

## The Nitrate Positions in Phase III of Thallous Nitrate

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The structure of  $\text{TlNO}_3$  III has been redetermined by X-ray diffractometry. The space group is  $Pnma$  with  $a = 12.355$  (6),  $b = 8.025$  (4),  $c = 6.298$  (3) Å,  $Z = 8$ . There is a CsCl-related arrangement of anions and cations. Alternate nitrate ions lie respectively parallel and perpendicular to mirror planes, as found previously, but the new results show that the planes of these anions are almost parallel to the faces of primitive pseudo-tetragonal subcells. An  $R$  of 0.063, based on 659 reflexions, was obtained. The structure is unique. The packing in this structure and in the alkali iodates is discussed. It is suggested that in  $\text{TlNO}_3$  the structure of phase II is closely related to that of III, and that there is not necessarily any great reorientation of the planes of the anions in the structural transformation  $\text{III} \rightarrow \text{II}$ .

### Introduction

Determination of the structures of thallous nitrate should help to clarify both the crystal-chemistry of compounds of planar and nearly planar anions, and the mechanisms of the structural transformations in such compounds. Three polymorphs of  $\text{TlNO}_3$  exist at normal pressure:  $\text{III}^{76^\circ\text{C}}$ ,  $\text{II}^{143^\circ\text{C}}$ ,  $\text{I}^{206^\circ\text{C}}$  melt. In contrast to the well known  $\text{NaNO}_3$  (calcite-related) and  $\text{KNO}_3$  II (aragonite-type) structures (both also known in the lanthanide orthoborates), in which the planes of the anions are parallel, the three structures of thallous nitrate belong to a group of structures of nitrates of the larger cations  $\text{Tl}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  ( $r_c > 1.33$  Å) in which the planes of neighbouring anions are differently oriented. The pressure forms of  $\text{KNO}_3$ , such as  $\text{KNO}_3$  IV (Davis & Adams, 1962), may also belong to this group. All the structures are related to the cubic  $\text{CsNO}_3$  I structure which was determined (with some doubt about the anion orientations) by Korhonen (1954). Each anion is contained within a coordination cage of eight cations. This cage is cubic in form I of  $\text{TlNO}_3$ , and pseudo-cubic in form II. The observed mechanisms of polymorphic transformation in  $\text{TlNO}_3$  are similar to martensitic mechanisms and preserve the array in a specific orientation despite changing dimensions. The further observation that III can transform directly to I in an almost continuous manner shows that quite small differences in the dimensional changes are accompanied by substantial differences in mechanism (Kennedy & Patterson, 1965; Kennedy, Taylor & Patterson, 1966). It remained to be ascertained whether such a difference in mechanism was due to slight differences in lattice misregistry, or to electrical polarization effects, or to differences in the reorientation of the planes of the anions. If a large reorientation of the planes of the anions were associated with the observed mere deformation of the cation array, this would have important implications for the aragonite-calcite and other transformations.

Within this whole group only the structure of  $\text{TlNO}_3$  III has been determined by single-crystal methods (Kennedy & Patterson, 1961). Although the general arrangement in space group  $Pnma$ ,  $Z = 8$ , has been supported by single-crystal polarized infrared and Raman spectroscopy (Pogarev & Shultin, 1973), some doubt remained about the orientations of the planes of the anions, because of the high scattering power of  $\text{Tl}^+$ . In the present work, in which a larger set of data has been collected by diffractometry, new positions within this space group have been assigned to the light atoms in form III.

### Experimental

Crystals were grown by slow evaporation of an aqueous solution of previously recrystallized thallous nitrate. The two crystals used showed  $\{111\}$  and  $\{001\}$  faces. All X-ray data were collected at  $21^\circ\text{C}$  on a Stoe automatic Weissenberg diffractometer fitted with a graphite monochromator. The lattice parameters were determined from the  $\omega$  scans of  $h00$ ,  $0k0$ , and  $00l$  reflexions, and are shown in Table 1. The intensities were measured by the  $\omega$ -scan technique with a take-off angle of  $4^\circ$ . The scan range  $\Delta\omega$  for upper levels was varied according to  $\Delta\omega = A + B[\sin \mu / \tan(\psi/2)]$  (Phillips, 1954), where  $\mu$  is the equi-inclination angle,  $\psi$  is the detector angle and  $A$  and  $B$  are constants. Values of  $A = 0.7$  and  $B = 0.9$  were used. Pairs of crossed aperture slits (1 to 3 mm) were chosen to avoid truncation of reflexions. The procedure is described elsewhere (Snow, 1974). All possible reflexions for one octant were collected about  $b$  of one crystal and about  $c$  of another for  $2\theta < 60^\circ$ . Reciprocal lattice levels of reflexions about  $b$  were alternately strong when  $k$  was even and weak when  $k$  was odd. Collection of data proceeded to  $k = 10$  for  $k$  even and to  $k = 5$  for  $k$  odd. Strong and weak reflexions occurred in the same level about  $c$ : data were collected to  $l = 6$ . A standard reflexion was monitored after every 30 reflexions. There was no significant change in the standards for the  $c$ -axis crystal but

