THE CRYSTAL STRUCTURE OF TETRAMMINOPALLADOUS CHLORIDE
THE CRYSTAL STRUCTURE OF POTASSIUM BROMOSELENITE
THE NORMAL STATE OF THE HYDROGEN MOLECULE-ION

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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 compound.

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 Mo $K\alpha$ 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 IA are given the data obtained from an oscillation photograph from (001). The value of c_o 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 IA. 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 IB, 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 an 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. By choosing $a_0 =$ 10.302 Å we require that the a-axis make an angle of 45° with the normals to the developed prism faces which as a result belong to the form $\{110\}$.

Table IB. 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	7.291
		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 two forms were reflecting in the first order. 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/cm^3, which agrees satisfactorily with the experimental value of 1.93 ± 0.1 g/cm^3 measured by the suspension method using a mixture of methylene iodide and benzene.

The reflection 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 $a = 7.284$ Å and $c = 4.34$ Å. Eleven reflections of this type are given in Table II which contains the data from a single Laue photograph.

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 $(\bar{1}22)$, $(4\bar{3}0)$, $(\bar{5}6\bar{2})$, $(4\bar{3}\bar{2})$, $(6\bar{3}2)$, 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. Each of these three kinds of lattices is also ruled out by the appearance of reflections of other types. 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.

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 $\{0k\ell\}$ 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 $\{0k\ell\}$ 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 (0k0) where $k = 1,3,5 \ldots 13$, (0k1) where $k = 1,3,5 \ldots 13$, (0k2) where $k = 1,3,5 \ldots 13$, and (0k3) 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.

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

Plane	$n\lambda$	Plane	$n\lambda$	Plane	$n\lambda$	Plane	$n\lambda$
023	0.318 Å	155	0.411 Å	$7\bar{3}3$	0.322 Å	$9\bar{5}1$	0.366 Å
203	0.250	515	0.364	$7\bar{3}\bar{4}$	0.423	$9\bar{5}\bar{1}$	0.443
$02\bar{5}$	0.355	$3\bar{2}1$	0.268	$\bar{3}7\bar{5}$	0.438	$9\bar{5}\bar{2}$	0.416
$20\bar{5}$	0.328	$\bar{2}43$	0.301	$\bar{3}94$	0.450	$\bar{5}93$	0.372
065	0.398	$4\bar{2}\bar{5}$	0.280	$\bar{4}4\bar{1}$	0.316	$11\cdot\bar{5}\cdot\bar{2}$	0.474
$1\bar{1}\bar{1}$	0.368	$\bar{2}4\bar{5}$	0.345	$4\bar{5}1$	0.406	$\bar{6}81$	0.352
$\bar{1}1\bar{2}$	0.430	245	0.413	$6\bar{4}1$	0.266	$\bar{6}8\bar{1}$	0.436
$1\bar{1}\bar{2}$	0.266	425	0.390	$6\bar{4}\bar{1}$	0.419	$\bar{6}8\bar{3}$	0.366
113	0.296	$6\bar{2}3$	0.408	$6\bar{4}\bar{3}$	0.313	$10\cdot\bar{6}\cdot\bar{1}$	0.340
$\bar{1}1\bar{3}$	0.282	$\bar{3}3\bar{1}$	0.426	$\bar{4}83$	0.434	$\bar{6}\cdot10\cdot\bar{3}$	0.458
$11\bar{5}$	0.349	$\bar{3}3\bar{2}$	0.356	$8\bar{4}\bar{3}$	0.456	$\bar{7}90$	0.345
$\bar{1}22$	0.268	335	0.406	$10\cdot\bar{4}\cdot3$	0.363	$\bar{7}9\bar{1}$	0.362
$2\bar{1}\bar{3}$	0.440	$4\bar{3}0$	0.315	$\bar{5}60$	0.419	$\bar{7}9\bar{2}$	0.349
$\bar{1}33$	0.319	$4\bar{3}\bar{2}$	0.352	$\bar{5}6\bar{2}$	0.414	$\bar{7}\cdot11\cdot1$	0.407
314	0.380	$\bar{3}4\bar{3}$	0.448	$\bar{5}71$	0.460	$\bar{7}\cdot11\cdot\bar{1}$	0.453
$3\bar{1}\bar{4}$	0.417	$5\bar{3}1$	0.436	$\bar{5}72$	0.329	$\bar{7}\cdot11\cdot\bar{2}$	0.434
$4\bar{1}3$	0.374	$5\bar{3}\bar{3}$	0.401	$7\bar{5}\bar{2}$	0.276	$\bar{7}\cdot11\cdot\bar{3}$	0.396
$\bar{1}54$	0.395	$\bar{3}5\bar{4}$	0.423	$\bar{5}7\bar{3}$	0.425	$\bar{8}\cdot10\cdot\bar{1}$	0.306
$5\bar{1}4$	0.298	$5\bar{3}\bar{4}$	0.308	$\bar{5}7\bar{4}$	0.346	$\bar{8}\cdot12\cdot\bar{1}$	0.376
$5\bar{1}\bar{5}$	0.434	$6\bar{3}2$	0.382	$9\bar{5}0$	0.424		

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 $n\lambda = 0.318$ A	Eliminated

TABLE III Continued

Space Groups	Representative Data	Conclusion
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 absence of an observable pyroelectric effect* 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.

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*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.

The Atomic Arrangement

The space group D_{4h}^5 offers the following sets of equivalent positions:

Two equivalent positions:

(a) $000; \frac{1}{2}\frac{1}{2}0$

(c) $0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$

(b) $\frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}$

(d) $\frac{1}{2}00; 0\frac{1}{2}0$

Four equivalent positions:

(e) $0\ 0\ u;\ 0\ 0\ \bar{u};\ \frac{1}{2}\ \frac{1}{2}\ \bar{u};\ \frac{1}{2}\ \frac{1}{2}\ u.$

(f) $0\ \frac{1}{2}\ u;\ 0\ \frac{1}{2}\ \bar{u};\ \frac{1}{2}\ 0\ \bar{u};\ \frac{1}{2}\ 0\ u.$

(g) $u,\ u+\frac{1}{2},\ 0;\ \frac{1}{2}-u,\ u,\ 0;\ u+\frac{1}{2},\ \bar{u},\ 0;\ \bar{u},\ \frac{1}{2}-u,\ 0.$

(h) $u,\ u+\frac{1}{2},\ \frac{1}{2};\ \frac{1}{2}-u,\ u,\ \frac{1}{2};\ u+\frac{1}{2},\ \bar{u},\ \frac{1}{2};\ \bar{u},\ \frac{1}{2}-u,\ \frac{1}{2}.$

Eight equivalent positions:

