $v_N = 0.027$. The factors ω and $(1 + \cos^2 2\theta)/2 \sin 2\theta$ have been used in the calculated intensities.

We have the two following types of reflections:

Type I: $h + k$ even for which $S_{hk0} = 2f_{Pd} + S_{Cl} + S_N \pm 2f_0$,
Type II: $h + k$ odd for which $S_{hk0} = S_{Cl} + S_N$.

Unless individual temperature corrections are used for the different kinds of atoms the calculated intensities for lines of Type II are too high when compared with the computed intensities from planes of Type I. It is very likely that due to the great difference in masses of the various kinds of atoms we should use individual temperature factors which fall off more slowly with increasing values of $(\sin \theta)/\lambda$ for the heavier atoms for the lighter ones. Since the palladium atoms are much heavier than any other kind in $Pd(NH_3)_4Cl_2 \cdot H_2O$ it is seen that an effect of this nature could cause the discrepancies noted above. If the scattering factor used for palladium is too small we can also account in some measure for these discrepancies since S_{Pd} is zero for planes with $h + k$ odd but not for the ones with $h + k$ even. Either of these effects or a combination of the two could also explain the observation that the calculated intensities, using a common temperature factor for all atoms, are too small for lines such as (730), (950), (11.7.0), (330), (550), (770), and (990) for which chlorine is scattering to a marked extent in opposition to palladium. Errors in the chlorine scattering factor might be important in this case.

In the calculated data of Tables IV and V we have arbitrarily included the temperature factor found for potassium chloride (10) in the structure factors of chlorine, nitrogen, and oxygen, but have used no temperature correction in the palladium structure factor. With these assumptions the agreement between planes of Types I and II is good.

Although the planar $Pd(NH_3)_4$ arrangement was assumed in the derivation of the structure, the final agreement found between the observed and calculated intensities justifies the assumption and can be considered to show the existence of this arrangement in the crystals under consideration.

Absorption in the crystal will probably increase regularly as the order of the reflections lying in the same zone line increases because of the fact that the angles between the planes of this sequence and the developed

face (110) increase as the order of the reflection increases and this is also true for reflections in the same "diagonal" line such as the sequence (220), (420), (620), etc.

It should be noted that a one-molecule unit with $a = 7.284$ Å and $c = 4.34$ Å cannot account for the reflections lying in the odd order layer lines but that these reflections require at least a two-molecule unit with $a_0 = 10.302$ Å and $c_0 = 4.34$ Å.

It was found that an appreciable variation of the Pd-N separation from 2.02 Å which was assumed in evaluating the nitrogen parameters would seriously impair the agreement between calculated and observed intensities. Therefore, we have verified that this separation has the value Pd-$N = 2.02 \pm 0.05$ Å.

Discussion of the Structure.

Figure 3 is a projection of the structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$ on the plane (001). The palladium, nitrogen, and oxygen atoms lie in the same plane but the chlorine atoms are displaced from the first plane by one-half the depth of the unit along c.
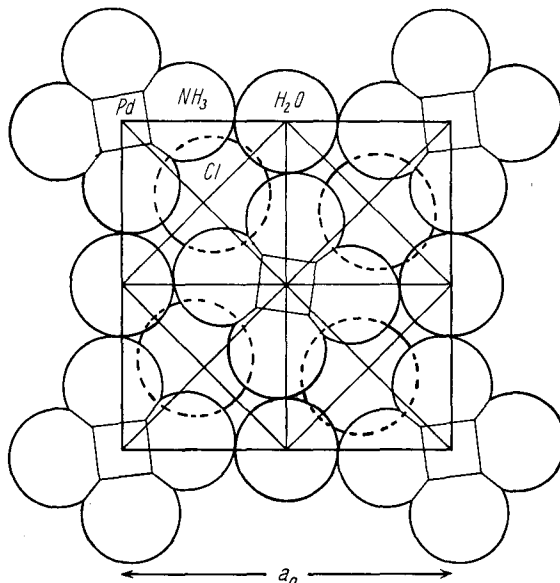

Fig. 3. Projection of the structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$ on the plane (001).

In Table VI are given the atoms or groups coordinated about each atom or group and the corresponding separations.