an upward drift of approximately 5% was observed in the first level of intense reflexions ( $h2l$ ) collected from the  $b$ -axis crystal. Although step scans of the standard reflexion before and after this run showed no difference in the width at half-height ( $0.18^\circ$ ) there was a slight broadening above this height. The drift of the standard was therefore attributed to an initial change in the extinction properties of the crystal.

Table 1. *Crystal data*

TlNO <sub>3</sub>	F.W. 266.37
Orthorhombic	Space group $Pnma$ or $Pna2_1$
$a = 12.355$ (6) Å	$F(000) = 896$
$b = 8.025$ (4)	$D_m = 5.556$ g cm <sup>-3</sup>
$c = 6.298$ (3)	$D_c = 5.666$
$Z = 8$	$\mu(\text{Mo } K\alpha) = 509$ cm <sup>-1</sup>
$[\lambda(\text{Mo } K\alpha) = 0.7107$ Å]	

Absorption corrections were made by an analytical method (Alcock, 1969). The dimensions of the crystals were measured at  $70\times$  magnification. They were  $0.009$  ( $a$ ),  $0.023$  ( $b$ ),  $0.017$  cm ( $c$ ) for the  $b$ -axis crystal and  $0.010$  ( $a$ ),  $0.019$  ( $b$ ),  $0.024$  cm ( $c$ ) for the  $c$ -axis crystal. Transmission factors ranged from  $0.0385$  to  $0.0850$  ( $b$  axis) and  $0.0274$  to  $0.0621$  ( $c$  axis). Lorentz and polarization corrections for use with a highly mosaic monochromator (Whittaker, 1953) were then applied and the data collected about the two axes were scaled together by a non-iterative least-squares method (Rae, 1965) to yield 659 unique reflexions.

### Solution and refinement of the structure

It was confirmed that the space group was  $Pnma$  or  $Pna2_1$ . As the previous work had shown that the array of thallium atoms was centrosymmetric (Kennedy & Patterson, 1961), the presence or absence of a centre of symmetry depends upon the positions of the N and O atoms. A difference map was obtained with reflexions phased by contributions from thallium atoms (refined positions, isotropic temperature factors). The peaks were best accounted for if adjacent nitrate ions lay alternately in and across mirror planes perpendicular to  $b$  at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ . Atomic positions were refined by least-squares minimization of the function  $\sum w(|F_o| - |F_c|)^2$  where  $F_o$  and  $F_c$  are the observed and calculated structure factors and the weights ( $w$ ) were

unity. The conventional  $R$  value ( $\sum[|F_o| - |F_c|]/\sum|F_o|$ ) and the  $R$  value ( $\sum w(|F_o| - |F_c|)^2/wF_o^2$ )<sup>1/2</sup> are designated  $R_1$  and  $R_2$  respectively. Values of  $0.170$  for  $R_1$  and  $0.171$  for  $R_2$  were obtained at this stage.

### Refinement in space group $Pnma$

The asymmetric unit consists of one thallium atom and two half-nitrate groups. One cycle of refinement of approximate nitrogen and oxygen positions obtained from the difference map reduced  $R_1$  to  $0.121$ . Refinement of an anisotropic temperature factor for the thallium atom further reduced  $R_1$  to  $0.103$ .

