The Structure of $(NH_4)_3ClS_2O_6$

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The crystal structure of $(NH_4)_3ClS_2O_6$ has been determined. The cell dimensions are $a = 12 \cdot 64$, $b = 12 \cdot 48$, $c = 6 \cdot 08$ Å and the space group is *Pbam*. The structure is pseudo-tetragonal and is isostructural with the mixed salts $NaK_5Cl_2(S_2O_6)_2$ and $NaK_2ClS_2O_6$.

Introduction

A mixed salt of ammonium dithionate and ammonium chloride has been described by Foch & Klus (1888). It turns out to be the compound $(NH_4)_3ClS_2O_6$. There are two other known compounds of the general formula $R_3ClS_2O_6$, where R is one or more monovalent cations. These were described by Buckley (1951) and analysed in detail by Stanley (1953). Their formulae were $NaK_5Cl_2(S_2O_6)_2$ and $NaK_2ClS_2O_6$. The two compounds were very similar in structure.

Experimental

Ammonium dithionate was prepared from equimolar solutions of ammonium sulphate and barium dithionate. The barium sulphate was removed by filtering and an equimolar solution of ammonium chloride added to the filtrate. The crystals which formed on evaporation were unlike those of either ammonium chloride, barium dithionate or ammonium dithionate. The crystals were badly formed needles.

Precession and Weissenberg photographs demonstrate that the crystal is orthorhombic and the systematic absences, $0kl$ with k odd and $h0l$ with h odd indicate that the space group is either *Pba*2 or *Pbam*. The crystals did not exhibit a measurable piezo-electric effect. The unit-cell dimensions are $a = 12 \cdot 64 \pm 0 \cdot 04$, $b = 12 \cdot 48 \pm 0 \cdot 04$, $c = 6 \cdot 08 \pm 0 \cdot 06$ Å. The calculated volume of the unit cell is $959 \cdot 1$ Å^3 and the density, measured by flotation is $1 \cdot 71 \pm 0 \cdot 1$ g.cm^{-3}. There is only one possible formula for the unit-cell contents to satisfy these measurements; this is: $4[(NH_4)_3ClS_2O_6]$.

The intensities of the reflexions in the [001] and the [010] zones were recorded on multiple film Weissenberg photographs with Cu $K\alpha$ radiation, and were estimated visually. The crystals were small and ill formed and no correction was made for absorption. The intensities were put on an approximate absolute scale using the method of Wilson (1942).

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Determination of the structure

The Patterson projection on (001) gave a very good idea of the orientation of the dithionate ions and of the position of the chlorine ions. A trial structure was postulated with the dithionate ion lying on twofold axes in two non-equivalent sets of positions at $0,0$ and $\frac{1}{2},\frac{1}{2}$ and at $\frac{1}{2},0$ and $0,\frac{1}{2}$. The chlorine ion was put at $\frac{1}{4},\frac{1}{4}$. The phases of the structure factors were calculated using the positions of these ions only, and a synthesis of the projection of the electron density calculated using these phases showed the main features of the structure. One of the ammonium ions appeared to be coincident (in projection) with the chlorine ion at $\frac{1}{4},\frac{1}{4}$. Refinement of this projection was continued using difference syntheses (Cochran, 1951) until the residual, $R = \Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|$, was reduced to $0 \cdot 20$.

The projection on (010) was assumed to be centrosymmetric (*i.e.* space group *Pbam*) and using the x coordinates for the projection on (001) and packing considerations, a satisfactory set of initial coordinates was determined. There is a great deal of overlap in this projection and refinement by Fourier and difference-Fourier syntheses would be slow and uncertain.

The final refinement of both projections was completed using the method of Bhuiya & Stanley (1963). The residuals were reduced to $0 \cdot 18$ and $0 \cdot 14$ in the projections on (001) and (010) respectively, and the final general isotropic temperature coefficients were $4 \cdot 1$ Å^2 and $3 \cdot 7$Å^2. The analytical scattering factors of Forsyth & Wells (1959) were used throughout the calculations. The final coordinates are given in Table 1, and the observed and final calculated structure factors in Table 2.

