The Crystal Structure of Ammonium Trihydrogen Paraperiodate, $(NH_4)_2H_3IO_6$

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Introduction.—An investigation of the crystal structure of ammonium paraperiodate has been carried out to settle definitely the question of the formula of the substance as $(NH_4)_2H_3IO_6$ or $(NH_4)_4I_2O_9 \cdot 3H_2O$, to determine the nature of the IO_6^{5-} group and to investigate the role of hydrogen bonds in this crystal. In addition, it is felt that the recent development of methods for interpreting bond distances[1] makes complete structure determinations of some of the salts of halogen oxy acids desirable for the purpose of discussing the irregularities in this series of compounds.

The results of this work show that the formula $(NH_4)_2H_3IO_6$ is correct, and that the configuration of the oxygen atoms around the iodine atoms is that of a nearly regular octahedron. The structure indicates clearly the existence of hydrogen bonds between pairs of oxygen atoms. These bonds are of decided importance in determining the structure.

Procedure.—Single crystals of ammonium paraperiodate were prepared by crystallization from ammonium periodate solution on the addition of an excess of concentrated ammonia. The crystals obtained in this way were small truncated rhombohedra about 0.5 mm. on an edge, with the most frequently developed faces (10·1) and (00·1) (relative to hexagonal axes). Goniometric measurements on these faces gave the angle (10·1):(00·1) equal to 61°38'. The value given by Groth[2] is 61°45'. This agreement was taken as sufficient evidence of the identity of the crystals and no analysis was made.

The crystals were found to decompose on exposure to moist air, probably giving ammonia, water, and ammonium periodate. This last compound was identified by means of a powder pattern obtained in the course of an X-ray exposure of a decomposing crystal. It was originally proposed by Eakle[3] that this decomposition involved the loss of water from crystals having the formula $(NH_4)_4I_2O_9 \cdot 3H_2O$.

Unit and Space Group.—Laue photographs were prepared using general radiation from a tungsten target. The symmetric photographs taken with the beam normal to the (00·1) face gave the Laue symmetry C_{3i}. The absence of planes of symmetry was quite marked, eliminating the higher symmetry D_{3d}.

(1) Pauling, Brockway and Beach, THIS JOURNAL, **57**, 2705 (1935).
(2) Groth, "Chem. Krist.," Vol. II, p. 181.
(3) Eakle, Z. Krist., **26**, 574 (1896).

Oscillation pictures gave the following values for the dimensions of the unit:

$$a_0 = 6.88 \pm 0.005 \text{ Å.}, \quad c_0 = 11.10 \pm 0.05 \text{ Å.}$$

The data are given in Table I; the c-dimension is obtained from layer line measurements as indicated.

TABLE I

EQUATORIAL MEASUREMENTS

$(hk \cdot l)$	$d_{exptl.}$	$d_{calcd.}$
(30·0)	1.784 Å.	1.784 Å.
(60·0)	0.991	0.993
(14·0)	1.300	1.300
(25·0)	0.953	0.954
(17·0)	.787	.789
(36·0)	.750	.751
(55·0)	.686	.688
(28·0)	.650	.650

Layer Line Measurements

Layer line	$d_{(00 \cdot 1)}$, Å.
1	11.147
2	11.148
3	11.126
4	11.107
5	11.108
6	11.070
7	11.072
8	11.080
9	11.083

Average 11.10 Å.

Laue and oscillation pictures showed the regular absence of $(hk \cdot l)$ when $h - k + l \neq 3n$. Of the two possible space groups C_{3i}^2 and C_3^4, the choice of the higher symmetry C_{3i}^2 can be made on the basis of crystallographic data.

The density was measured only roughly and found to be 3.00 ± 0.5. This accuracy is sufficient to give the number of molecules in the unit since the smallest (rhombohedral) unit must contain one, two, three, etc., molecules. The assumption of one molecule of $(NH_4)_2H_3IO_6$ in this unit leads to a density 2.85. Obviously the formula $(NH_4)_4I_2O_9 \cdot 3H_2O$ is out of the question.

Determination of the Structure.—The atoms were assigned the positions given below (referred to hexagonal axes)[4]

(4) "Int. Tab. z. Bestimmung v. Kristalstrukturen."