For reflexions with  $F_o^2 > 100$ ,  $F_c^2$  values were significantly higher than  $F_o^2$ , and  $F_c^2$  increased linearly with  $F_o^2/F_o^2$ . This is consistent with the occurrence of extinction. The observed structure factor was replaced by the expression  $F_o K^{-1}[1 + f(\theta)K^2 F_c^2 G]^{1/4}$  where  $K$  is the scale factor normally applied to  $|F_c|$ ,  $f(\theta)$  is  $(1 + \cos^2 2\theta)/[\sin 2\theta(1 + \cos^2 2\theta)]$  and  $G$  is a secondary extinction parameter. Two cycles of refinement gave  $R_1 = 0.067$  with  $G = 1.66 \times 10^{-5}$ . Attempts at further refinement of  $G$  resulted in high correlation between  $G$  and  $K$ . Anisotropic temperature factor refinement of all atoms and the exclusion from the refinement (but not from  $R$  value calculation) of the six reflexions which showed the largest  $[|F_o| - |F_c|]$  values gave a final  $R_1 = 0.063$  and  $R_2 = 0.068$ . Examination of values of  $\sum w(|F_o| - |F_c|)^2$  averaged in ranges of  $|F_o|$  versus  $|F_c|$  showed that the unit weighting scheme assigned weights to the set of strongest reflexions which were relatively too large. Values ranged between  $6.4$  and  $35.2$  for all except the highest  $|F_c|$  range, but showed no systematic trend. A final difference map showed some residual density in the planes of the thallium atoms with a maximum peak of  $2.8$  e Å<sup>-3</sup>. All other peaks (positive and negative) were less than  $1.7$  e Å<sup>-3</sup>. This is approximately 16% of a nitrogen peak in the original difference map.

### Refinement in space group $Pna2_1$

The asymmetric unit in this space group consists of two thallium atoms and two nitrate groups. The  $z$  coordinates of the oxygen and nitrogen atoms were randomly perturbed from the values indicated by the difference map. Initial attempts at least-squares refinement were unsuccessful because of almost complete correlation between the  $z$  coordinates and temperature

Table 2. *Positional and thermal parameters* ( $\times 10^4$ ) for TlNO<sub>3</sub> III

The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Tl	1244 (1)	5039 (1)	2142 (1)	51 (1)	104 (2)	195 (3)	-1 (1)	-4 (1)	22 (2)
N(1)	3883 (21)	2500	2404 (36)	35 (20)	109 (43)	24 (51)	0	8 (25)	0
N(2)	3593 (18)	7500	1628 (42)	15 (15)	105 (46)	83 (60)	0	-19 (23)	0
O(1)	3576 (17)	1165 (25)	1703 (34)	83 (18)	118 (36)	247 (60)	-49 (19)	37 (27)	-53 (35)
O(2)	4607 (23)	2500	3884 (46)	60 (20)	145 (52)	193 (75)	0	10 (32)	0
O(3)	2897 (24)	7500	0209 (47)	61 (21)	145 (54)	223 (82)	0	-42 (34)	0
O(4)	3336 (29)	7500	3496 (45)	104 (28)	217 (67)	112 (64)	0	13 (39)	0
O(5)	4588 (22)	7500	1150 (54)	50 (19)	149 (54)	309 (98)	0	9 (37)	0

factors of atoms related by a mirror plane in the centrosymmetric space group. It was necessary to refine one member of each pair of correlated parameters in alternate cycles for the refinement to proceed. The same refinement scheme was followed as before to yield  $R$  values consistently about 0.005 higher. At convergence all  $x$  and  $y$  coordinates were the same as for  $Pnma$ . The  $z$  coordinates and thermal parameters agreed less well, though in most cases they were still within error limits of the previous values. Anisotropic temperature factor refinement for the nitrogen and oxygen atoms was not possible because of further very high correlations between  $z$  coordinates and thermal parameters of the same atoms. The final  $R$  values were  $R_1=0.069$  and  $R_2=0.067$ . The difficulties of refinement in  $Pna2_1$  can be ascribed to incipient mirror planes.\*

Scattering factors for O and N (neutral atoms) and  $Tl^+$  were from *International Tables for X-ray Crystallography* (1962). Anomalous scattering components  $\Delta f'$  and  $\Delta f''$  for  $Tl^+$  ( $-3.556$ ,  $9.659$ ) were from Cromer & Liberman (1970).

Programs used for solution, refinement and geometry were local modifications of the following: Busing & Levy's *ORFLS* and *ORFFE*, Zalkin's *FORDAP* and Johnson's *ORTEP II*.