Table VI. Interatomic Separations found for $Pd(NH_3)_4Cl_2 \cdot H_2O$.

Central atom or group	Atoms or groups in contact with central atom or group	Separation		
Pd	$4\,NH_3$	Pd-N	$= 2.02 \pm 0.05$ Å	
Cl	$8\,NH_3$	Cl-NH_3	$= 3.44 \pm 0.1$ Å	
Cl	$2\,H_2O$	Cl-H_2O	$= 3.81 \pm 0.1$ Å	
H_2O	$4\,Cl$	H_2O-Cl	$= 3.81 \pm 0.1$ Å	
H_2O	$4\,NH_3$	H_2O-NH_3	$= 3.16 \pm 0.1$ Å	
NH_3	$4\,Cl$	NH_3-Cl	$= 3.44 \pm 0.1$ Å	
NH_3	$1\,H_2O$	NH_3-H_2O	$= 3.16 \pm 0.1$ Å	
NH_3	$2\,NH_3$	NH_3-NH_3	$= 2.86 \pm 0.05$ Å	(in the same cation)
NH_3	$1\,NH_3$	NH_3-NH_3	$= 4.06 \pm 0.1$ Å	(in different cations)

It was assumed that each ammonia of the surrounding eight is equidistant from the chlorine atom but from x-ray data it can only be shown that this condition is approximately satisfied. It may be that $4\,NH_3$ are slightly closer to Cl than the other $4\,NH_3$.

If the water molecules were placed in the plane of the chlorine atoms we would obtain a minimum Cl-H_2O separation of 3.1 to 3.2 Å which is somewhat smaller than we expect to find[1]). This probably accounts for the displacement of H_2O to positions half way between planes of Cl.

A structure very similar to that of K_2PdCl_4 and based on a one-molecule unit would be obtained from the structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$ by placing $u_{Cl} = 0.250$ and $v_N = 0.000$. In such a one-molecule structure interatomic distances would be essentially the same as was found in the two-molecule unit except for the NH_3-NH_3 separation in different cations. This separation would be about 4.44 Å in the one-molecule structure, whereas it is decreased to 4.06 Å in the structure found. In K_2PdCl_4 the large Cl atoms in different anions are in contact with one another (3.6 Å apart). When the Cl atoms are replaced by the smaller NH_3 groups, the structure becomes unstable and is deformed slightly in such a way as to regain contact between $Pd(NH_3)_4$ groups. From figure 3 it is seen that the two-molecule unit arises from small rotations of the square configurations of ammonia molecules and chlorine atoms about axes parallel to c.

Cox (3) has reported very briefly his investigation of the crystal $Pt(NH_3)_4Cl_2 \cdot H_2O$, which, because of the very close similarity in crystal-chemical properties of palladium and platinum, we expect to be completely isomorphous with $Pd(NH_3)_4Cl_2 \cdot H_2O$. The structure suggested by him,

---

1) From the radii of H_3O^+ and NH^+_4 Pauling (11) has estimated that H_2O has a radius of about 1.45 Å and that the Cl-H_2O separation will not be less than about 3.26 Å.

however, is the one-molecule structure obtained from our two-molecule structure by putting u_{Cl} and v_N equal to one-fourth and zero respectively, and by placing the water molecules in the plane of the chloride ions rather than between these planes. It seems probable to us that Cox's structure is incorrect, and that the platinum compound also crystalizes with the two-molecule unit. The reflections eliminating the smaller unit would be somewhat weaker relative to other lines than for the palladium crystal, and Cox presumably overlooked them on his oscillation and Laue photographs. The dimensions $a = 7.39 \pm 0.02$ Å and $c = 4.21 \pm 0.02$ Å reported by him correspond to $a_0 = 10.46 \pm 0.03$ Å and $c_0 = 4.21 \pm 0.02$ Å respectively, which are nearly the same as was found for $Pd(NH_3)_4Cl_2 \cdot H_2O$. The parameter value $u_N = \frac{1}{4}$ approximately and the location of the water molecules in the plane of the chlorine ions are not supported by any published comparison of observed and calculated intensities, and in any case the effects of the deviation of u_{Cl} from 0.250 would vitiate such a treatment. The parameter value given by him also leads to a Pt-N separation, 2.62 Å, which is much larger than we expect[1]) on the assumption that nitrogen is bonded to platinum by a covalent bond. It is probable that the structure of $Pt(NH_3)_4Cl_2 \cdot H_2O$ is identical with that of $Pd(NH_3)_4Cl_2 \cdot H_2O$, even to the values of the parameters[2]).

