Acta Cryst. (1980). B**36**, 2517–2519

The Low-Temperature Forms of some $M_3^{\mathrm{I}}M'^{\mathrm{III}}(XO_4)_3$ Compounds: Structure of Triammonium Indium(III) Trisulfate

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(*Received* 6 *March* 1980; *accepted* 16 *April* 1980)

Abstract

The low-temperature form of $(NH_4)_3In(SO_4)_3$ is monoclinic, $P2_1/c$, with $a = 8{\cdot}963\,(7)$, $b = 15{\cdot}644\,(15)$, $c = 9{\cdot}131\,(6)$ Å, $\beta = 108{\cdot}28\,(5)^\circ$, $Z = 4$. Final $R = 0{\cdot}015$ for 1936 observed reflections. The In atoms have distorted octahedral coordination with an average In—O distance of 2·125 Å. InO_6 octahedra are linked together by SO_4 tetrahedra to form infinite chains along *c*. NH_4^+ ions connect these chains. An extensive hydrogen-bond network is proposed. The arrangement of $In(SO_4)_3$ columns exhibits pseudo-trigonal symmetry.

Introduction

Numerous compounds of general formula $M_3^{\mathrm{I}}\,M'^{\mathrm{III}}\,(XO_4)_3$ with X = S or Se; M^{I} = K, Cs, Rb, NH_4, Tl; M'^{III} = Al, Ga, In, Tl, Sc, V, Fe, Cr, rare earth, have been isolated and characterized. The most commonly adopted structure is of trigonal symmetry (Valkonen & Niinistö, 1978) but some compounds have a monoclinic cell (Kudin, Efremov, Pokrovsky, Trunov & Dertirev, 1977; Laplace & Jolibois, 1979). During the investigation of $M_2^{\mathrm{I}}SO_4$–$M_2^{\mathrm{III}}(SO_4)_3$ systems we have synthesized one compound $(NH_4)_3In(SO_4)_3$ (Tudo, Tudo & Perret, 1974) which exhibits a low-temperature reversible transition between monoclinic and trigonal forms. The slight modification observed on the powder diffractogram suggests only a small distortion between the two structures. This paper deals with the structural determination of the low-temperature monoclinic form.

Experimental

Single crystals of $(NH_4)_3In(SO_4)_3$ were obtained as previously described (Laplace & Jolibois, 1979).

The crystals are prismatic with hexagonal cross-section limited by the planes $(\bar{1}03)$, (100), (130) and $(\bar{1}30)$. A crystal with dimensions 0·190 mm between the lateral faces and 0·390 mm between hexagonal sections $(\bar{1}03)$ was selected for intensity collection. A Philips PW 1100 automated diffractometer at the University of Lille I with graphite-monochromated Mo $K\alpha$ radiation was used for the data collection. Half of reciprocal space was explored to $\theta = 25^\circ$. Of the 4561 reflections measured, 4036 were considered significant from the criterion $I > 3\sigma(I)$, where $\sigma(I)$ is the e.s.d. of the measured intensity. Three standard reflections were measured every two hours. The data were corrected for background, Lorentz and polarization effects. Absorption corrections were made (de Meulenaer & Tompa, 1965); the transmission factor ranged from 0·65 to 0·69 [μ(Mo $K\alpha$) = 2·5 mm^{-1}]. Averaging of equivalent reflections led to the 1978 independent planes used in the structure determination.

Structure determination and refinement

The structure was solved by the heavy-atom method. Two positions for In atoms were consistent with the Patterson map. For the two solutions, a Fourier map calculated with $(F_o - F_{\mathrm{In}})$ revealed the positions of all the S atoms. The refinement of the In and S coordinates permitted the elimination of one of the two solutions since R was very different in the two cases: 0·246 and 0·319; furthermore, a $(F_o - F_{\mathrm{In+S}})$ synthesis revealed O and N atoms only in the case corresponding to R = 0·246. The coordinates and anisotropic temperature factors for all non-H atoms were refined. R dropped to 0·022. A difference synthesis at this stage revealed all the H atoms. Introduction of their coordinates with isotropic temperature factors led to R = 0·017; however, the value of B for H(8) was too large (13 Å^2). 42 reflections with $|F_o - F_c| > 3\sigma$ $\{\sigma = [\sum (|F_o| - |F_c|)^2/N]^{1/2}\}$ were then rejected: B of H(8) dropped to 6·6 Å^2; the final R was 0·015 for the remaining reflections (0·017 if the 1978 initial reflections were included). The coordinates and thermal parameters are