### The structure

The correct space group is  $Pnma$  since worse agreement was obtained at equivalent stages by the refinement of 52 parameters in  $Pna2_1$  compared with 38 in  $Pnma$ . All data given are therefore the results of the refinement in  $Pnma$ . Atomic positions and thermal parameters at convergence are given in Table 2. Table 3 shows interatomic distances and angles. Two reflexions (221, 420) were excluded from all refinements because of suspected faulty data collection. Table 4 shows r.m.s. amplitudes of vibration.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30664 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Crystal geometry*

Interatomic distances (less than 4.0 Å)			
N(1 <sup>1</sup> )-O(1 <sup>1</sup> )	1.22 (2)	Tl <sup>1</sup> -O(3 <sup>1</sup> )	3.09 (2)
N(1 <sup>1</sup> )-O(2 <sup>1</sup> )	1.29 (4)	Tl <sup>1</sup> -O(4 <sup>1</sup> )	3.36 (3)
N(1 <sup>1</sup> )-O(1 <sup>1'</sup> )	1.22 (2)	Tl <sup>1</sup> -O(5 <sup>11</sup> )	3.04 (2)
O(1 <sup>1</sup> )-O(2 <sup>1</sup> )	2.16 (3)	Tl <sup>1</sup> -O(1 <sup>111</sup> )	3.51 (3)
O(1 <sup>1</sup> )-O(2 <sup>1'</sup> )	2.16 (3)	Tl <sup>1</sup> -O(2 <sup>111</sup> )	2.94 (2)
O(1 <sup>1</sup> )-O(1 <sup>1'</sup> )	2.14 (3)	Tl <sup>1</sup> -O(3 <sup>111</sup> )	3.00 (2)
N(2 <sup>1</sup> )-O(3 <sup>1</sup> )	1.22 (4)	Tl <sup>1</sup> -O(5 <sup>111</sup> )	3.41 (3)
N(2 <sup>1</sup> )-O(4 <sup>1</sup> )	1.24 (3)	Tl <sup>1</sup> -O(2 <sup>111</sup> )	3.04 (2)
N(2 <sup>1</sup> )-O(5 <sup>1</sup> )	1.27 (3)	Tl <sup>1</sup> -O(4 <sup>111</sup> )	3.12 (2)
O(3 <sup>1</sup> )-O(4 <sup>1</sup> )	2.14 (4)	Tl <sup>1</sup> -O(1 <sup>11</sup> )	3.02 (2)
O(4 <sup>1</sup> )-O(5 <sup>1</sup> )	2.14 (5)	Tl <sup>1</sup> -O(1 <sup>1'</sup> )	3.55 (3)
O(3 <sup>1</sup> )-O(5 <sup>1</sup> )	2.17 (4)	Tl <sup>1</sup> -O(1 <sup>1'</sup> )	3.05 (2)
Bond angles (°)			
O(1 <sup>1</sup> )-N(1 <sup>1</sup> )-O(2 <sup>1</sup> )	118.5 (1.6)	O(3 <sup>1</sup> )-N(2 <sup>1</sup> )-O(4 <sup>1</sup> )	121.0 (3.0)
O(1 <sup>1</sup> )-N(1 <sup>1</sup> )-O(1 <sup>1'</sup> )	123.0 (1.6)	O(3 <sup>1</sup> )-N(2 <sup>1</sup> )-O(5 <sup>1</sup> )	120.2 (3.0)
O(1 <sup>1</sup> )-N(1 <sup>1</sup> )-O(2 <sup>1'</sup> )	118.5 (1.6)	O(4 <sup>1</sup> )-N(2 <sup>1</sup> )-O(5 <sup>1</sup> )	118.8 (3.0)

i:  $x, y, z$ ; ii:  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$ ; iii:  $\frac{1}{2} - x, -y, -\frac{1}{2} + z$ ;  
iv:  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ; v:  $x, \frac{1}{2} - y, z$ .