(i) $u\ v\ 0;\ v\ \bar{u}\ 0;\ v+\frac{1}{2},u+\frac{1}{2},0;\ u+\frac{1}{2},\frac{1}{2}-v,0;$

$\bar{u}\ \bar{v}\ 0;\ \bar{v}\ u\ 0;\ \frac{1}{2}-v,\frac{1}{2}-u,0;\ \frac{1}{2}-u,v+\frac{1}{2},0.$

(j) $u\ v\ \frac{1}{2};\ v\ \bar{u}\ \frac{1}{2};\ v+\frac{1}{2},u+\frac{1}{2},\frac{1}{2};\ u+\frac{1}{2},\frac{1}{2}-v,\frac{1}{2};$
$\bar{u}\ \bar{v}\ \frac{1}{2};\ \bar{v}\ u\ \frac{1}{2};\ \frac{1}{2}-v,\frac{1}{2}-u,\frac{1}{2};\frac{1}{2}-u,\ v+\frac{1}{2},\frac{1}{2}$

(k) $u,\frac{1}{2}-u,v;\ u+\frac{1}{2},u,v;\ \frac{1}{2}-u,\bar{u},v;\ \bar{u},u+\frac{1}{2},v$
$\bar{u},u+\frac{1}{2},\bar{v};\ \frac{1}{2}-u,\bar{u},\bar{v};\ u+\frac{1}{2},u,\bar{v};\ u,\frac{1}{2}-u,\bar{v}.$

Sixteen equivalent positions:

(l) x y z, etc.

With two molecules in the unit cell, there must be placed 2 Pd, 2 O, 4 Cl, and 8 N. 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 (hk0) and (hk2), although having approximately the same intensity, frequently differed greatly in intensity from (hk1). 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 $e^{\pi i \ell}$. The scattering power of the two oxygen atoms is too small to 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 (hk0), (hk1), and (hk2). 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.

An arrangement equivalent to the one just selected is obtained by placing palladium in (b), chlorine in (g), nitrogen in (j), and oxygen in (c).

Evaluation of the Parameters

Using the atomic arrangement (2 Pd in (a), 8 N in (i), 4 Cl in (h), and 2 O in (d)) selected in the preceding section, the individual structure factors are as follows:

$$\begin{aligned}
S_{Pd} &= f_{Pd}\left\{1 + e^{\pi i(h+k)}\right\},\\
S_{Cl} &= 2f_{Cl}\, e^{\pi i l}\left\{e^{\pi i k}\cos(h+k)u_{Cl} + e^{\pi i h}\cos(h-k)u_{Cl}\right\},\\
S_{N} &= 2f_{N}\Big[\cos(hu_N + kv_N) + \cos(hv_N - ku_N)\\
&\qquad e^{\pi i(h+k)}\left\{\cos(hu_N - kv_N) + \cos(hv_N + ku_N)\right\}\Big],\\
S_{O} &= f_{O}(e^{\pi i h} + e^{\pi i k}).
\end{aligned}$$

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 $e^{\pi i l}$ entering in S_{Cl} the chlorine atoms will contribute in the same sense to all reflections lying in the same zone line (planes (hkl) 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 $S_{Pd} + S_N + S_0$ will be positive, since $2f_{Pd} > 8f_N + 2f_0$ for all values of $\frac{\sin\theta}{\lambda}$.

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

(1) (hk2) > (hk1)

(2) (hk1) > (hk0) and (hk3) > (hk2)

(3) (hk0) > (hk1) > (hk2) > (hk3)

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 (hk0) > (hk2) and (hk1) > (hk3) 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 (hk0) and (hk2), 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 (hk0), (hk1), (hk2), and (hk3). If the inequalities (2) hold we conclude that S_{Cl} for (hk0) and (hk2) is negative. Except in the sequence (680), (681), (682), and (683) which will be discussed later it was found that if one of the inequalities of case (2) held the other did also. 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.

Having devised a method for ascertaining the sign of S_{Cl} for a large number of lines, we can now evaluate the chlorine parameter in the following manner. The sign of S_{Cl} is determined by the factor [illegible]

$\{e^{\pi ik} \cos(h+k)u_{Cl} + e^{\pi ih} \cos(h-k)u_{Cl}\}$ and therefore u_{Cl} can have only such values as will give this factor the proper sign in all cases.

Figure 1 is a device for representing the results of the procedure we have just given. Each arrow marks the region eliminated by the inequality 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. It will be shown later that equivalent structures arise from the choice of either range.

From the relative intensities of the lines (hkℓ) where $\ell = 0,1,2,3$ the size of S_{Cl} for (hk0) can be roughly estimated. These estimations for several planes are compared in Table IV with the corresponding calculated values of S_{Cl}. The chlorine structure factor for each given plane has been computed for four values of u_{Cl} lying in the range between 0.275 and 0.292 in order to determine which portion of the range is most suitable. No corrections for the temperature effect and absorption have been introduced in these calculations but the Lorentz and polarization factors are included.

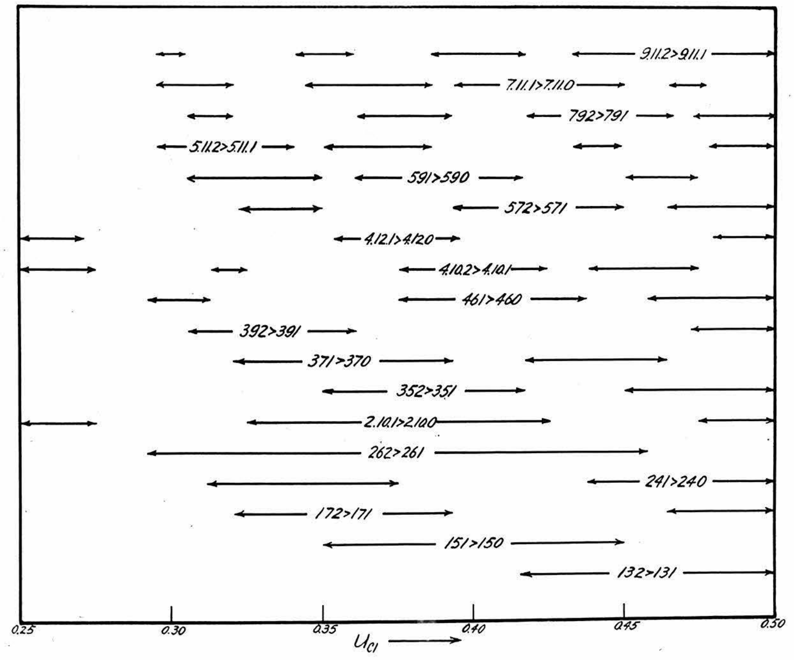

Figure 1

Regions eliminated for u_{Cl} by considering the sign of S_{Cl} for planes (hk0)