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Table 1. *Fractional atomic coordinates* ($\times 10^5$; *for* H $\times 10^3$) *and isotropic* (H) *or isotropic equivalent* (In, S, O *and* N) *temperature factors*

	x	y	z	B (Å^2)
In	21519 (2)	25002 (1)	22474 (2)	0·9
S(1)	25436 (7)	9155 (4)	47552 (6)	1·1
S(2)	44729 (7)	34724 (4)	53964 (6)	1·1
S(3)	−4120 (7)	32909 (4)	39422 (6)	1·2
O(1)	17615 (23)	1057 (12)	47641 (22)	2·6
O(2)	40834 (21)	7958 (13)	46155 (21)	2·4
O(3)	15451 (19)	14349 (11)	34323 (19)	1·7
O(4)	27239 (24)	13703 (12)	62235 (20)	2·5
O(5)	38732 (32)	42679 (12)	46306 (22)	2·6
O(6)	61420 (22)	35057 (13)	61423 (23)	2·7
O(7)	37074 (27)	32968 (14)	65744 (23)	3·3
O(8)	41130 (19)	27590 (11)	42505 (19)	1·9
O(9)	−6172 (29)	41503 (13)	44100 (27)	3·7
O(10)	7426 (21)	33220 (11)	30978 (21)	2·1
O(11)	−18738 (23)	29385 (17)	29640 (23)	3·8
O(12)	1589 (21)	27205 (12)	53042 (19)	2·2
N(1)	87639 (30)	2490 (17)	21238 (30)	2·2
N(2)	60214 (34)	4200 (20)	78375 (32)	2·4
N(3)	69791 (30)	17078 (16)	47053 (29)	1·8
H(1)	935 (6)	39 (3)	162 (6)	5·0 (1·3)
H(2)	943 (7)	18 (4)	296 (7)	4·7 (1·4)
H(3)	790 (5)	67 (3)	182 (5)	2·5 (0·9)
H(4)	820 (7)	−25 (4)	182 (7)	6·2 (1·5)
H(5)	593 (5)	9 (3)	712 (5)	2·3 (1·0)
H(6)	569 (6)	22 (3)	852 (6)	3·1 (1·1)
H(7)	684 (5)	72 (3)	819 (5)	1·8 (0·8)
H(8)	531 (8)	73 (4)	771 (7)	6·6 (1·7)
H(9)	742 (4)	110 (3)	481 (4)	1·8 (0·8)
H(10)	599 (6)	167 (3)	447 (6)	3·1 (1·2)
H(11)	738 (4)	196 (2)	572 (5)	1·5 (0·7)
H(12)	731 (4)	199 (2)	398 (4)	1·5 (0·8)

in Table 1.* Refinement was performed with *SFLS*-5 (Prewitt, 1966). The function minimized was $\sum(|F_o| - |F_c|)^2$. An extinction correction was applied of the form $F^2_{\text{corr}} = F^2_c/(1 + SF^2_o)$, with a final S of 0·52(2) × 10^{-7}. Scattering factors were from Cromer & Waber (1965). Anomalous-dispersion corrections were made (Cromer & Liberman, 1970).

Description of the structure and discussion

The most significant bond lengths and angles in the In, S and N coordination polyhedra are listed in Table 2. In atoms are surrounded by six O atoms of six different sulfate groups (Fig. 1), forming a slightly deformed octahedron. The six In—O distances are close and the mean value (2·125 ± 0·025 Å) is consistent with previously reported values (Johansson, 1961; Tudo, Jolibois, Laplace, Nowogrocki & Abraham, 1979).

In the three crystallographically independent SO_4 tetrahedra, the S—O distances are distributed in two groups: two long bonds (mean length 1·484 ± 0·014 Å) with O atoms linked to In, and two shorter bonds (mean length 1·442 ± 0·007 Å) with O not bonded to In (Fig. 1). Two InO_6 octahedra are linked together by three SO_4 tetrahedra to form infinite chains along *c*