Table 4. *Root-mean-square amplitudes of vibration* (Å)

	Minimum	Intermediate	Maximum
Tl	0.174 (2)	0.197 (1)	0.209 (2)
N(1)	0.07 (7)	0.17 (4)	0.19 (4)
N(2)	0.08 (7)	0.15 (4)	0.18 (4)
O(1)	0.15 (3)	0.20 (3)	0.30 (3)
O(2)	0.19 (4)	0.21 (4)	0.22 (4)
O(3)	0.17 (4)	0.22 (4)	0.25 (4)
O(4)	0.15 (4)	0.26 (4)	0.28 (4)
O(5)	0.19 (4)	0.22 (4)	0.26 (4)

A stereo view of the unit cell is shown in Fig. 1. Thallium ions are in sheets normal to  $b$ . The planes of the nitrate ions are alternately parallel and normal to the mirror (010) planes of the structure. Their orientations can more clearly be described in terms of the thallium sublattice (Fig. 2). Each nitrate group is contained within a pseudo-tetragonal subcell of thallium ions, and is aligned with its plane parallel to a face of the subcell. Neighbouring subcells have the nitrate ions parallel to different faces. No face is associated with more than one oxygen. There is no evidence for distortion of the nitrate ions. The average N-O and O-O distances are 1.24 (1) and 2.15 (1) Å respectively.

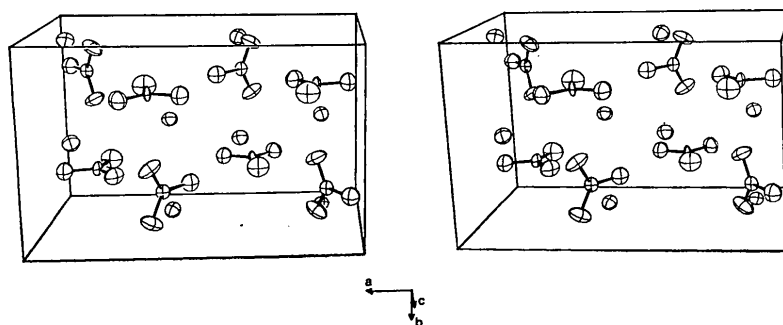


Fig. 1. A stereoscopic view of the unit cell of the structure of  $TlNO_3$ , III. The direction of view is approximately along  $c$ . All atoms are drawn with 50% probability ellipsoids.

Both nitrate ions are planar (although only one is required to be so by symmetry); the average O–N–O angle is  $120.0 (1.8)^\circ$ ; each thallium ion is surrounded by eight oxygen atoms in a shell formed by the limiting radii  $2.94$  and  $3.12 \text{ \AA}$ , and there are a further four oxygen atoms within  $3.55 \text{ \AA}$ .

### Discussion

Two ways of placing a triangular ion within an approximately cubic subcell are shown in Fig. 3 (a) and (b). In (a) the plane of the anion is normal to a body diagonal; in (b) it is parallel to a face of the cell. Arrangement (a) has been proposed for  $\text{RbNO}_3$ ,  $\text{CsNO}_3$  and  $\text{TlNO}_3$  II (Strømme, 1971) and observed in  $\text{RbIO}_3$  (Alcock, 1972). It follows that if the arrangement (a) proposed for the other phases of  $\text{TlNO}_3$  is correct, then in the structural transformations  $\text{TlNO}_3$  III  $\rightarrow$  II and II  $\rightarrow$  I the plane of the anion must undergo a substantial reorientation in which the oxygen atoms change their nearest neighbour cations. However, proposed (but not fully determined) nitrate structures based on arrangement (a) should be re-examined.

In phase III the present work confirms the presence of two non-equivalent nitrate groups, in agreement with the results of infrared and Raman spectroscopy (Pogarev & Shultin, 1973).

### Ionic packing

In considering packing there are two main approaches to the coordination of a planar oxy-ion. One approach is to consider the oxy-ion as a single packing unit, and to assign to it an effective average radius, and to enquire whether, on the basis of radius ratio, it will tend to take up (distorted) sixfold (usually octahedral), or eightfold coordination (Kennedy, 1970, 1974). The value of the effective radius previously taken for the nitrate ion was  $r_a = 1.89 \text{ \AA}$  for six coordination. If  $r_{\text{Tl}} = 1.48 \text{ \AA}$ , then the radius ratio  $\rho = 0.78$ , a value which favours the eightfold (CsCl-type) coordination, which is observed in  $\text{TlNO}_3$  III. (The argument based on the analogy between the packing of the alkali nitrate in eight and six coordination, and the CsCl and NaCl structures of alkali halides is supported by the similarity in the volume change associated with the coordination change. In most alkali halides  $\Delta V$  is close to 16% (Fraser & Kennedy, 1974) and in the total change  $\text{RbNO}_3$  III (CsCl-related) to I (NaCl-related) it is also 16%.) In arrangement (a) although the anion is within a cage of eight cations, nevertheless the coordination approximates significantly to the equivalent, for a flat ion, of octahedral six coordination [shaded atoms of Fig 3(a)]. In the arrangement shown in Fig. 3(b) the anion is coordinated by the eight cations, four from each face parallel to the plane of the anion. This arrangement might therefore be favoured when the anion-ation radius ratio favours eight coordination.