TABLE IV

Calculated and Estimated Sizes of S_{Cl} for Planes (hk0)

Plane	Observed Magnitude of S_{Cl}	Observed Sign of S_{Cl}	Calculated Values of S_{Cl}			
			$u_{Cl} =$ 0.275	0.280	0.285	0.290
130	s	+	8.2	11.6	15.5	19.7
150	s	−	−7.5	−10.3	−13.3	−16.1
170	s	+	6.7	8.7	10.5	11.7
240	l	−	−62.2	−54.8	−46.6	−37.9
260	s	+	29.5	20.9	11.9	2.9
280	v s		−12.2	−2.4	7.1	15.5
2·10·0	m	−	0.0	−9.9	−18.3	−24.4
350	l	+	18.4	25.0	31.2	37.2
370	l	−	−18.2	−23.4	−27.6	−30.3
390	m	+	16.5	19.6	20.7	19.4
440	m	+	38.7	31.5	24.1	17.3
460	s	−	−22.4	−14.7	−7.5	−1.6
480	v s		9.7	1.8	−4.6	−8.8
4·10·0	s	+	0.0	7.4	12.3	14.2
4·12·0	m	−	−6.7	−12.4	−15.0	−14.2
550	l	−	−24.0	−31.4	−38.1	−43.4
570	l	+	25.2	31.3	35.6	37.4
590	l	−	−23.9	−27.5	−28.0	−25.1
5·11·0	m	+	19.8	20.1	16.7	9.9

TABLE IV Continued

Plane	Observed Magnitude of S_{Cl}	Observed Sign of S_{Cl}	Calculated Values of S_{Cl}				
			u_{Cl}	0.275	0.280	0.285	0.290
660	v s	+		14.1	7.4	2.5	0.2
680	s	−		−6.3	−0.9	1.6	0.9
6·10.0	v s			0.0	−3.9	−4.3	−1.5
6·12·0	v s			4.4	6.6	5.3	1.6
770	l	−		−27.9	−32.8	−35.0	−33.8
790	l	+		26.8	29.2	27.9	23.0
7·11·0	m	−		−22.2	−21.4	−16.7	−9.1
880	v s	+		2.9	0.1	1.1	5.6
8·10·0	s	−		0.0	0.5	−2.9	−9.0
990	m	−		−25.8	−26.0	−22.2	−15.7
9·11·0	m	+		21.5	19.1	13.4	6.2
10·10·0	s	+		0.0	2.1	7.5	14.1

The abbreviations l, m, s, and v s are used to denote large, medium, small, and very small respectively.

The most serious of the various small discrepancies which appear in the data of Table IV is found for the planes (680) and (8·10·0). Thus 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. 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 (hkl)$>$ (hk0) appeared the inequality (hk3) $>$ (hk2) was also found even when it was judged from the first inequality that $|S_{Cl}|$ is small.

The general agreement we have obtained so far seems to justify the procedure adopted to evaluate the chlorine parameter and this conclusion is also supported by the fact that a completely different type of comparison which will be given later leads to practically the same value of u_{Cl}.

The best agreement seems to be obtained for values of u_{Cl} in the upper portion of the range and therefore at this time we place $u_{Cl} = 0.285 \pm 0.01$.

We have already mentioned that there was some difficulty in discriminating between (c) and (d) as positions for the oxygen atoms. So far the latter positions have been assumed to be the correct set. If (c) were selected the oxygen structure factor would become $S_0 = f_0 e^{\pi i l}(e^{\pi ih} + e^{\pi ik})$ and we would need to consider that the difference in intensity between lines with l even and with l odd, where h and k are the same for all these planes, arose from $S_0 + S_{Cl}$ rather than from S_{Cl} alone. With this assumption the chlorine parameter would be evaluated in a manner similar to the one we have already described. Thus the sign of $S_0 + S_{Cl}$ for (hk0) would be determined from the relative intensities of (hk0), (hk1), (hk2), and (hk3), and we should find in which regions of the chlorine parameter $S_{Cl} + S_0$ would have the proper sign for (hk0) by plotting $S_{Cl} + S_0$ as a function of u_{Cl}. This process was carried out and gave the values between 0.277 and 0.284 as the best parameter range. Throughout this range, however, the calculated values of $S_{Cl} + S_0$ for the planes (130), (170), (680), and (8·10·0) definitely disagreed with the experimental observations and for these reasons the oxygen atoms were placed in the positions (d).

Using the Pd-N separation* of 2.02 Å we can

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*The single-bond covalent radius of nitrogen is given by Pauling (6) as 0.70 Å. Pauling and Huggins (7) have found the covalent radius of bivalent palladium to be 1.32 Å.

reduce the number of independent nitrogen parameters to one by writing

$$(I) \quad u_N^2 + v_N^2 = \left(\frac{2.02}{10.302}\right)^2$$

From the equation

$$S_N = 2f_N \Big[\cos(hu_N + kv_N) + \cos(hv_N - ku_N) + e^{\pi i(h+k)}\big\{\cos(hu_N - kv_N) + \cos(hv_N + ku_N)\big\}\Big]$$

it is seen that S_N is unaffected by the exchange of u_N and v_N for planes with $h+k$ even while this operation will change the sign but not the absolute value of S_N if $h+k$ is odd. From expression (I) we infer that for each point (u_N, v_N) a corresponding point (v_N, u_N) will come under consideration. 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. From the foregoing discussion we see that two possible ranges for u_N must always arise from intensity comparisons between planes with $h+k$ even, i.e.,

(1) a range for u_N such that $u_N > v_N$ and, correspondingly,

(2) a range such that $u_N < v_N$.

Now it has been noted already that the value u_{Cl} is ambiguous in that

(3) u_{Cl} may lie between 0.208 and 0.225,

or (4) u_{Cl} may be between 0.275 and 0.292.

The combinations (1) with (4) and (2) with (3) give rise to equivalent structures as do the combinations (1) with (3) and (2) with (4). The latter possibility may be eliminated by considering the intensity data for lines with $h+k$ odd. Thus it was observed that $(410) > (210)$, whereas for any value of u_{Cl} lying in the range 0.208 to 0.225 it was calculated that $|S_{210}| > |S_{410}|$ when u_N is in the range between 0.139 ($u_N = v_N$) and 0.196 ($v_N = 0$). We conclude that u_{Cl} has a value between 0.275 and 0.292 and that $u_N > v_N$.

The comparisons $(660) > (330)$ and $(550) > (330)$ can be employed to further limit the nitrogen parameter u_N. When $u_{Cl} = 0.285$ the first inequality restricts u_N to the values between 0.184 and 0.196 while the other inequality 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 0.0 to 0.068 and 0.0 to 0.044. Only these comparisons and the inequality $(410) > (210)$ were to be found useful for evaluating the nitrogen parameter.

