JOURNAL OF SOLID STATE CHEMISTRY **40**, 69–74 (1981)

Monoclinic–Trigonal Transition in Some $M_3^{I}M'^{III}(XO_4)_3$ Compounds: The High Temperature Form of $(NH_4)_3In(SO_4)_3$

B. JOLIBOIS AND G. LAPLACE

U.E.R. Sciences Exactes et Naturelles, 33, rue Saint-Leu,
80039 Amiens, France

AND F. ABRAHAM AND G. NOWOGROCKI

Université des Sciences et Techniques de Lille, B.P. 36, 59655 Villeneuve
d'Ascq Cedex, France

Received March 23, 1981; in revised form June 25, 1981

The high-temperature form of $(NH_4)_3In(SO_4)_3$ is rhombohedral, $R3c$, with a = 15.531 (12), c = 9.163 (8) Å, Z = 6. The structure was solved to R = 0.023 for 570 independent reflections measured at about 140°C. The structure is built up of $[In(SO_4)_3]_\infty$ columns extending along the c axis and composed of InO_6 octahedra and SO_4 tetrahedra linked together; this arrangement is very similar to that found in the low-temperature form. To explain the transition mechanism, the existence of an intermediate phase of point symmetry $\bar{3}$ is postulated and the whole sequence of possible forms would be $2/m \rightarrow \bar{3} \rightarrow 3m \rightarrow \bar{3}m$. This last phase would be the prototypic structure of the possibly ferroelastic low-temperature modification, which can apparently exist only with nonspherical monovalent cations.

Introduction

Some compounds of general formula $M_3^{I}M'^{III}(XO_4)_3$ undergo at low temperature (about 100°C) a reversible transition between monoclinic and trigonal symmetry. During the investigations of the thermal behavior of some double sulfates, Tudo *et al.* (*1*) showed by means of DTA that such a transition occurs in $(NH_4)_3In(SO_4)_3$ at 80°C. These authors have confirmed this result by a study in a heating powder Guinier–Lenne camera.

We previously reported (*2*) the crystal structure of the low-temperature form of triammonium indium III trisulfate (space group $P2_1/c$). This paper deals with the structural determination of the high-temperature trigonal form of this compound and with the characteristics of the transition.

Experimental

Single crystals of the high-temperature modification of $(NH_4)_3In(SO_4)_3$ can be obtained by slow heating of single crystals of the low-temperature phase prepared as previously described (*3*). For diffraction measurements, a prismatic crystal with a hexagonal cross section was enclosed in a glass capillary and mounted on the Philips PW 1100 automated diffractometer of the University of Lille I. The heating device con-

0022-4596/81/130069-06$02.00/0

sists of a gas-blower which supplies a temperature-regulated flow of air on the crystal. The intensity of the 221 reflection of the monoclinic cell was monitored during the heating. At the transition, the diffracted intensity suddenly dropped to zero. The temperature of the air flow was then regulated at about 20°C above the transition to prevent return to the monoclinic form during the intensity measurements. The peak hunting program of the diffractometer then found the rhombohedral cell.

A fourth of reciprocal space was explored to $\theta = 25°$ using graphite-monochromated Mo*K*α radiation. Monitoring of three standard reflections every 2 hr showed no deterioration of the crystal throughout the data collection. Of the 1850 reflections measured, 1599 were considered significant from the criterion $I > 3\sigma(I)$, where $\sigma(I)$ is the *SD* of the measured intensity.

The data were corrected for background, Lorentz, and polarization effects. Absorption corrections were made using De Meulenaer and Tompa method (4); the crystal was limited by the pair of planes $(1\ \bar{1}\ 2)$, $(2\ \bar{1}\ 0)$, $(1\ \bar{2}\ 0)$, and $(1\ 1\ 0)$, the distance between the parallel planes being respectively 0.385, 0.252, 0.230, and 0.232 mm; the trasmission factor ranged from 0.54 to 0.61 (μ(Mo$K\alpha$) = 2.5 mm^{-1}). Averaging of the equivalent reflections led to 579 independent planes which were used in the structure determination.

Structure Determination and Refinement

The hexagonal parameters of the rhombohedral cell were obtained by refinement of diffraction angles measured on a powder Guinier spectrum realized at 120°C: a = 15.531 (12) c = 9.163 (8) Å. These values are in good agreement with the parameters obtained during data collection by means of the single crystal diffractometer.