Table 2. *Principal distances* (Å) *and angles* (°) *in* $(NH_4)_3In(SO_4)_3$

E.s.d.'s are in parentheses. The symmetry code (i) stands for $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Indium octahedron			
In—O(3)	2·148 (2)	In—O(8)	2·141 (2)
In—O(4)$^{\text{i}}$	2·135 (2)	In—O(10)	2·113 (2)
In—O(7)$^{\text{i}}$	2·101 (2)	In—O(12)$^{\text{i}}$	2·114 (2)
Sulfate tetrahedra			
S(1)—O(1)	1·449 (2)	O(1)—S(1)—O(2)	111·5 (3)
S(1)—O(2)	1·438 (2)	O(1)—S(1)—O(3)	108·1 (2)
S(1)—O(3)	1·497 (2)	O(1)—S(1)—O(4)	109·3 (2)
S(1)—O(4)	1·481 (2)	O(2)—S(1)—O(3)	110·3 (2)
		O(2)—S(1)—O(4)	107·9 (3)
		O(3)—S(1)—O(4)	109·7 (2)
S(2)—O(5)	1·446 (2)	O(5)—S(2)—O(6)	111·8 (2)
S(2)—O(6)	1·437 (2)	O(5)—S(2)—O(7)	109·0 (3)
S(2)—O(7)	1·472 (2)	O(5)—S(2)—O(8)	109·8 (2)
S(2)—O(8)	1·494 (2)	O(6)—S(2)—O(7)	108·4 (3)
		O(6)—S(2)—O(8)	108·8 (2)
		O(7)—S(2)—O(8)	108·9 (3)
S(3)—O(9)	1·440 (2)	O(9)—S(3)—O(10)	107·5 (3)
S(3)—O(10)	1·473 (2)	O(9)—S(3)—O(11)	111·4 (3)
S(3)—O(11)	1·444 (2)	O(9)—S(3)—O(12)	110·8 (2)
S(3)—O(12)	1·485 (2)	O(10)—S(3)—O(11)	109·8 (3)
		O(10)—S(3)—O(12)	110·1 (3)
		O(11)—S(3)—O(12)	107·2 (2)
Ammonium ions			
N(1)—H(1)	0·83 (6)	N(3)—H(9)	1·02 (4)
N(1)—H(2)	0·82 (5)	N(3)—H(10)	0·85 (5)
N(1)—H(3)	0·99 (4)	N(3)—H(11)	0·97 (4)
N(1)—H(4)	0·93 (6)	N(3)—H(12)	0·92 (4)
N(2)—H(5)	0·81 (5)		
N(2)—H(6)	0·84 (6)		
N(2)—H(7)	0·84 (4)		
N(2)—H(8)	0·79 (6)		

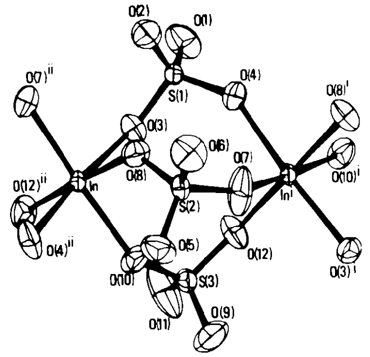

Fig. 1. Coordination polyhedra around the In and S atoms. The symmetry codes (i) and (ii) stand for $x, \frac{1}{2} - y, \frac{1}{2} + z$ and $x, \frac{1}{2} - y, z - \frac{1}{2}$ respectively.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35342 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Fig. 2). Each sulfate shares two O atoms with In polyhedra. Such columns were found in triammonium scandium selenate, $(NH_4)_3Sc(SeO_4)_3$ (Valkonen & Niinistö, 1978), but the orientations of two consecutive octahedra along the column are different.

The inaccuracy of the H coordinates precludes an assessment of the regularity of the NH_4^+ tetrahedra. However, the mean N—H distance of 0·88 Å [0·87, 0·82 and 0·94 Å for N(1), N(2) and N(3) respectively] is acceptable.

The NH_4^+ ions link together the columns previously described. An extensive hydrogen-bond network can be proposed, the characteristics of which are summarized in Table 3. Some of the H atoms seem to participate in bifurcated bonds. However, the presence of this hydrogen-bond network does not exclude the existence of electrostatic interactions between the large NH_4^+ cations and the O atoms not involved in the column formation.

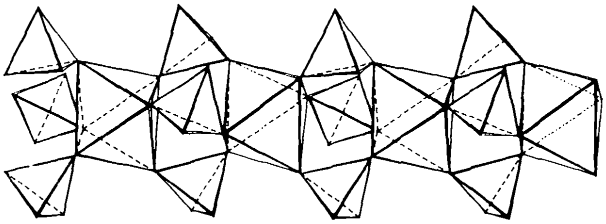

Fig. 2. Linking of InO_6 octahedra and SO_4 tetrahedra to form the $[In(SO_4)_3^{3-}]_\infty$ column along *c*.