Table 1. *Final fractional atomic coordinates*

	x	y	z
Cl⁻	0·247	0·262	0·500
S	0·415	0·482	0·000
S(1)	0·476	0·081	0·000
O(1)	0·356	0·075	0·000
O(2)	0·518	0·126	0·218
O(1′)	0·423	0·367	0·000
O(2′)	0·380	0·532	0·211
NH₄⁺	0·313	0·006	0·500
NH₄⁺	0·497	0·315	0·500
NH₄⁺	0·217	0·245	0·000

Table 2. Observed and final calculated structure factors

h	k	ℓ	|F_o|	F_c	h	k	ℓ	|F_o|	F_c	h	k	ℓ	|F_o|	F_c	h	k	ℓ	|F_o|	F_c	h	k	ℓ	|F_o|	F_c	h	k	ℓ	|F_o|	F_c
2	0	0	73	72	2	3	0	49	42	1	6	0	10	-13	0	9	0	<2	0	5	12	0	<2	-1	0	0	2	175	151
4	0	0	63	54	3	3	0	9	9	2	6	0	29	30	1	9	0	2	-2	6	12	0	<2	-2	2	0	2	27	-34
6	0	0	17	-17	4	3	0	5	5	3	6	0	28	-36	2	9	0	2	-12	7	12	0	5	6	4	0	2	48	56
8	0	0	54	54	5	3	0	51	-39	4	6	0	57	-51	3	9	0	5	-6	8	12	0	3	-1	6	0	2	25	-36
10	0	0	4	11	6	3	0	31	30	5	6	0	21	13	4	9	0	3	7	9	12	0	8	-3	8	0	2	3	-3
12	0	0	15	16	7	3	0	5	5	6	6	0	4	-3	5	9	0	19	-20	10	12	0	3	-4	10	0	2	7	-8
14	0	0	4	-4	8	3	0	5	-2	7	6	0	11	-10	6	9	0	9	-7						12	0	2	24	33
					9	3	0	8	15	8	6	0	32	-23	7	9	0	9	-11	0	13	0	<2	0	14	0	2	<2	2
0	1	0	<1	0	10	3	0	6	4	9	6	0	9	-11	8	9	0	22	-23	1	13	0	12	-12					
1	1	0	2	1	11	3	0	<2	1	10	6	0	25	24	9	9	0	3	-5	2	13	0	6	3	0	0	3	5	6
2	1	0	14	15	12	3	0	2	-2	11	6	0	17	-18	10	9	0	32	-31	3	13	0	3	2	2	0	3	54	46
3	1	0	52	-56	13	3	0	5	3	12	6	0	9	7	11	9	0	<2	0	4	13	0	8	9	4	0	3	30	-30
4	1	0	39	36	14	3	0	11	8	13	6	0	4	3	12	9	0	7	-6	5	13	0	5	-1	6	0	3	5	-5
5	1	0	132	-117						14	6	0	11	3	13	9	0	2	2	6	13	0	4	5	8	0	3	32	-32
6	1	0	9	-13	0	4	0	58	58											7	13	0	4	-5	10	0	3	10	9
7	1	0	48	-42	1	4	0	47	-53	0	7	0	<1	0	0	10	0	2	-5	8	13	0	<2	3	12	0	3	<2	2
8	1	0	9	9	2	4	0	122	-120	1	7	0	34	34	1	10	0	21	19	9	13	0	1	-2	14	0	3	12	13
9	1	0	11	9	3	4	0	19	-25	2	7	0	1	-7	2	10	0	24	22										
10	1	0	4	-10	4	4	0	22	-26	3	7	0	3	-3	3	10	0	18	14	0	14	0	2	-1	0	0	4	140	137
11	1	0	18	12	5	4	0	2	0	4	7	0	0	-1	4	10	0	6	-5	1	14	0	6	5	2	0	4	9	20
12	1	0	3	3	6	4	0	63	-63	5	7	0	28	-32	5	10	0	36	31	2	14	0	13	4	4	0	4	32	31
13	1	0	12	10	7	4	0	9	-4	6	7	0	20	-24	6	10	0	12	13	3	14	0	4	-5	6	0	4	17	-13
14	1	0	4	1	8	4	0	<2	1	7	7	0	6	-9	7	10	0	<2	2	4	14	0	2	-1	8	0	4	11	21
15	1	0	6	4	9	4	0	49	-39	8	7	0	10	-11	8	10	0	6	-11	5	14	0	4	4	10	0	4	<2	1
16	1	0	3	3	10	4	0	6	-7	9	7	0	<2	-1	9	10	0	8	9	6	14	0	5	5	12	0	4	13	15
					11	4	0	16	-15	10	7	0	13	-9	10	10	0	9	5	7	14	0	13	-12					
0	2	0	60	71	12	4	0	15	8	11	7	0	0	-4	11	10	0	1	-4						0	0	5	40	46
1	2	0	8	-8	13	4	0	5	-13	12	7	0	5	-2						0	15	0	<2	0	2	0	5	47	47
2	2	0	94	93						13	7	0	3	3	0	11	0	<2	0	1	15	0	4	-7	4	0	5	19	-20
3	2	0	<1	0	0	5	0	<2	0	14	7	0	4	8	1	11	0	5	-6	2	15	0	11	9	6	0	5	4	4
4	2	0	149	-121	1	5	0	99	102						2	11	0	4	-1	3	15	0	<2	1	8	0	5	7	-3
5	2	0	31	38	2	5	0	<2	-11	0	8	0	49	48	3	11	0	2	10	4	15	0	7	5	10	0	5	12	10
6	2	0	15	15	3	5	0	46	46	1	8	0	8	-9	4	11	0	<2	0	5	15	0	3	-2	12	0	5	9	-5
7	2	0	13	-7	4	5	0	23	22	2	8	0	20	-19	5	11	0	<2	4										
8	2	0	22	-18	5	5	0	2	2	3	8	0	32	29	6	11	0	<2	5	0	16	0	4	4	0	0	6	54	50
9	2	0	26	-20	6	5	0	19	19	4	8	0	10	17	7	11	0	<2	1	1	16	0	3	-3	2	0	6	<2	1
10	2	0	20	20	7	5	0	15	25	5	8	0	15	15	8	11	0	19	-17						4	0	6	15	14
11	2	0	15	-11	8	5	0	25	27	6	8	0	32	-29	9	11	0	0	3	0	0	1	107	107	6	0	6	8	-11
12	2	0	7	-10	9	5	0	13	18	7	8	0	19	20	10	11	0	12	-14	2	0	1	103	122	8	0	6	4	6
13	2	0	2	8	10	5	0	<2	-1	8	8	0	3	-2	11	11	0	2	3	4	0	1	59	-63					
14	2	0	6	4	11	5	0	3	3	9	8	0	6	-9						6	0	1	2	-2	0	0	7	<2	0
15	2	0	<1	0	12	5	0	3	8	10	8	0	<2	0	0	12	0	22	14	8	0	1	22	-22	2	0	7	19	12
16	2	0	6	-5	13	5	0	3	3	11	8	0	4	4	1	12	0	6	-6	10	0	1	16	17	4	0	7	6	-7
					14	5	0	7	7	12	8	0	16	13	2	12	0	4	-9	12	0	1	12	-5					
0	3	0	<1	0						13	8	0	3	3	3	12	0	19	15	14	0	1	13	13					
1	3	0	42	55	0	6	0	24	-25	14	8	0	1	-1	4	12	0	15	12	16	0	1	20	-17					