Absence of reflections $h\ 0\ l$ with l odd

TABLE I

REFINED POSITIONAL (× 10^4) AND THERMAL PARAMETERS[a] IN $(NH_4)_3In(SO_4)_3$ HIGH-TEMPERATURE MODIFICATION

Atom	Position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq} (Å^2)[b]
In	6*a*	0	0	0	0.00279(2)	$= \beta_{11}$	0.00287(4)	$= \frac{1}{2}\beta_{11}$	0	0	1.67
S	18*b*	1738(1)	261(1)	2479(2)	0.00199(5)	0.00334(7)	0.00476(9)	0.00133(5)	0.00018(7)	0.00024(9)	1.82
O(1)	18*b*	291(4)	1241(4)	1367(6)	0.0046(3)	0.0037(3)	0.0091(6)	0.0013(2)	0.0016(3)	−0.0018(3)	3.31
O(2)	18*b*	1282(4)	209(7)	3882(6)	0.0057(4)	0.0174(8)	0.0064(6)	0.0055(5)	0.0018(4)	−0.0024(5)	6.41
O(3)	18*b*	2309(5)	−224(6)	2653(10)	0.0095(5)	0.0148(8)	0.0214(11)	0.0106(6)	−0.0064(7)	−0.0053(8)	6.81
O(4)	18*b*	2357(5)	1269(5)	2038(8)	0.0086(5)	0.0059(4)	0.0191(10)	−0.0020(4)	−0.0053(6)	0.0044(5)	7.42
N	18*b*	4148(4)	−260(4)	2761(7)	0.0042(3)	0.0048(4)	0.0116(8)	0.0023(3)	0.0000(4)	0.0006(4)	3.45

[a] The anisotropic temperature factor is defined by $\exp\left(-\sum_{ij} \beta_{ij} h_i h_j\right)$.

[b] B_{eq}: equivalent isotropic temperature factors are computed according to the relation $B_{eq} = \frac{4}{3} \sum_{ij} \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

indicates the presence of c glide planes and limits the possibilities to space groups $R3c$ or $R\bar{3}c$. Presence of a second-order harmonic signal above 110°C proves the noncentrosymmetry of the structure and therefore the structural determination was performed in space group $R3c$. The volume of the monoclinic cell being 1216 Å^3 for four formula units, the calculated volume of the hexagonal cell (1914 Å^3) implies that $Z = 6$.

Therefore, the indium atoms can only be located in a $6a$ position $0, 0, z$, with $z = 0$ to fix the origin. The structure was solved by successive difference Fourier synthesis and least-squares refinements to $R = 0.026$ ($R_w = 0.030$) for all nonhydrogen atoms with anisotropic thermal vibration parameters.

Attempts to determine the absolute configuration failed: the slight increase of R to 0.027 ($R_w = 0.031$), brought by changing the $\Delta f''$ signs, was not considered as significant. A secondary extinction correction was introduced in the form $F^2_{\mathrm{corr}} = F^2_{\mathrm{calc.}}/(1 + SF^2_{\mathrm{obs}})$, the final value of S being $0.24\ (8) \times 10^{-7}$. After rejection of nine reflections such that $|F_{\mathrm{obs}} - F_{\mathrm{calc}}| > 3\sigma$ (σ is defined by $\sigma = [\Sigma(F_{\mathrm{obs}} - F_{\mathrm{calc}})^2/N]^{1/2}$, N = number of independent planes), the final reliability factors are $R = 0.023$ and $R_w = 0.024$. Despite these minor improvements, the H atoms could not be located on the subsequent difference synthesis.

Atomic coordinates and anisotropic temperature factors are listed in Table I. F_{obs} and F_{calc} values are listed in Table II.[1]

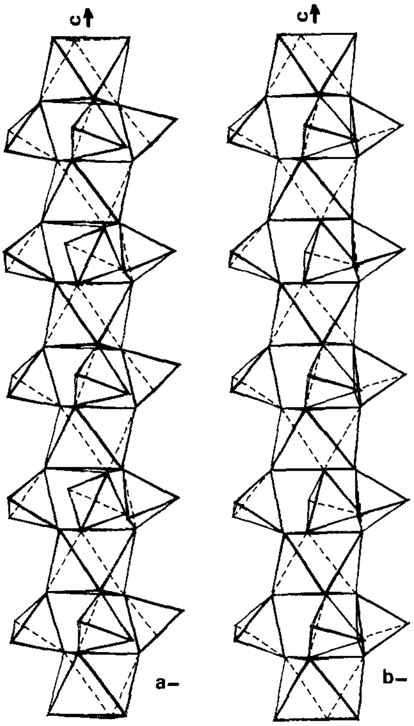

FIG. 1. $[In(SO_4)_3]_\infty$ columns in (a) low-temperature and (b) high-temperature forms of $(NH_4)_3In(SO_4)_3$.