Table 3. *Characteristics of hydrogen bonds*

The notation $O(n)^x_{pqr}$ represents atom O(*n*) to which the symmetry *x* has been applied, followed by a translation of $p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$. Symmetry code: (i) x,y,z; (ii) $\bar{x},\bar{y},\bar{z}$; (iii) $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

	N—O (Å) (e.s.d. 0·002 Å)	H—O (Å) (e.s.d. 0·06 Å)	N—H—O (°) (e.s.d. 3–4°)
$N(1)-H(1)-O(9)^{iv}_{10\bar{1}}$	2·862	2·154	143
$N(1)-H(1)-O(9)^{iii}_{1\bar{1}0}$	3·022	2·567	116
	$[O(9)^{iv}_{10\bar{1}}-H(1)-O(9)^{iii}_{1\bar{1}0}$		77]
$N(1)-H(2)-O(1)^{i}_{100}$	3·003	2·221	160
$N(1)-H(3)-O(6)^{iv}_{00\bar{1}}$	2·966	1·977	178
$N(1)-H(4)-O(5)^{iii}_{1\bar{1}0}$	2·852	2·052	143
$N(1)-H(4)-O(10)^{iii}_{1\bar{1}0}$	3·063	2·413	127
	$[O(5)^{iii}_{1\bar{1}0}-H(4)-O(10)^{iii}_{1\bar{1}0}$		87]
$N(2)-H(5)-O(2)^{ii}_{101}$	2·917	2·107	174
$N(2)-H(6)-O(5)^{iii}_{1\bar{1}1}$	2·902	2·187	146
$N(2)-H(6)-O(5)^{iv}_{000}$	2·933	2·313	131
	$[O(5)^{iii}_{1\bar{1}1}-H(6)-O(5)^{iv}_{000}$		83]
$N(2)-H(7)-O(9)^{iv}_{100}$	2·979	2·212	151
$N(2)-H(7)-O(11)^{iv}_{100}$	3·167	2·431	146
	$[O(9)^{iv}_{100}-H(7)-O(11)^{iv}_{100}$		62]
$N(3)-H(9)-O(1)^{ii}_{101}$	3·036	2·016	174
$N(3)-H(10)-O(2)^{i}_{000}$	2·940	2·225	142
$N(3)-H(10)-O(8)^{i}_{000}$	2·968	2·359	129
	$[O(2)^{i}_{000}-H(10)-O(8)^{i}_{000}$		85]
$N(3)-H(11)-O(11)^{iv}_{100}$	2·880	1·952	161
$N(3)-H(12)-O(11)^{i}_{100}$	2·884	2·001	160

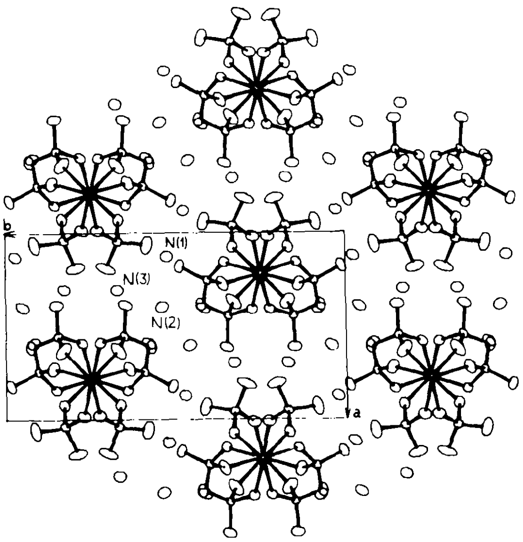

Fig. 3. Packing of the $[In(SO_4)_3^{3-}]_\infty$ columns viewed along *c* showing the pseudo-trigonal symmetry.

The arrangement of the $In(SO_4)_3$ chains is shown in Fig. 3. For clarity, only N positions have been represented for NH_4^+ ions.

It is obvious in Fig. 3 that an $In(SO_4)_3$ column exhibits pseudo-trigonal symmetry and that the neighboring columns form a pseudo-regular-hexagonal arrangement; this fact is probably related to the low-temperature transition from monoclinic to trigonal symmetry. The structure of the high-temperature form is presently under investigation.

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