Discussion

The accuracy of the bond lengths given in Table 3 was determined from the figures given by Stanley (1964, 1965) relating the standard deviation of a coordinate to the residual. Although these figures relate to an all carbon atom structure a good approximation in a structure containing a variety of atoms should be obtained by weighting the standard deviation of the coordinates of the atoms according to the inverse of their atomic number. The dimensions of the dithionate ion given in Table 3 are compared with other determinations in Table 4.

Table 3. Dimensions of the dithionate ion

Bond	Ion 1 (Å)	Ion 2 (Å)
S——S	2·13 ± 0·04	2·16 ± 0·04
S——O(1)	1·41 ± 0·06	1·44 ± 0·06
S——O(2)	1·53 ± 0·06	1·50 ± 0·06
O(1)–O(2)	2·45 ± 0·07	2·47 ± 0·07
O(2)–O(2)	2·65 ± 0·07	2·57 ± 0·07

The chlorine ions are octahedrally coordinated to six ammonium ions with an average distance of 3·2 Å (variation 3·08 to 3·34 Å) and to eight oxygen atoms from the dithionate ions, in the form of a distorted cube, at an average distance of 3·87 Å (variation 4·11 to 3·69 Å).

The crystal is isostructural with the salts in the series previously investigated. Table 5 gives the unit-cell dimensions and the space groups of the three materials, in the same orientation, for comparison, and projections of the three structures in the same orientation are given in Fig. 1.