Scaterring factors were taken from Cromer and Waber (5). Anomalous dispersion corrections were made according to Cromer and Liberman (6). Full matrix least-

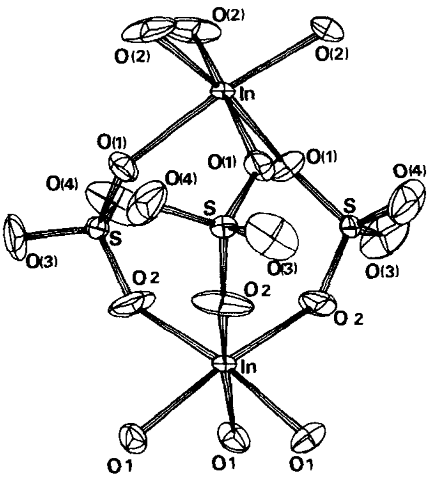

FIG. 2. Coordination polyhedra around In and S atoms in $(NH_4)_3In(SO_4)_3$ high-temperature form.

---

[1] See NAPS document No. 03893 for 4 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance in U.S. funds only for each NAPS Accession Number. Institutions may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of the U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

squares refinements were performed with a local modification of ORFLS (*7*).

Description of the Structure

Building blocks of the structure are InO_6 octahedra and SO_4 tetrahedra which are linked together to form infinite columns $[In(SO_4)_3]_\infty$ along the *c* axis (Fig. 1b). This arrangement is closely related to that found in the low-temperature phase (Fig. 1a). However, the position of the In atoms on the threefold axis implies that all the sulfate tetrahedra are crystallographically equivalent.

Inside its octahedron, the In atom is slightly off-center with three In–O(1) distances of 2.149 (6) Å and three smaller In–O(2) of 2.115 (8) Å (Fig. 2). The mean distance In–O (2.132 Å) is very close to the value found in the low-temperature modification (2.125 Å). The SO_4 geometry is quite similar in the two phases (Table III) with two shorter S–O distances with oxygen atoms not bonded to In (mean: 1.43 Å) and two slightly longer with 0 bonded to Indium (mean: 1.47 Å). The surroundings of nitrogen atom consist of eight oxygen atoms at distances less than 3.5 Å but no specific hydrogen bonds can be deduced. The failure to locate hydrogen atoms can be due either to very high thermal parameters at the measuring temperature or to dynamical disorder around N atoms.

TABLE III

PRINCIPAL DISTANCES (Å) AND ANGLES (°) IN HIGH-TEMPERATURE FORM OF $(NH_4)_3In(SO_4)_3$

	Indium octahedron		
In–O(1)(3x)	2.149(6)		
In–O(2)(3x)	2.115(8)		
	Sulfate tetrahedron		
S–O(1)	1.491(6)	O(1)–S–O(2)	109.6(7)
S–O(2)	1.450(6)	O(1)–S–O(3)	108.7(1.1)
S–O(3)	1.431(11)	O(1)–S–O(4)	110.3(7)
S–O(4)	1.426(7)	O(2)–S–O(3)	106.6(1.1)
		O(2)–S–O(4)	110.8(8)
		O(3)–S–O(4)	110.8(1.2)
	Ammonium ions[a]		
N–O(1)	$(\frac{1}{3} + y - x, y - \frac{1}{3}, z + \frac{1}{6})$		2.97(1)
N–O(2)	$(\frac{1}{3} - y, x - y - \frac{1}{3}, z - \frac{1}{3})$		3.37(1)
N–O(3)	(x, y, z)		2.89(1)
N–O(3)	$(\frac{1}{3} - y, x - y - \frac{1}{3}, z - \frac{1}{3})$		3.27(1)
N–O(3)	$(\frac{1}{3} + x, x - y - \frac{1}{3}, z + \frac{1}{6})$		3.17(1)
N–O(4)	$(\frac{1}{3} + y - x, y - \frac{1}{3}, z + \frac{1}{6})$		3.01(1)
N–O(4)	$(y - x + \frac{2}{3}, \frac{1}{3} - x, z + \frac{1}{3})$		3.17(1)
N–O(4)	$(\frac{2}{3} - y, \frac{1}{3} - x, z - \frac{1}{6})$		2.92(1)

[a] Symmetry codes are in parentheses.