In  $\text{TlNO}_3$  III the anions are entirely contained within the coordination polyhedron of eight cations. The O–O

distance within the triangular anion is  $2.15 \text{ \AA}$ . This fits into the approximately square cross section of the subcell the edge lengths of which vary from  $4.1$  to  $4.7 \text{ \AA}$  (Fig. 2). Since the anion is thus enclosed, an apparent

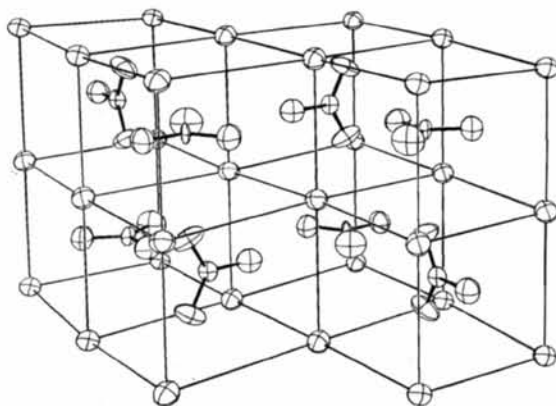


Fig. 2. The structure of  $\text{TlNO}_3$  III drawn to emphasize the subcells. The direction of view is the same as in Fig. 1.

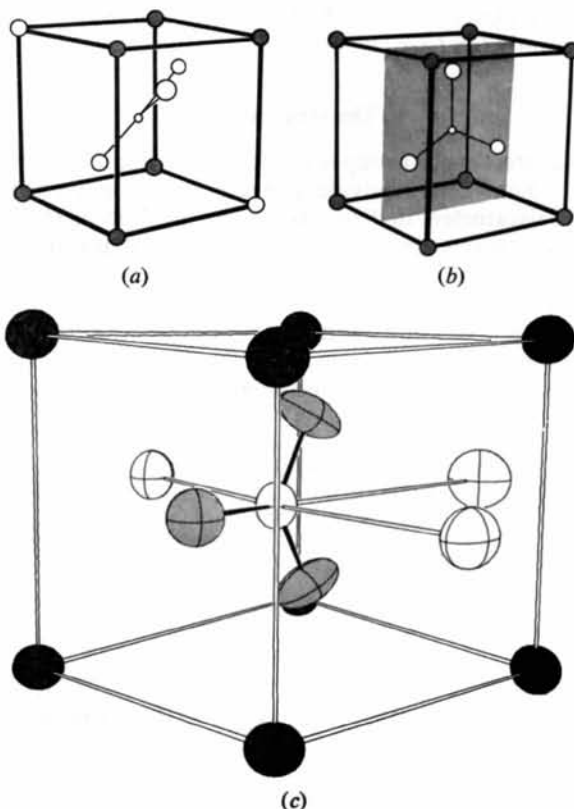


Fig. 3. Two ways of arranging a nitrate ion within an approximately cubic primitive array of cations. In (a) the plane of the anion is parallel to a (111) plane of the subcell. The flat anion is more closely coordinated to the six cations shown by shaded circles, than the other two. In (b), the plane of the anion is parallel to the face of the subcell. The observed arrangement in  $\text{TlNO}_3$  III is shown in (c), which also permits comparison with a perovskite arrangement; filled links are  $1.24 \text{ \AA}$ , open links  $2.8 \text{ \AA}$ .

effective mean radius for packing of the nitrate ion in eight coordination can be derived by defining a mean cubic subcell having an edge equal to the cube root of the molar volume in  $\text{TlNO}_3$  II. The empirical radius of  $\text{Tl}^+$  for eight coordination is  $r = 1.60 \text{ \AA}$  (Shannon & Prewitt, 1969). The apparent 'packing' radius of  $\text{NO}_3^-$  is then  $2.10 \text{ \AA}$ , and the radius ratio  $\rho = 0.76$ , which is indeed within the range for CN 8 ( $\rho > 0.73$ ).