8I   at 0 0 0; $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{3}$; $\frac{2}{3}$ $\frac{1}{3}$ $\frac{2}{3}$

6NH₄ at 0 0 0; $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{3}$; $\frac{2}{3}$ $\frac{1}{3}$ $\frac{2}{3}$; +0 0 w; 0 0 $\bar{w}$

180   at 0 0 0; $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{3}$; $\frac{2}{3}$ $\frac{1}{3}$ $\frac{2}{3}$; $\pm x\, y\, z$

$\bar{y}\, x - y\, z;\ y - x\, \bar{x}\, z$

The effect of the nine hydrogen atoms on the intensities of reflection was neglected, and a consideration of their positions will come later in the discussion of the structure.

An evaluation of the parameters was first made using the reflections ($hk\cdot0$). Oscillation pictures were taken with Mo K radiation using a small crystal with the c-axis vertical. It was found that as a first approximation the crystal could be considered as spherical so that absorption effects could be neglected in spite of the presence of iodine in the crystal. Only in the cases of some of the weaker, more complicated reflections was there any evidence that absorption might be causing difficulty. The crystals were covered with a thin layer of vaseline which apparently served to prevent decomposition since no powder lines were observed when this was done.

The relative intensities were obtained by taking pictures at different exposure times and comparing spots of equal intensity in the usual way. The reflections were also compared with a calibrated scale. The results of the two methods were checked one against the other and the agreement found satisfactory. The relative intensities obtained in this way are probably reliable to 30% for the reasonably intense reflections. Theoretical values for the relative intensities of reflection from the prism planes were calculated as functions of x and y by means of the formula

$$I = C \frac{1 + \cos^2 2\Theta}{\sin 2\Theta} |S|^2 \exp. - \beta \left(\frac{\sin \Theta}{\lambda}\right)^2$$

where Θ is the Bragg angle, $|S|^2$ the square of the absolute values of the structure factor and $\exp. - (\sin \Theta/\lambda)^2$ the temperature factor. The factor β was assigned arbitrarily the value 1.5, which accounts satisfactorily for the decrease in the intensities with increasing sin Θ. The f-values for iodine and oxygen were taken from the tables of Pauling and Sherman.[5] The experimentally determined f-curve for NH₄ was taken from the work of Wyckoff and Armstrong on ammonium chloride.[6]

By comparing the relative intensities of the 15 available prism reflections with the calculated values in the usual way, the parameters x and y were evaluated: $x = 0.235 \pm 0.01$; $y = 0.215 \pm 0.01$.

(5) Pauling and Sherman, Z. Krist., 81, 1 (1932).
(6) Wyckoff and Armstrong, ibid., 72, 319 (1930).

A similar procedure was carried out to obtain the values of w and z. Since the form of the crystals made it difficult to obtain basal plane reflections uninfluenced by absorption, the layer line reflections were used in this determination. Layer lines beyond the sixth were not used. The evaluation of w was necessarily inaccurate because of the low scattering power of NH₄⁺ and the small percentage of the ion in the crystal. The values obtained are

$z = 0.105 \pm 0.015$ $w = 0.34 \pm 0.025$

In order to obtain more accurate parameter values and to check the limits of error, an analysis of the Laue photographs was made with the use of an Astbury alpha-ray integrating microphotometer[7] constructed by Dr. J. H. Sturdivant of this Laboratory. The relative intensities obtained by this method are probably reliable to 15%. The final parameter values obtained are

$x = 0.232 \pm 0.003$ $z = 0.105 \pm 0.005$

$y = .216 \pm .003$ $w = .34 \pm .01$

TABLE II

Planes considered ($hk\cdot l$)/($hk\cdot l$)	Ratio of intensities Calcd.	Obsd.
($\bar{3}4\cdot1$)/($\bar{4}3\cdot1$)	0.98	1.00
($\bar{6}5\cdot2$)/($\bar{5}6\cdot2$)	1.56	1.62
($\bar{7}5\cdot3$)/($\bar{5}7\cdot3$)	2.07	2.11
($\bar{7}2\cdot3$)/($\bar{2}7\cdot3$)	1.96	1.70