Discussion

Ferroelastic Nature of the Transition

Apart from the crystallographic studies, the transition was also investigated by several methods: permitivity measurements exhibited a well-defined peak at 110°C; attempts at characterization of hydrogen atoms behavior by wide-line NMR of protons were not conclusive due to broadening of the signal. Second-order harmonic tests were realized at different temperatures: at 20°C, the absence of signal is compatible with the centrosymmetric space group $P2_1/c$ of the low-temperature form; on heating a second-order harmonic signal appears at about 110°C—On cooling, this signal disappears at about 85°C, thus confirming the reversibility of the transition.

The transformation matrix between the monoclinic and hexagonal cell is:

$$\begin{vmatrix} a \\ b \\ c \end{vmatrix}_{\text{hex.}} = \begin{vmatrix} \frac{3}{2} & \frac{1}{2} & \frac{1}{2} \\ -\frac{3}{2} & \frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & 1 \end{vmatrix} \cdot \begin{vmatrix} a \\ b \\ c \end{vmatrix}_{\text{monocl.}} .$$

The reverse transformation can proceed in three different directions (Fig. 3) thus conferring to the transition a ferroelastic nature. However, the crystallographic conditions (*8*) are not fulfilled: point group $2/m$ is not a subgroup of point group $3m$. Thus the rhombohedral cell cannot be the prototypic phase of the monoclinic form. (As

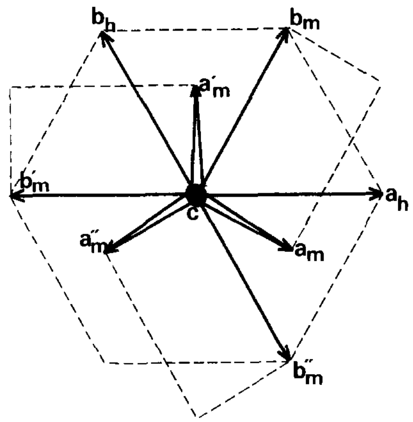

FIG. 3. Relation between low-temperature monoclinic cell and high-temperature hexagonal cell.

pointed out by Toledano (*8*), the prototypic phase does not necessarily exist as a stable state of the crystal).

Examination of Fig. 4 shows that, so long as we consider one single column, the direct transition between the two phases can be accomplished by a slight tilting of two symmetry related SO_4 tetrahedra A and B (and a very slight movement of the other SO_4 groups).

When we consider neighboring columns, several path can be imagined:

—tilting of the A′ and B′ tetrahedra (Fig. 4a) followed by a $\pi/3$ rotation of half the columns to obtain the rhomboedral arrangement (Fig. 4b): such a procedure is evidently incompatible with the conservation of the monocrystallinity across the transition.

—tilting of different SO_4 tetrahedra in adjacent columns, which are initially symmetry related: in half the columns, all the tetrahedra would be notably displaced; in the other half, only two would move.

—A physically more acceptable path could be a first transition to perfectly symmetrical columns (Fig. 5) followed by a further tilting of all SO_4 groups: that would preserve the relation of symmetry between the different columns. Thus the intermediate phase would be of point symmetry $\bar{3}$.

If the relationship between the phases is considered as follows: $2/m \rightarrow \bar{3} \rightarrow 3m \rightarrow \bar{3}m$, the space groups of the low-, intermediate-, and high-temperature forms belong to subgroups of the prototype $\bar{3}m$. This prototypic phase, with the highest symmetry, however, could not be observed due to decomposition of the compound at about 200°C; compounds of the same formula, stable at higher temperatures are actually