The orientation of the anion within the subcell can be further related to the coordination of Tl and O. Since the nearest cation–oxygen distances in other nitrates are the sums of the ionic radii of cation and  $\text{O}^{2-}$ , the ionic radius of oxygen can be used to examine the coordination of  $\text{Tl}^+$ . The radius ratio is  $\rho = 0.95$ . This is in the range for eight or 12 coordination. In the observed structure the  $\text{Tl}^+$  is coordinated by eight nearest-neighbour oxygen atoms and they are at the expected distance,  $3.0 (1) \text{ \AA}$ , which is the sum of the ionic radii corrected for eight coordination. The general arrangement of the structure can thus be attributed to eight coordination of anion and cation, together with eight coordination of the cation by oxygen.

#### *Relationship to perovskite and iodates*

Since one oxygen is associated with each face of the subcell, there is some similarity to the perovskite structure-type, in which the cation and oxygen atoms would together be in 12-coordination. A tendency to form such 12-coordination in accordance with the radius ratio would therefore further favour the general arrangement observed. The difference from the perovskite structure is shown by the difference between the bonding and non-bonding N–O distances, which are  $1.24$  and  $2.8 \text{ \AA}$  respectively [Fig. 3(c)]. A similar arrangement of cations (most similar to that in  $\text{TlNO}_3$  II) occurs in the corresponding iodates. These, including  $\text{KIO}_3$  (Hamid, 1973), have been described as perovskite type, with distorted octahedral coordination of iodine. In these the analogy is closer, because the iodate ion is larger. The perovskite structure would require  $t = (r_K + r_O) / \sqrt{2}(r_I + r_O)$ , where the tolerance factor  $t$  in known structures must lie in the range  $0.7 < t < 0.9$  (Galasso, 1969). For  $\text{KIO}_3$ , with 12-coordinated K and O, and  $r_I + r_O$  as the measured distance ( $\sim 1.8 \text{ \AA}$ ),  $t \simeq 1.26$ ; or  $t \simeq 1.1$  if the radius of  $\text{O}^{2-}$  for six coordination is used. When the packing of the iodate ion, as a rigid group, with the cations is considered, the radius ratio falls in the range for six coordination and could favour the arrangement shown in Fig. 3(a). This view would support the structure suggested by Crane (1972).  $\text{CsIO}_3$  could however resemble  $\text{TlNO}_3$  III.

#### *Phase II*

Packing geometry, the entropy of phase transformation, and the observed mechanism of structural transformation all show that the structure of phase II could be similar to that of phase III.

In phase II the cation subcell has become rhombohedral pseudo-cubic with  $a = 4.31_6 \text{ \AA}$ ,  $\alpha = 89.84^\circ$ . As the

volume change in the transformation  $\text{III} \rightarrow \text{II}$  is small,  $\sim 1\%$  (Taylor, 1966), and the arguments about packing in phase III again apply, a similar arrangement could be expected in II.

The entropy change in the transformation  $\text{TlNO}_3$   $\text{III} \rightarrow \text{II}$  (Arell & Varteva, 1962) corresponds to  $S = R \ln 1.4$ . This value could correspond to an increase in librational and lattice modes, or to a different ordered structure, but is too small to allow disordering of the anions, unless two thirds only of the anions can show twofold disorder. Newns & Staveley (1966) (who did not have the entropy value for  $\text{TlNO}_3$ ) considered the arrangement now found in  $\text{TlNO}_3$  III [Fig. 3(b)], even though there was no evidence for it until the present work, and showed that it could readily explain an entropy of transformation of  $\text{CsNO}_3$   $\text{II} \rightarrow \text{I}$  of  $R \ln 3$ . As this is the measured value (Arell & Varteva, 1962) for the corresponding transformation  $\text{TlNO}_3$   $\text{II} \rightarrow \text{I}$ , an arrangement in phase II similar to that in phase III is consistent with the data. In II, two thirds of the nitrate ions may differ in their local force fields from the other one third, as in  $\text{CsNO}_3$  II (Karpov & Shultin, 1970) which gives a similar precession single-crystal diffraction pattern (Patterson, 1962).