I wish to thank Professor Linus Pauling for many valuable suggestions received during this investigation. I am also indebted to Dr. J. L. Hoard for much helpful assistance.

1) We expect that the Pt-N separation will be about 2.02 Å since the single-bond covalent radius of nitrogen is given as 0.70 Å (6) and the radius of bivalent platinum as 1.32 Å (7).

2) Since submitting this paper for publication, I have learned that E. G. Cox and G. H. Preston have published corrections for Cox's earlier report on the structure of $Pt(NH_3)_4Cl_2 \cdot H_2O$, as well as their results on the structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$, in the J. chem. Soc., **1933**, 1089.

For both compounds they find the space group D_{4h}^5. For $Pd(NH_3)_4Cl_2 \cdot H_2O$ they give $a_0 = 14.30$ Å and $c_0 = 4.27$ Å while for $Pt(NH_3)_4Cl_2 \cdot H_2O$ they give $a_0 = 14.76$ Å and $c_0 = 4.21$ Å.

After stating that the symmetry of the complex is either three mutually perpendicular planes or a four-fold axis, they conclude, "The latter (a four-fold axis) would mean that the four Pd-N valencies were equivalent, but that the ion would be arranged unsymmetrically in the lattice relative to the chlorine ions. This is unlikely, since it would imply distortion of the chlorine ions, resulting in color and reduced solubility, whereas actually the tetrammines are typically ionic substances, colorless and highly soluble. Thus we conclude that the tetrammine ion has three planes of symmetry, so that again the four nitrogens must be coplanar with the central atom, and the valencies must be paired . . . ."

No intensity data are given.

Summary.

The crystal structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$ was investigated using oscillation and Laue photographs. The structure was found to be based on a simple tetragonal unit containing two molecules with $a_0 = 10.302 \pm 0.03$ Å and $c_0 = 4.34 \pm 0.02$ Å. The space group was shown to be C_{4v}^2, V_d^7, or D_{4h}^5, the latter being further indicated by the observed absence of a pyroelectric effect. It was found possible to base a satisfactory structure on the space group D_{4h}^5.

The palladium atoms occupy positions (a), nitrogen (i), chlorine (h) and oxygen (d) of Wyckoff's tables. The ranges 0.275 to 0.292 and 0.278 to 0.293 were determined for u_{Cl} by two independent methods. Using $u_{Cl} = 0.285$ and an assumed Pd-N separation, u_N was found by intensity comparisons to lie between 0.191 and 0.196 and v_N between 0.000 and 0.044. With the following parameter values a good general agreement between the calculated and observed intensities was obtained:

$$u_{Cl} = 0.285 \pm 0.01, \quad u_N = 0.194 \pm 0.02, \quad v_N = 0.027 \pm 0.02.$$

Werner's assumption that bivalent palladium coordinates four groups in a planar configuration about itself was verified in this case.

The following interatomic distances were found:

$$
\begin{aligned}
Pd\text{-}N &= 2.02 \pm 0.05 \text{ Å,} \\
Cl\text{-}H_2O &= 3.81 \pm 0.1 \text{ Å,} \\
H_2O\text{-}NH_3 &= 3.16 \pm 0.1 \text{ Å,} \\
Cl\text{-}NH_3 &= 3.44 \pm 0.1 \text{ Å,} \\
NH_3\text{-}NH_3 &= 2.86 \pm 0.05 \text{ Å (in the same cation),} \\
NH_3\text{-}NH_3 &= 4.06 \pm 0.1 \text{ Å (in different cations).}
\end{aligned}
$$

It is pointed out that the corresponding platinum compound $Pt(NH_3)_4Cl_2 \cdot H_2O$ probably has the same structure, rather than the simpler structure reported by Cox.

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