TABLE III

($hk\cdot l$)	$I^{1/2}_{calcd.}$	$I^{1/2}_{obsd.}$	($hk\cdot l$)	$I^{1/2}_{calcd.}$	$I^{1/2}_{obsd.}$
($03\cdot0$)	3.78	3.38	($25\cdot6$)	0.69	0.72
($06\cdot0$)	1.13	1.16	($25\cdot\bar{6}$)	1.04	1.05
($09\cdot0$)	0.56	0.61	($\bar{2}6\cdot1$)	0.68	0.89
($22\cdot0$)	2.38	2.24	($\bar{2}6\cdot2$)	1.50	1.48
($33\cdot0$)	1.12	1.17	($\bar{2}6\cdot4$)	1.04	1.09
($44\cdot0$)	1.04	1.02	($26\cdot5$)	1.16	1.34
($55\cdot0$)	0.55	0.59	($\bar{2}5\cdot1$)	1.62	1.67
($14\cdot0$)	2.75	2.41	($\bar{2}5\cdot2$)	0.95	1.18
($41\cdot0$)	2.25	2.24	($\bar{2}5\cdot4$)	1.83	1.73
($25\cdot0$)	0.88	0.89	($\bar{2}5\cdot5$)	1.62	1.61
($52\cdot0$)	.95	.95	($\bar{2}7\cdot3$)	.97	0.97
($17\cdot0$)	.69	.67	($\bar{2}7\cdot\bar{3}$)	1.15	1.18
($71\cdot0$)	.59	.62	($\bar{2}7\cdot6$)	0.89	1.00
($28\cdot0$)	.48	.45	($\bar{2}7\cdot\bar{6}$)	.79	0.95
($82\cdot0$)	.30	.39	($15\cdot1$)	1.22	1.31
($06\cdot3$)	.99	1.09	($15\cdot\bar{2}$)	0.90	1.02
($06\cdot\bar{3}$)	1.25	1.24	($03\cdot3$)	2.70	2.64
($04\cdot1$)	3.12	2.65	($03\cdot\bar{3}$)	2.92	3.02
($04\cdot\bar{2}$)	2.48	2.35	($17\cdot3$)	0.71	0.71
($05\cdot\bar{1}$)	1.81	1.79	($17\cdot\bar{3}$)	.57	.50
($05\cdot\bar{2}$)	1.38	1.52	($\bar{2}4\cdot3$)	1.64	1.76
($14\cdot3$)	1.39	1.45	($\bar{2}4\cdot\bar{3}$)	3.20	3.20
($14\cdot\bar{3}$)	1.50	1.58	($36\cdot3$)	0.62	0.63
($25\cdot3$)	1.37	1.37	($36\cdot\bar{3}$)	.60	.64
($25\cdot\bar{3}$)	0.77	0.67	($45\cdot1$)	.63	.67

(7) Astbury, Proc. Roy. Soc. (London), 123, 575 (1929).