The small volume change and the observed shear-type mode of transformation  $\text{III} \rightleftharpoons \text{II}$  (Kennedy & Patterson, 1965) again suggest a deformation of the structure, as in the transformations of the perovskite type ferroelectrics, with no exchange of neighbours. The substantially continuous nature of the metastable direct transformation  $\text{III} \rightarrow \text{I}$  suggests a gradual increase in disorder within the same basic coordination. Thus the transformation mechanisms suggest, and the other data are consistent with, the view that the structures of forms II and I of  $\text{TlNO}_3$  are based upon the arrangement found in form III.

Whilst some disordering is expected in the cubic phase I, there need not be a large reorientation of the planes of the nitrate ions in the transformations, and little such reorientation is to be expected in  $\text{III} \rightarrow \text{II}$ .

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## The Crystal and Molecular Structure of Ethylenediammonium Bis- $\{cis\text{-[ethylenediaminedisulphitoaurate(III)]}\}^*$

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$(C_2H_{10}N_2)^{2+}[Au(SO_3)_2en]_2^-$  is triclinic with  $a=7.975$  (1),  $b=7.872$  (1),  $c=9.198$  (1) Å;  $\alpha=93.88$  (2),  $\beta=94.90$  (2),  $\gamma=100.07$  (1)°;  $Z=1$ ; space group  $P\bar{1}$ . The structure was solved by Patterson and Fourier techniques and refined to a final  $R$  of 0.047. The aurate ion is essentially square-planar; the ligands are two N atoms from an ethylenediamine molecule and two S atoms from the sulphito groups. The geometry of the  $SO_3$  groups is that of coordinated groups through the sulphur atoms to the metal, rather than the geometry of sulphite ions. All the H atoms of ethylenediamine, as well as those attached to the carbon atoms of ethylenediammonium, were located from a difference synthesis. Only one H atom of the  $NH_3^+$  group was clearly located; this was sufficient to define the orientation of the group and to obtain a complete view of the three-dimensional network of hydrogen bonds in the crystal.

### Introduction

The gold(III) complexes  $X^{n+}[Au(SO_3)_2en]_n^-$  ( $n=1$ ,  $X=Na, K, NH_4$ ;  $n=2$ ,  $X=C_2H_{10}N_2$ ) display interesting electrochemical properties and have gained technological importance in electrodeposition of gold and its alloys (Zuntini, Aliprandini, Gioria, Meyer & Losi, 1974). The present X-ray structure analysis was prompted by the general lack of crystallographic information on gold(III) sulphito complexes and by the need to disclose the stereochemical arrangement in the coordination sphere of gold to relate function to structure. The oxidation state of gold was ascertained by photoelectron spectroscopy (Jørgensen, 1973).

### Experimental

The monocationic complexes are unstable in the solid state and form exceedingly thin flakes which are not

suitable for X-ray investigation. On the other hand the ethylenediammonium derivative proved to be quite adequate. On cooling, large colourless prisms, elongated along  $a$ , were obtained from moderately warm aqueous solutions of any of the monocationic complexes with an excess of ethylenediamine. The crystals decompose slowly with formation of metallic gold, but remain stable long enough for data collection when sealed under argon in Lindemann capillaries. The lattice parameters and the intensities were measured at room temperature on an automatic four-circle Philips PW1100 diffractometer with graphite-monochromatized  $Mo K\alpha$  radiation ( $\lambda=0.71069$  Å).

### Crystal data

$(C_2H_{10}N_2)[Au(SO_3)_2(C_2H_8N_2)]_2$ ;  $M=896.31$ . Triclinic; space group  $P\bar{1}$ ,  $a=7.975$  (1),  $b=7.872$  (1),  $c=9.198$  (1) Å,  $\alpha=93.88$  (2),  $\beta=94.90$  (2),  $\gamma=100.07$  (1)°;  $V=566.7$  Å<sup>3</sup>;  $Z=1$ ;  $D_m=2.737$ ;  $D_x=2.627$  g cm<sup>-3</sup>;  $\mu=143.24$  cm<sup>-1</sup>.

With a crystal of dimensions  $0.19 \times 0.16 \times 0.16$  mm, 3609 independent reflexions were scanned in the  $\theta$ - $2\theta$  mode (scan width  $1.0^\circ$  in  $2\theta$ ; scan speed  $0.04$  s<sup>-1</sup>) with

\* A summary of this work was presented at the meeting of the Swiss Crystallographical Society, October 1973, Treviso/Lugano (Dunand & Gerdil, 1974).