All three inequalities are taken from Table V, containing data obtained from an oscillation photograph prepared from (110) with $[1\bar{1}0]$ 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)

$$\omega = \left[1 - (\mu\lambda / d \sin 2\theta)^2\right]^{-1/2}$$

where u is the order of the layer line and d is the unit translation along the axis of rotation. Since $[1\bar{1}0]$ 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-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-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-NH_3 separation is 3.44 Å. The validity of the conclusions reached in this paragraph depends, of course, upon the correctness of the assumed Pd-N separation, 2.02 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

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

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.

The comparisons used were taken from the data given in Tables V and VI. 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}. A temperature correction was omitted as a measure of safety and in all comparisons employed except (750) > (640) it seemed fairly certain that the stronger line was absorbed to the greater extent in the crystal. The calculated structure factors contain the Lorentz and polarization factors and are corrected for the varying specific exposure times of lines by including the factor $\sqrt{\omega}$.

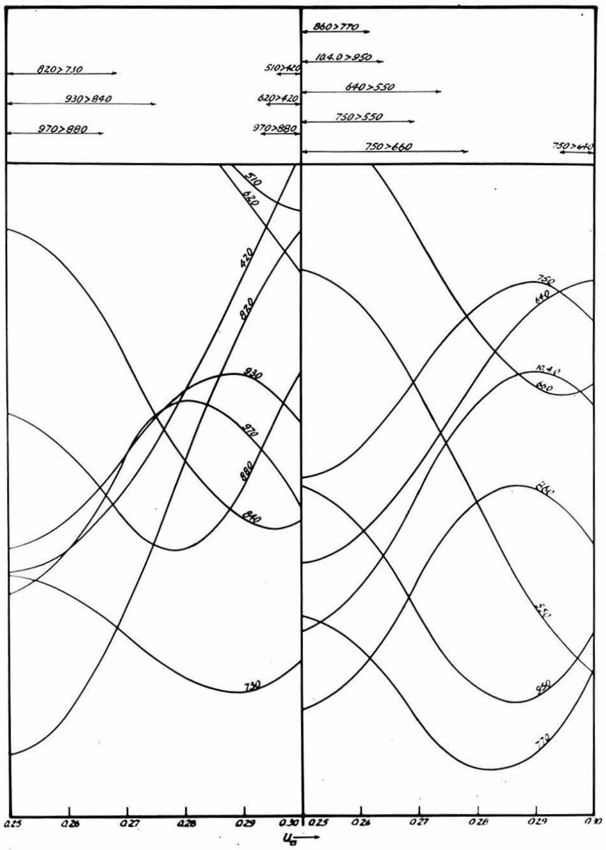

Figure 2

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

TABLE V†

Intensity data for an Oscillation Photograph from (110) with $[\bar{1}10]$ vertical; oscillation 0 - 30°.

Layer Line								
8th				910 2.9 3.2	10·2·0 2.0 2.9	11·3·0 1.15 1.94	12·4·0 0.70 1.38	
7th				810 1.9 1.8	920 A 0.005	10·3·0 A 0.14	11·4·0 A 0.23	
6th			710 4.8 6.0	820 3.8 5.0	930 3.8 4.7	10·4·0 2.8 4.2	11·5·0 1.10 2.77	
5th			610 2.1 1.3	720 A 0.01	830 0.65 0.61	940 A 0.02	10·5·0 A 0.04	
4th		510 15.0 13.1	620 12.0 11.6	730 2.2 1.2	840 3.1 3.2	950 1.0 1.0	10·6·0 1.10 2.2	
3rd		410 10.0 8.9	520 0.80 0.50	630 0.55 0.40	740 0.50 0.13	850 A 0.12	960 A 0.00	
2nd	310 * 20.0 26.9	420 8.5 7.2	530 14.0 12.3	640 5.5 6.2	750 5.7 6.5	860 2.0 3.0	970 2.1 3.5	
1st	210 * 3.3 4.2	320 A 0.20	430 1.85 1.14	540 1.2 0.55	650 0.60 0.44	760 A 0.00	870 A 0.02	
Equator	220 * >30.0 36.2	330 2.2 1.0	440 16.0 16.5	550 4.0 2.7	660 5.0 5.2	770 0.75 0.66	880 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 VI

Intensity Data for an Oscillation Photograph from (110) with $[1\bar{1}0]$ vertical; oscillation 15 - 45°.

<table>
<tr><th>Layer Line</th><th colspan="10"></th></tr>
<tr><td>8th</td><td colspan="2">10·2·0
3.2 2.9</td><td colspan="2">11·3·0
2.55 1.94</td><td colspan="2">12·4·0
1.20 1.38</td><td colspan="2">13·5·0
0.85 0.97</td><td colspan="2">14·6·0
0.70 0.98</td></tr>
<tr><td>7th</td><td></td><td colspan="2">10·3·0
0.30 0.14</td><td colspan="2">11·4·0
0.60 0.23</td><td colspan="2">12·5·0
A 0.005</td><td colspan="2">13·6·0
A 0.03</td><td></td></tr>
<tr><td>6th</td><td colspan="2">930
5.8 4.7</td><td colspan="2">10·4·0
4.5 4.2</td><td colspan="2">11·5·0
2.5 2.8</td><td colspan="2">12·6·0
1.10 1.79</td><td colspan="2">13·7·0
0.00 1.23</td></tr>
<tr><td>5th</td><td></td><td colspan="2">940
A 0.02</td><td colspan="2">10·5·0
A 0.04</td><td colspan="2">11·6·0
A 0.12</td><td colspan="2">12·7·0
A 0.00</td><td></td></tr>
<tr><td>4th</td><td colspan="2">840
5.0 3.2</td><td colspan="2">950
1.8 1.0</td><td colspan="2">10·6·0
2.5 2.2</td><td colspan="2">11·7·0
0.90 1.04</td><td colspan="2">12·8·0
0.95 1.45</td></tr>
<tr><td>3rd</td><td></td><td colspan="2">850
0.40 0.12</td><td colspan="2">960
A 0.00</td><td colspan="2">10·7·0
A 0.05</td><td colspan="2">11·8·0
A 0.17</td><td></td></tr>
<tr><td>2nd</td><td colspan="2">750
7.0 6.5</td><td colspan="2">860
3.2 3.0</td><td colspan="2">970
3.5 3.5</td><td colspan="2">10·8·0
1.20 1.74</td><td colspan="2">11·9·0
1.10 1.61</td></tr>
<tr><td>1st</td><td></td><td colspan="2">760
A 0.00</td><td colspan="2">870
A 0.02</td><td colspan="2">980
A 0.05</td><td colspan="2">10·9·0
A 0.00</td><td></td></tr>
<tr><td>Equator</td><td colspan="2">660
6.4 5.2</td><td colspan="2">770
1.25 0.66</td><td colspan="2">880
2.6 2.3</td><td colspan="2">990
0.90 0.80</td><td colspan="2">10·10·0
1.05 1.55</td></tr>
</table>

In figure 2, S_{hk0} for several planes are plotted against the chlorine parameter for values between 0.25 and 0.30. All the inequalities used are given in the figure and the arrows designate the regions eliminated by these comparisons. 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}.