Table II gives the results of the work with the alpha-ray photometer. The comparisons are not numerous, but many pairs of spots had to be eliminated since the values of λ were in the neighborhood of 0.37 Å., the absorption limit of iodine. A comparison of observed intensities and intensities calculated on the basis of the final parameter values is given in Table III.
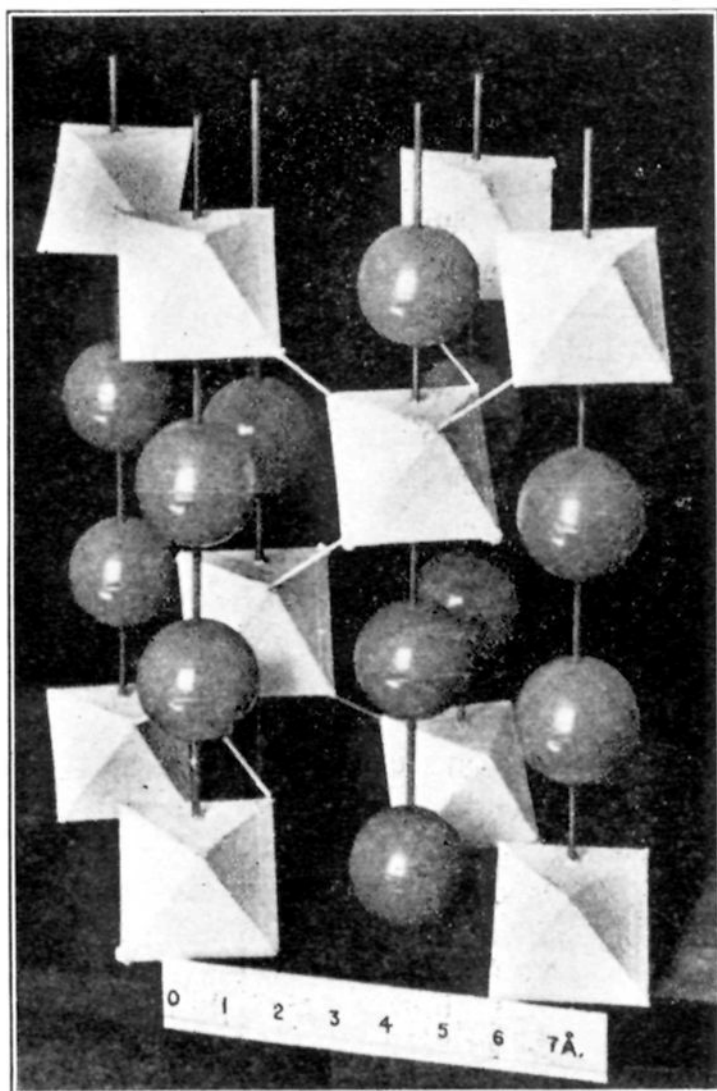

Fig. 1.—Photograph of the hexagonal unit cell of ammonium paraperiodate. The IO_6 groups are represented by the white octahedra, the NH_4^+ ions by darker balls. Hydrogen bonds are indicated by small metal tubes connecting corners of the octahedra.

Discussion of Structure

The Paraperiodate Group.—The parameter values obtained as indicated lead to the structure shown in Fig. 1, where the IO_6^{5-} ions are shown as white octahedra. The iodine to oxygen distance is found to be 1.93 $\pm$ 0.03 Å. Each oxygen atom has four near neighbors in the same octahedron: two at 2.67 $\pm$ 0.02 Å. in a plane parallel to the basal plane, and two above (or below) at a distance of 2.75 $\pm$ 0.05 Å. It is difficult to say anything definite about the apparent stretching of the IO_6^{5-} group along the c-axis since the deviation from regularity is just on the borderline of experimental error; nevertheless it seems probable that this small distortion exists, because of the fact that the forces in the crystal would tend to produce just the distortion indicated by the parameter determination. This effect will be discussed later.

The bond distance I–O = 1.93 Å. may be discussed in two ways. From the ionic point of view one might anticipate a distance of about 1.90 Å., the sum of the ionic radii. The distance of closest approach of the oxygen atoms is also approximately what one would expect.

If the IO_6^{5-} group is considered to be a covalent radical the I–O bond would be regarded as having about 10% double-bond character causing the shortening of the bond distance from the sum of the covalent radii[8] 1.99 to 1.93 Å. The value given for the sum of the covalent radii is the sum of the normal radii. This is open to some question because of the difference between the nature of the bonds in IO_6^{5-} and the compounds from which the normal radius was obtained. One would, however, expect an increase in interatomic distance over the sum of the tetrahedral radii 1.93 Å. due to increase in coördination number, so that it may be said that, from this point of view, some double bond character must be attributed to the I–O bond to account for the interatomic distance. The oxygen–oxygen distances in the octahedra are of the magnitude to be expected.

Hydrogen Bonds.—Each oxygen atom has three close oxygen neighbors in other IO_6 groups— one at a distance 2.60 $\pm$ 0.05 Å. and two at 3.02 $\pm$ 0.05 Å. The short distance corresponds to a relatively strong hydrogen bond and the longer distances to non-bonded contacts. The hydrogen bonds are indicated in Fig. 1 by small metal tubes connecting the corners of octahedra. The angle between the O–H–O bond and the I–O bond is calculated to be 112°30′.