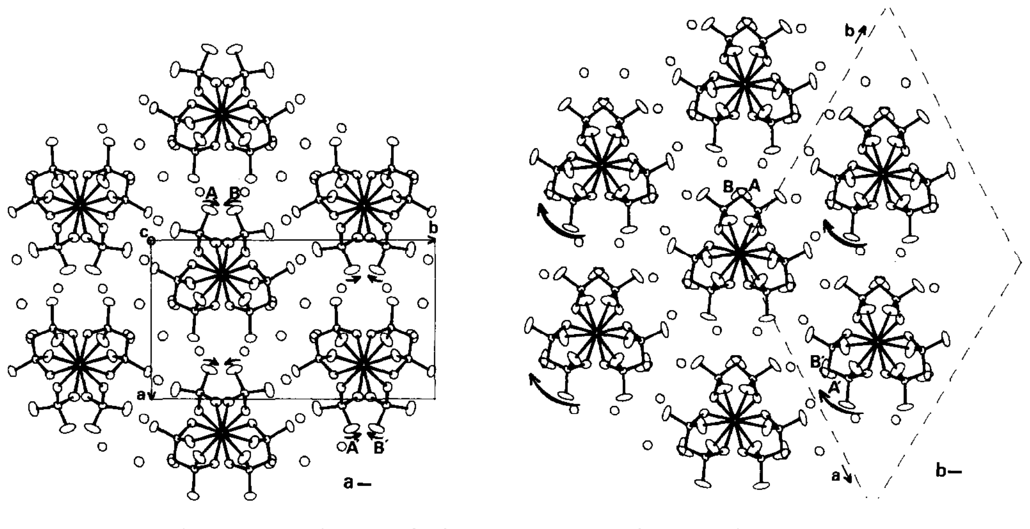

FIG. 4. Projection along *c* axis of (a) the low-temperature and (b) the high-temperature forms of $(NH_4)_3In(SO_4)_3$.

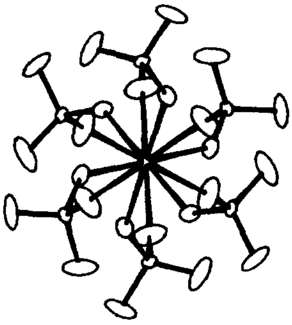

FIG. 5. Intermediate centrosymmetric arrangement.

under study to confirm this hypothesis.

A possible proof of the proposed mechanism is brought by the micro DTA realized with a Perkin–Elmer DSC2 apparatus which shows that, indeed, the transition proceeds in two steps (Fig. 6). In addition, a very close examination of the film obtained in the heating Guinier–Lenne camera shows that the transition is not a simple one: Some X-ray reflections of the low-temperature phase are slightly shifted before complete extinction. However, isolation of the intermediate spectra does not seem possible.

Appropriate substitutions of cations are presently under investigation in the hope of separating these two steps.

Comparison with Other $M_3^{\mathrm{I}}M'^{\mathrm{III}}(XO_4)_3$ Compounds

The majority of such compounds are only known in the rhomboedral symmetry (M^{I} = K, Rb, Cs; M'^{III} = In, Tl, Cr, Fe, V, *R.E.*). The known transitions from monoclinic to rhomboedral symmetry occur when M^{I} = NH_4 or Tl. Therefore it appears that the low-temperature geometry is governed by the symmetry of the monovalent cation: the spherical ions led to rhomboedral compounds, nonspherical to monoclinic. At higher temperature, dynamical disorder can confer to NH_4^+ or lone pair of Tl^+ a pseudospherical symmetry and thus stabilize the rhombohedral form. This hypothesis is under investigation by the study of other compounds of the family.

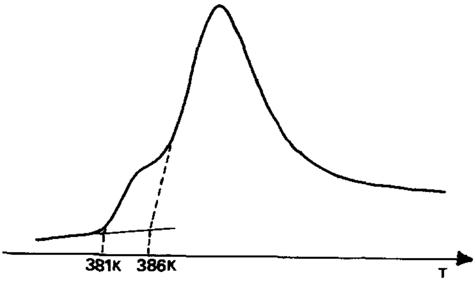

FIG. 6. DTA of $(NH_4)_3In(SO_4)_3$.

Acknowledgments

The authors wish to thank Mr. D. Bernard (Laboratoire Chimie Minerale D, Rennes) for second-order harmonic tests, Pr. F. Rietsch (Laboratoire de Physique Macromoléculaire, Lille) for use of Perkin–Elmer D S C 2 apparatus and Mr. G. Odou (Laboratoire de Dynamique des Cristaux, Lille) for the technical assistance in the high-temperature diffraction measurements.

References

1. J. TUDO, M. TUDO, AND R. PERRET, *C.R. Acad. Sci. Paris Ser. C* **278**, 117 (1974).
2. B. JOLIBOIS, G. LAPLACE, F. ABRAHAM, AND G. NOWOGROCKI, *Acta Crystallogr.* **36**, 2517 (1980).
3. G. LAPLACE AND B. JOLIBOIS, *J. Appl. Crystallogr.* **12**, 615 (1979).
4. J. DE MEULENAER AND H. TOMPA, *Acta Crystallogr.* **19**, 1014 (1965).
5. D. T. CROMER AND J. T. WABER, *Acta Crystallogr.* **18**, 104 (1965).
6. D. T. CROMER AND D. LIBERMAN, *J. Chem. Phys.* **53**, 1891 (1970).
7. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, "ORFLS, Report ORNL—TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn.
8. J. C. TOLEDANO, *Ann. Telecommun.* **29**, 249 (1974).