In Tables V and VI we have listed the data obtained from two oscillation photographs from (110) with $[1\bar{1}0]$ as the axis of oscillation. They differ in that the data of Table VI are from a photograph prepared with the prism face making an angle of about 15° with the beam in the starting position. 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 times 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 $\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$ have been used in the calculated intensities as well as a temperature correction the nature of which will be explained later.

It will be noted that the structure factors of the two following classes of reflections are quite different:

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

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 $\frac{\sin\theta}{\lambda}$ for the heavier atoms than 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.

The palladium atoms contribute far more than any other kind of atoms to the intensity of lines with h + k even and hence errors in f_{Pd} could cause quite serious disagreements of the kind stated. 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 V and VI 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 crystal 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.

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

In the cation the four ammonia groups form a square configuration about each palladium atom and with the Pd-N separation 2.02 ± 0.05 Å the distance between the NH_3 molecules belonging to the same cation is 2.86 ± 0.05 Å.

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.* This probably accounts for the displacement of H_2O to positions half way between planes of Cl.

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*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.

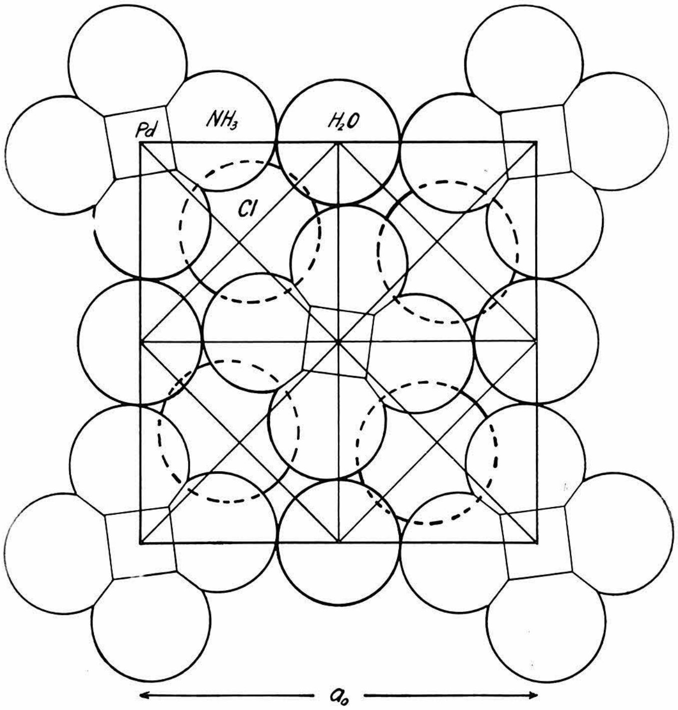

Figure 3

Projection of the structure of

$Pd(NH_3)_4Cl_2 \cdot H_2O$ on the plane (001).

TABLE VII

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 ± 0.05 Å
Cl	8 NH_3	$Cl-NH_3$	3.44 ± 0.1 Å
Cl	2 H_2O	$Cl-H_2O$	3.81 ± 0.1 Å
H_2O	4 Cl	H_2O-Cl	3.81 ± 0.1 Å
H_2O	4 NH_3	H_2O-NH_3	3.16 ± 0.1 Å
NH_3	4 Cl	NH_3-Cl	3.44 ± 0.1 Å
NH_3	1 H_2O	NH_3-H_2O	3.16 ± 0.1 Å
NH_3	2 NH_3	NH_3-NH_3	2.86 ± 0.05 Å
NH_3	1 NH_3	NH_3-NH_3	4.06 ± 0.1 Å

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, 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 crystallizes 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 * 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.

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.

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*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).

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 $a_o = 10.302 \pm 0.03$ Å and $c_o = 4.34 \pm 0.05$ Å. The space group was shown to be C_{4v}^2, V_d^7, or D_{4h}^5, the last 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 0.0 and 0.044. With the following parameter values a good general agreement between the calculated and observed intensities was obtained:

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

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:

Pd-N = 2.02 ± 0.05 Å,
Cl-H_2O = 3.81 ± 0.1 Å,
H_2O-NH_3 = 3.16 ± 0.1 Å,
Cl-NH_3 = 3.44 ± 0.1 Å,
NH_3-NH_3 = 2.86 ± 0.05 Å (in the same cation)
NH_3-NH_3 = 4.06 ± 0.1 Å (in different cations).

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.

REFERENCES

1. R. G. Dickinson, J. Am. Chem. Soc., 44, 774 & 2404 (1922).
2. Linus Pauling, ibid., 53, 1367 (1931).
3. E. G. Cox, J. Chem. Soc., 134, 1912 (1932).
4. A.J.P. Martin, Min. Mag., 22, 519 (1931).
5. L. Pauling and J. Sherman, Z. Krist., 81, 1 (1932).
6. L. Pauling, Proc. Nat. Acad. Sci., 18, 293 (1932).
7. L. Pauling and M.L. Huggins, Z. Krist., to be published.
8. H. Ott, Z. Physik, 22, 201 (1924).
9. R.J. Havighurst, E. Mack, Jr., and F.C. Blake, J. Am. Chem. Soc., 46, 2368 (1924).
10. James and Brindley, Proc. Roy. Soc., A 121, 155 (1928).
11. L. Pauling, Z. Krist., 72, 482 (1930).

The Crystal Structure of Potassium Bromoselenite.

By

J. L. Hoard and **B. N. Dickinson** in Pasadena.

(With 2 figures.)

Potassium bromoselenite is one of a group of compounds of the general formula R_2MX_6 which crystallize as regular octahedra, and presumably have the potassium chlorostannate structure[1]). It has been of interest to confirm this hypothesis in the case of potassium bromoselenite and to determine the single parameter with such care that an accurate value of the bromine-selenium separation in the complex is obtained.

Determination of the Unit Cell and Space Group.