With the hydrogen bonds located in this way it is possible to give approximate positions to the hydrogen atoms. If one uses the nine special positions of C_{3i}^2: $\frac{1}{2} 0 \frac{1}{2}$; $0 \frac{1}{2} \frac{1}{2}$; $\frac{1}{2} \frac{1}{2} \frac{1}{2}$; + $0\ 0\ 0$; $\frac{1}{3} \frac{2}{3} \frac{1}{3}$; $\frac{2}{3} \frac{1}{3} \frac{2}{3}$, the hydrogen atoms may be placed half way between the centers of the oxygen atoms assumed to be connected by hydrogen bonds. Other work shows that the hydrogen atoms in hydrogen bonds are generally associated more closely with one or the other of

(8) Pauling and Huggins, Z. Krist., **87**, 205 (1934).

the bonded oxygen atoms; these positions of the atoms above may represent mean positions of the hydrogen atoms in the crystal.

Structure in General.—If it is assumed for the purpose of comparison that in the absence of hydrogen bonds the structure of this crystal would be determined by the ammonium and paraperiodate ions then the crystal might well have the structure of $(NH_4)_2PtCl_6$. The structure described above is closely similar to the structure of ammonium chloroplatinate, the differences being that the axial ratio (considering the hexagonal unit of $(NH_4)_2PtCl_6$) has greatly decreased and the IX_6 groups have been rotated nearly 30° about the threefold axis leading to a more nearly close packed arrangement of the X atoms. The effects seem to be directly attributable to the introduction of hydrogen bonds into the hypothetical structure proposed. As can be seen in Fig. 1 the hydrogen bonds are tending to pull the IO_6^{5-} groups closer together along the c-axis and to rotate them. The decrease in the c-dimension probably necessitates closer packing and an increase in the a-dimension, contributing to the decrease in the axial ratio. The distortion of the IO_6 mentioned previously may well arise from the disposition of hydrogen bonds.

The effect of this decrease in the axial ratio is to bring the ammonium ions very close together particularly in the c-direction, where the N–N distance is 3.55 Å. compared to 4.92 in $(NH_4)_2$-$PtCl_6$ (3.84 in NH_4Cl). The N–N separation in $(NH_4)_2H_3IO_6$ in planes parallel to the basal plane is 3.97 Å. This effect may be of some importance in accounting for the basal cleavage of this crystal, since the repulsive forces between ammonium ions will be greater parallel to the c-axis than perpendicular to it, as can readily be seen from the distances given above. In this connection it is interesting to note the observations of Eakle on the growth of the crystals. He found that when a great excess of ammonium hydroxide was added to ammonium periodate solutions the resulting crystals showed about equal develop-

ment of (10·1) and (00·1) faces. When the solution became more dilute with respect to ammonium hydroxide the crystals developed in the form of plates perpendicular to the c-axis corresponding to a small rate of growth in the c-direction. This suggests that the close packing together of ammonium ions along the c-axis is attended by a considerable potential energy increase and that in the presence of a great excess of ammonium hydroxide the growth of the crystal is determined by factors other than the NH_4^+ concentration. In dilute ammonia solutions the packing of NH_4^+ along the c-axis becomes the rate determining step. This consideration may well have some bearing on the cleavage of the crystal although the explanation is unquestionably greatly oversimplified, particularly since the effect of hydrogen bonds and the structure in general has not been taken into account.

I am indebted to Professor Linus Pauling for his suggestion of this research and the interest he has taken in it.

Summary

A determination of the structure of ammonium trihydrogen paraperiodate has been carried out to establish the formula of the substance and investigate the IO_6^{5-} group and the role of hydrogen bonds in the structure. The formula has been shown definitely to be $(NH_4)_2H_3IO_6$.

The paraperiodate group has been found to have an octahedral arrangement of oxygen atoms around the iodine, possibly somewhat distorted by the hydrogen bonds. The iodine–oxygen separation is 1.93 ± 0.03 Å., as determined in this work.

Each oxygen atom has three oxygen neighbors in other octahedra, one at 2.60 Å., and two at 3.02 Å. The short O–O distance is believed to be attributable to the existence of a hydrogen bond. The influence of the hydrogen bonds on the structure and on some of the properties of the crystal is discussed.