Note added in proof: – The results given in this paper appear to verify those of Alvarez, Sotoca & Verdier (1966), which were not known to the present authors until the paper was about to appear in print.

Table 4. *Comparison with other determinations*

Bond	Mean length					
	(1)	(2)	(3)	(4)	(5)	(6)
S–S	2·15 ± 0·03	2·08 ± 0·04	2·15 ± 0·0	2·16	2·17	2·08
S–O	1·50 ± 0·04	1·48 ± 0·06	1·43 ± 0·05	1·45	1·47	1·50

(1) Present work.
(2) Stanley (1953).
(3) Stanley (1956).
(4) Martinez, Garcia-Blanco & Rivoir (1950).
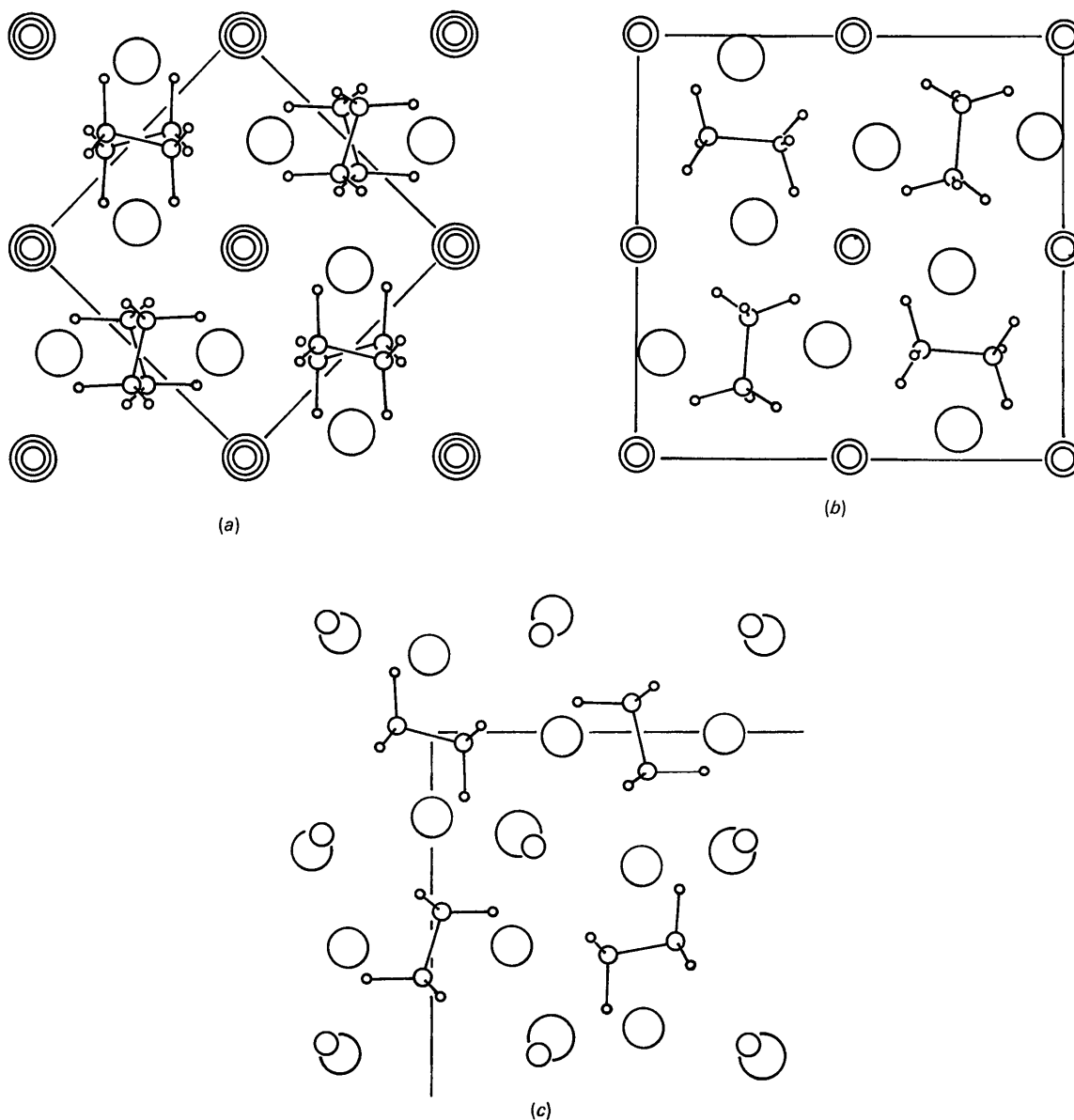(5) Garcia-Blanco, Gomis & Abbad (1953).
(6) Barnes & Wendling (1938).