We are indebted to Professor R. G. Dickinson of this Institute for the potassium bromoselenite crystals used in this study. The crystals were octahedra from 1—4 mm. on an edge and were isotropic under a polarizing microscope. Data from an oscillation photograph prepared by reflecting $MoK\alpha$ radiation from a (111) face lead to the spacing $d_{111}/n = 5.983 \pm 0.01$ Å. These data are recorded in Table I. Laue photographs were prepared using radiation from a tube with a tungsten anticathode operated at a peak voltage of about 52 kV, the beam being inclined at various small angles with the normal to (111). Using $a = 10.363 \pm 0.02$ Å, no value of $n\lambda$ calculated from two completely indexed Laue photographs was found to be less than the short wave length limit, 0.24 Å. From this value of the edge of the unit cube and the measured density, 3.61, four molecules were found to exist in the unit cell.

Table I.
Oscillation data from different orders of (111).

Plane	Line	sin θ	d/n
(111)	α	.0594	5.971
(222)	α	.1184	5.991
(444)	α_1	.2366	5.983
	α_2	.2378	5.988

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1) R. G. Dickinson, J. Am. chem. Soc. 44, 276. 1922.

The only planes giving first order reflection on the two Laue photographs were those with all indices odd, so that the structure may be assumed to be based on a face-centered lattice. The Laue photographs through (111) showed a three-fold axis and three planes of symmetry, so that the point-group symmetry is that of T_d, O, or O_h. The space groups isomorphous with these point groups and based upon a face-centered lattice are O^3, O^4, T_d^2, T_d^5, O_h^5, O_h^6, O_h^7, and O_h^8. The observed reflections from planes such as $(\bar{9}95)$ at $n\lambda = 0.40$ Å eliminate T_d^5, O_h^6, and O_h^8; and those from planes such as $(\bar{4}05)$ at $n\lambda = 0.72$ Å eliminate O_h^7 and O_h^8. This leaves O^3, O^4, T_d^2 and O_h^5 to be considered. Since O^4 furnishes no fewer than eight equivalent positions in the unit cell, and four *Se* must be placed, only T_d^2, O^3, and O_h^5 (all without special criteria) remain as possible space groups.

Determination of the Atomic Arrangement.

With four molecules in the unit cell, there must be placed 8 *K*, 4 *Se*, and 24 *Br*. O_h^5 and O^3 furnish exactly the same possibilities in this case. Furthermore there are only two non-equivalent arrangements based upon O_h^5 and O^3, and one of these is immediately eliminated by the observation that (555) reflects more strongly than (333), whereas the structure factor for both of these planes is the same, $\pm 4 f_{Se}$. There remains, therefore, only the following possibility which is also obtainable from T_d^2:

8 *K* in 8e: Face-centered arrangeemnt starting in $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$;
4 *Se* in 4b: Face-centered arrangement starting in $(0, 0, 0)$;
24 *Br* in 24a: Face-centered arrangement starting in $\pm(u, 0, 0; 0, u, 0; 0, 0, u)$.

The above arrangement leads to a structure which gives complete qualitative agreement between calculated and observed intensities for $u = 0.245 \pm 0.003$. All of the remaining essentially distinct structures based on T_d^2 may be eliminated as follows. It is found that the modulus of the structure factors calculated for (111) and (333) for these arrangements cannot be less than $4 f_{Se} - 4 f_K$ ($4 f_K$ and $4 f_{Se}$ for some), whereas (111) is observed to be very weak and (333) is not observed at all. The scattering power of selenium is nearly twice that of potassium, so that it is highly probable that these possibilities are to be excluded and that the first proposed arrangement, which permits the bromine atoms to scatter in opposition to the selenium atoms for odd orders from (111) (the contribution of the potassium atoms being zero), is to be accepted as correct.

Using a horizontal slit system, oscillation photographs for use in making intensity comparisons were prepared by reflecting $MoK\alpha$ radiation filtered through zirconia from a (111) face of potassium bromoselenite. Only orders of (111) were used, the calculated intensity for (nnn) being obtained as follows. The structure factor calculated from the f_0 values of Pauling and Sherman[1]) for the given value of $\frac{\sin\theta}{\lambda}$ was multiplied by the Lorentz and polarization factors, $\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right)^{\frac{1}{2}}$, and by $\sqrt{n}$, and the absolute value of this so-obtained result was taken as the square root of the relative intensity. The factor $\sqrt{n}$ enters since if a horizontal slit system is employed the fraction of the total beam intercepted by the strongly absorbing crystal when in position to reflect is proportional to $\sin\theta$ and so to n. As the temperature factor was not included only intensity inequalities were used for which a plane with a given value of d_{nnn} was observed to reflect more strongly than another with larger d_{nnn}. The procedure is illustrated in Fig. 1, in which $S_{nnn} = \sqrt{I_{nnn}}$ is plotted against the value of the bromine parameter. Thus as (555) is observed to reflect more strongly than (333), only those values for n are possible for which S_{555} is calculated to be larger than S_{333}.

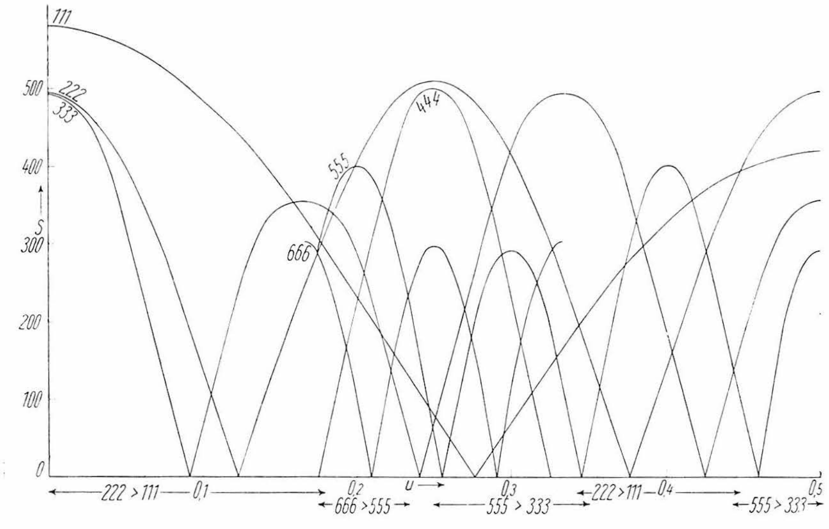

Fig. 1. Calculated intensities for different orders of (111), as functions of the parameter u.

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1) Linus Pauling and J. Sherman, Z. Krist. **81**, 1. 1932.

The visually estimated observed intensities of reflection from various orders of (111) on photographs taken with a horizontal slit system are:

$$(111) = 0.5; \quad (222) = 7.0; \quad (333) = 0;$$
$$(444) = 2.5; \quad (555) = 0.08; \quad (666) = 0.1.$$

The regions eliminated by the observed intensity inequalities are marked with arrows on Fig. 1. As a result the parameter is limited to the range of values between 0.233 and 0.250. Assuming the intensity of (333) to be zero, the calculated value of u is 0.241.

Intensity inequalities appearing on the Laue photographs were used to further limit the possible range of values for the parameter. The procedure was analogous to that employed for the spectral comparisons, except for the omission of the factor $\sqrt{n}$ and $\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right)^{\frac{1}{2}}$. Only intensity inequalities between planes reflecting in the first order with very nearly the same value of $n\lambda$ and with a plane of given d_{hkl} reflecting more strongly than another of larger d_{hkl} were used. The omission of the temperature, polarization, and Lorentz corrections served as factors of safety in making such comparisons.

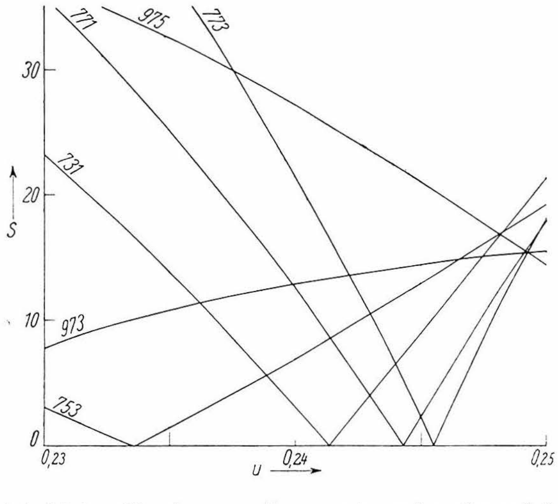

Fig. 2. Calculated intensities for some Laue spots, as functions of the parameter u.

The curves used for the Laue comparisons are plotted in Fig. 2 and the intensity data are listed in Table II. The intensity inequalities used from Table II and the range of values they permit for the parameter are as follows:

$\{753\} \geqq \{731\}$ $0.2388 \leqq u \leqq 0.2482$
$\{975\} > \{773\}$ $0.2375 < u < 0.2495$
$\{975\} > \{771\}$ $u < 0.2491$
$\{973\} > \{773\}$ $0.2422 < u < 0.2495$.

Table II.

Laue intensities used for calculating the parameter.

Plane	d_{hkl}	$n\lambda$	Estimated intensity
$(7\bar{1}\bar{3})$	1.35	0.32	0.075
$(\bar{1}7\bar{3})$	1.35	0.38	0.1
$(7\bar{3}\bar{1})$	1.35	0.43	0.1
$(\bar{7}35)$	1.14	0.38	0.1
$(3\bar{7}5)$	1.14	0.32	0.085
$(73\bar{5})$	1.14	0.41	0.1
$(1\bar{7}7)$	1.04	0.35	0.02
$(7\bar{7}3)$	1.03	0.38	0.03
$(\bar{7}73)$	1.03	0.45	0.05
$(9\bar{7}3)$	0.88	0.43	0.07
$(\bar{9}75)$	0.83	0.35	0.05
$(5\bar{9}7)$	0.83	0.35	0.05
$(\bar{9}57)$	0.83	0.39	0.04

These comparisons justify the selection of 0.245 ± 0.003 as the value of the parameter. The corresponding selenium-bromine separation is 2.54 ± 0.03 Å. Subtracting the value of the normal electron-pair-bond radius of bromine¹), 1,14 Å, a value of 1.40 Å is found for the "octahedral" electron-pair-bond radius of quadrivalent selenium. Using powder and Laue photographs, Sieg²) has recently shown that ammonium bromoselenite has the potassium chlorostannate structure, with $a = 10.46$ Å. He finds 0.24 to 0.25 as the possible range of values for the bromine parameter, the range for the corresponding selenium-bromine separation being 2.51 to 2.63 Å, which includes the range found by us. Subtracting the value $a = 10.36$ for potassium bromoselenite from that $a = 10.46$ for ammonium bromoselenite, 0.10 Å is obtained, which is in agreement with the corresponding difference, 0.09 Å, obtained from potassium and ammonium chlorostannates³).

We are indebted to Professor Linus Pauling for suggesting the study of potassium bromoselenite.

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1) Linus Pauling, Pr. Nat. Acad. Sci. **18**, 293. 1932.

2) Lothar Sieg, Z. anorg. Ch. **207**, 93. 1932.

3) R. G. Dickinson, J. Am. chem. Soc. **44**, 276. 1922.

Summary.

With the aid of oscillation and Laue photographs, potassium bromoselenite has been shown to have the potassium chlorostannate structure. The value of the edge of the unit cell was found to be 10.363 ± 0.02 Å. Complete qualitative agreement between calculated and observed intensities was obtained for $u = 0.245 \pm 0.003$ Å. By substracting the normal electron-pair-bond radius of bromine, 1.14 Å, from the selenium-bromine separation, 2.54 Å, the "octahedral" electron-pair-bond radius of quadrivalent selenium was found to be 1.40 Å.

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The Normal State of the Hydrogen Molecule-Ion*

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A variation function somewhat similar to that applied by Rosen to H_2 is used in the discussion of the normal state of H_2^+.

IN treating the normal state of the hydrogen molecule by the variational method, N. Rosen[1] used an eigenfunction involving the one-electron function

$$\psi=\psi^0+\sigma\psi',$$

in which $\psi^0=(\alpha^3/\pi)^{\frac{1}{2}}e^{-\alpha r_a}$ is a hydrogen-like $1s$ wave function for nucleus a, with effective nuclear charge (in units e) $Z=\alpha a_0$, and $\psi'=(\alpha^5/\pi)^{\frac{1}{2}}r_a e^{-\alpha r_a}\cos\theta_a$ is a hydrogen-like $2p$ function for nuclear charge $2Z$, θ_a being the angle between the nuclear axis and the radius vector from nucleus a to the electron, and σ a parameter. In order to see to what extent this method of treatment of molecules could be expected to be satisfactory in other cases, and whether or not pronounced improvement could be obtained by varying the ratio of the effective nuclear charges in ψ^0 and ψ', we have treated the hydrogen molecule-ion (which has previously been well investigated) by methods similar to Rosen's.

For this purpose we replace Z by $Z'=\epsilon Z$ in ψ'. ψ^0 and ψ' satisfy the equations

$$H_a{}^0\psi^0=Z^2E_0\psi^0 \quad\text{and}\quad H_a{}'\psi'=\epsilon^2Z^2E_0\psi',$$

where

$$H_a{}^0=\frac{-h^2}{8\pi^2m}\nabla^2-\frac{Ze^2}{r_a}\quad\text{and}\quad H_a{}'=\frac{-h^2}{8\pi^2m}\nabla^2-\frac{2Z\epsilon e^2}{r_a},$$

and are normalized and mutually orthogonal.