(a)

(b)

(c)

Fig. 1. The structures of (a) $NaK_5Cl_2(S_2O_6)_2$, (b) $NaK_2ClS_2O_6$ and (c) $(NH_4)_3ClS_2O_6$ projected on to the (001) face. The edges of the true unit-cells are indicated in each structure.

Table 5. *Unit-cell dimensions and space groups of the isostructural salts*

Salt	a	b	c	Space group
$NaK_5Cl_2(S_2O_6)_2$	8·562	8·562	11·529	$P4/mnc$
Reoriented	12·107	12·107	11·529	$C4/mcn$
$NaK_2ClS_2O_6$	12·118	12·118	5·522	$P4/n$
$(NH_4)_3ClS_2O_6$	12·64	12·48	6·08	$Pbam$

References

ALVAREZ, SOTOCA, & VERDIER(1966). *An. Real Soc. esp. Fis. Quim.* **62A**, 285.

BARNES, W. H. & WEHDLING, A. V. (1938). *Z. Kristallogr.* **99**, 153.

BHUIYA, A. K. & STANLEY, E. (1963). *Acta Cryst.* **16**, 981.

BUCKLEY, H. E. (1951). *Crystal Growth.* London: Chapman & Hall.

COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.

FOCK, A. & KLUS, K. (1888). *Ber. dtsch. chem. Ges.* **246**, 179.

FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.

GARCIA-BLANCO, S., GOMIS, V. & ABBAD, M. (1953). *An. Soc. esp. Fis. Quim.* A3–4, 114.

MARTINEZ, S., GARCIA-BLANCO, S. & RIVOIR, L. (1956). *Acta Cryst.* **9**, 145.

STANLEY, E. (1953). *Acta Cryst.* **6**, 187.

STANLEY, E. (1956). *Acta Cryst.* **9**, 897.

STANLEY, E. (1964). *Acta Cryst.* **17**, 1028.

STANLEY, E. (1965). *Acta Cryst.* **19**, 1055.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

The Crystal Structure of POBr₃ and Intermolecular Bonding

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Crystals of $POBr_3$ are orthorhombic, space group $Pn2_1a$. The unit cell with dimensions $a=9·467$, $b=9·938$, $c=6·192$ Å contains four molecules. The structure was determined by vector analysis and refined by the least-squares method from photometered Cu $K\alpha$ data. The average P–Br distance is 2·14 Å, the P–O distance is 1·44 Å. The molecules form infinite chains by means of intermolecular Br–O bonds with a length of 3·08 Å.

Introduction

Raman spectra of solid $POBr_3$ and $POCl_3$ show an extra vibration line in the vicinity of the P–O stretching frequency (Smitskamp, Olie & Gerding, 1968). Since this vibration is non-degenerate in the free molecule the apparent splitting cannot be explained by the assumption of lower site symmetry in the crystal. In order to check our suspicion that strong intermolecular interactions might exist we started the present crystal structure determination.

Experimental

The crystals of $POBr_3$ are colourless and rapidly attacked by atmospheric moisture. Nearly spherical crystals with a diameter of 0·02 cm were selected and inserted into thin walled glass capillaries with the directions

defined as [100], [0$\bar{1}$1] and [001] parallel to the capillary axis. Zero-level Weissenberg photographs (Cu radiation) about [100] and [0$\bar{1}$1] were superposed with Al powder lines for calibration purposes. Carefully measured glancing angles corresponding to $0kl$ and hkk reflexions were used to determine the unit-cell dimensions by a least-squares procedure (Table 1). The listed errors correspond to three times the standard deviations.

Table 1. *Crystal data of* POBr₃

Cell dimensions: $a=9·467 \pm 0·006$
$b=9·938 \pm 0·006$
$c=6·192 \pm 0·003$
Space group: $Pn2_1a$
Number of molecules per cell: $Z=4$
Calculated density: 3·27 g.cm⁻³
Absorption coefficient: $\mu=307$ cm⁻¹