We write

$$\chi=\psi^0+\phi^0+\sigma(\psi'+\phi')$$

as the complete eigenfunction for the molecule-ion, with ϕ^0 and ϕ' replacing ψ^0 and ψ' for the nucleus b. The Hamiltonian for this problem is

$$H=\frac{-h^2}{8\pi^2m}\nabla^2+e^2\left(\frac{1}{R}-\frac{1}{r_a}-\frac{1}{r_b}\right).$$

The integrals arising from the expression for the energy

$$W=\int\chi H\chi d\tau\Big/\int\chi^2d\tau$$

are listed below using Rosen's notation.

$$I_{00}=\int\psi^0\phi^0d\tau,\quad F_1=\int\frac{(\psi')^2}{r_a}d\tau,\quad J_{00}=\int\frac{\psi^0\phi^0}{r_a}d\tau,$$

$$I_{01}=\int\psi^0\phi'd\tau,\quad G_{00}=\int\frac{(\psi^0)^2}{r_b}d\tau,\quad J_{01}=\int\frac{\psi^0\phi'}{r_a}d\tau,$$

$$I_{11}=\int\psi'\phi'd\tau,\quad G_{01}=\int\frac{\psi^0\psi'}{r_b}d\tau,\quad J_{10}=\int\frac{\psi'\psi^0}{r_a}d\tau,$$

$$F_0=\int\frac{(\psi^0)^2}{r_a}d\tau,\quad G_{11}=\int\frac{(\psi')^2}{r_b}d\tau,\quad J_{11}=\int\frac{\psi'\phi'}{r_a}d\tau.$$

The integrals (I_{01}, G_{01}, J_{01}, and J_{10}) not given in Rosen's paper were evaluated in elliptic coordinates and have the following forms in terms of ϵ and $\rho=\alpha R$:

$$I_{01}=(8\epsilon^{5/2}/(1-\epsilon^2)^4\rho^2)[e^{-\rho}\{(\epsilon^2-1)4\epsilon\rho^2-24\epsilon\rho-24\epsilon\}+e^{-\epsilon\rho}\{(1-\epsilon^2)^2\rho^3-8\epsilon\rho^2(1-\epsilon^2)+24\epsilon^2\rho+24\epsilon\}],$$

$$RJ_{01}=(4\epsilon^{5/2}/(1-\epsilon^2)^3\rho)[-8\epsilon e^{-\rho}(\rho+1)+e^{-\epsilon\rho}\{(1-\epsilon^2)^2\rho^3-4\epsilon(1-\epsilon^2)\rho^2+8\epsilon^2\rho+8\epsilon\}],$$

$$RJ_{10}=(8\epsilon^{5/2}/(1-\epsilon^2)^3\rho)[e^{-\rho}\{(1-\epsilon^2)\rho^2+4\rho+4\}+e^{-\epsilon\rho}\{(1-\epsilon^2)\rho^2-4\epsilon\rho-4\}],$$

$$RG_{01}=(4\epsilon^{5/2}/(1+\epsilon)^5\rho)[-e^{-(1+\epsilon)\rho}\{(1+\epsilon)^3\rho^3+4(1+\epsilon)^2\rho^2+8(1+\epsilon)\rho+8\}+8].$$

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* Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 363.

[1] N. Rosen, Phys. Rev. **38**, 2099 (1931).

The energy can be expressed as

$$W=2Z^2E_0A/d+2ZE_0B/d,$$

where

$$A=1+I_{00}+\sigma(1+\epsilon^2)I_{01}+\sigma^2\epsilon^2(1+I_{11})-(2/\rho)[RF_0+RJ_{00}+\sigma(RJ_{01}+2\epsilon RJ_{10})+2\epsilon\sigma^2(RF_1+RJ_{11})],$$

$$B=(2/\rho)[RF_0+RG_{00}-I_{00}-1+2RJ_{00}+2\sigma(RJ_{01}-I_{01}+RG_{01}+RJ_{10})+\sigma^2(RF_1-I_{11}+RG_{11}+2RJ_{11}-1)],$$

$$d=2[1+I_{00}+2\sigma I_{01}+\sigma^2(1+I_{11})].$$

This expression for the energy can be minimized with respect to Z, giving

$$Z=-B/2A,$$

which when combined with the expression for W gives

$$W=-E_0B^2/2dA.$$

RESULTS

On placing $\epsilon=1$ and minimizing the energy relative to Z, σ, and ρ, the values $\epsilon=1$, $\rho=2.50$, $\sigma=0.1605$, $Z=1.2537$, and $W=-16.242$ volt-electrons were obtained. The value given for W by Burrau's[2] and Hylleraas'[3] exact treatments is -16.30 volt-electrons. Consequently the Rosen-type function leads to an error of 0.06 volt-electron, which is rather unsatisfactory, in view of the fact that Guillemin and Zener[4] obtained the value $W=-16.30$ volt-electrons by using a two parameter function no more complicated than the Rosen-type function.

It was thought that the error of 0.06 volt-electron in W might be removed by varying ϵ. On carrying out this variation for the values of σ, Z, and ρ given above, then varying σ, and finally varying ϵ again, there were obtained the values

$$\rho=2.50,\qquad \epsilon=1.15,\qquad \sigma=0.145,$$
$$Z=1.247,\quad Z'=1.434,\quad r_0=1.06\text{A},$$

and $W=-16.257$ volt-electrons. The discrepancy in the energy has, it is seen, been reduced by only one-third by the variation of ϵ, being still 0.04 volt-electron. (The value of r_0 obtained is the same as that found by Burrau and Hylleraas and also found experimentally for excited states of H_2.) We accordingly conclude that the Rosen-type function for the hydrogen molecule-ion is not so satisfactory as the Guillemin-Zener-type function of equivalent complexity, and that no pronounced improvement results from a variation of ϵ from 1. Change of Rosen's treatment for the hydrogen molecule by introducing ϵ in his function and varying it can hence be expected to lead to little improvement over his results.

It must be mentioned that the error in W of 0.04 volt-electron is only about 8 percent as great as that for a function with $\sigma=0$, i.e., involving 1*s* functions alone, for which Finkelstein and Horowitz[5] obtained $Z=1.228$, $r_0\cong 1.06$A, and $W=-15.75$ volt-electrons, so that very marked improvement in the wave function is obtained by introducing the Rosen-type term ψ'.

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[2] An account of this work is given by Linus Pauling, Chem. Rev. **5**, 173 (1928).

[3] E. A. Hylleraas, Zeits. f. Physik, **71**, 739 (1931).

[4] V. Guillemin and C. Zener, Proc. Nat. Acad. **15**, 314 (1929).

[5] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).