On Basic Thallium Sulfates: Structure of $Tl_2Tl\ OH(SO_4)_2$

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The $Tl_2TlOH(SO_4)_2$ compound is monoclinic, $a = 7.758$ (3), $b = 17.587$ (9), $c = 7.356$ (3) Å, $\beta = 119.91$ (3)°, S. G. Cc, $Z = 4$. The structure was solved by full-matrix least square refinement to $R = 0.033$ from 1242 single-crystal reflections collected on an automated diffractometer. Tl^+ ions ensure bonding between $[Tl^{III}OH(SO_4)_2]_\infty$ sheets. These sheets may be viewed as criss-crossing Tl–SO₄ chains. In the [101] direction, the linking of Tl^{III} is reinforced by bidentate OH groups, so the usual hexacoordination of trivalent thallium is preserved. A transition occurring at 104°C is under investigation.

Introduction

In the course of a study of the existence conditions of basic thallium sulfates of monovalent ions (*1*) we have isolated some compounds of general formula $M_2^ITlOH(SO_4)_2$ ($M = K^+, NH_4^+, Rb^+, Tl^+$). Growing of good single crystals of $Tl_2TlOH(SO_4)_2$ has allowed determination of the crystal data: monoclinic cell $a = 7.758$ (3), $b = 17.587$ (9), $c = 7.356$ (3) Å, $\beta = 119.91$ (3)°, $Z = 4$. Systematic extinction conditions ($hkl: h + l = 2n$ and $h\ 0\ l: l = 2n$) point to space group Cc or $C2/c$. The other compounds of the series are isomorphous (*2*).

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Experimental

Single crystals of $Tl_2TlOH(SO_4)_2$ suitable for X-ray study were grown by a previously described method (*2*). For diffraction measurements a prismatic crystal with a pseudo hexagonal cross section was enclosed in a glass capillary and mounted on the Philips PW 1100 automated diffractometer of the University of Lille I. Half of the reciprocal space was explored to $\theta = 30°$ using graphite monochromated Mo $K\alpha$ radiation. Monitoring three standard reflections every 2 hr showed no deterioration of the crystal throughout the data collection. Of the 2732 reflections measured, 2363 were considered significant from the criterion $I > 3\ \sigma(I)$, where $\sigma(I)$ is the SD of the measured inten-

sity. The data were corrected for the background, Lorentz, and polarization effects. Because of the proportion of thallium in the compound (about 75%), the absorption coefficient was high (56.65 mm^{-1}). Rigorous absorption corrections were absolutely necessary: the De Meulenaer and Tompa (3) method is best adapted to well defined crystals. The selected crystal was limited by the pairs of planes (0 1 0), (1 0 0), ($\bar{2}$ $\bar{3}$ 2), and ($\bar{2}$ 3 2) at distances of 0.16, 0.06, 0.06, and 0.06 mm, respectively. The transmission factor on intensities ranged from 0.052 to 0.112. Averaging of the equivalent reflections led to 1242 independent planes which were used in the structure determination.

Structure Determination and Refinement

As the possible space groups were either Cc or $C2/c$, a second-order harmonic test was performed. The presence of a strong signal established the noncentrosymmetry of the structure; therefore, the structural determination was carried out in the space group Cc. In this space group, the Patterson map was readily interpreted by assuming that Tl atoms occupy three independent general positions. For the Tl(3) atom, x and z coordinates were held at 0.25 and 0, respectively, to fix the origin. S and O coordinates were deduced from subsequent refinement and difference synthesis. Refinement of all the position parameters, of anisotropic thermal parameters for Tl atoms, and of isotropic thermal parameters for S and O atoms, led to $R = 0.04$. and $R_w = 0.58$. After rejection of 17 reflections such that $|F_{obs} - F_{calc}| > 3\,\sigma$ (σ is defined by $\sigma = [\Sigma(F_{obs} - F_{calc})^2/N]^{1/2}$, N = number of independent planes), the reliability factors were 0.034 and 0.041 for the remaining reflections (0.038 and 0.061 if the 1242 initial reflections were included). Attempts to determine the absolute configuration failed: the slight decrease of R and R_w to 0.033 and 0.039 (0.037 and 0.059 for all reflections),

brought about by changing the $\Delta f''$ signs, was not considered as significant. A secondary extinction correction was introduced in the form $F_{cor}^2 = F_{calc}^2/(1 + SF_{obs}^2)$, the final value of S being 0.271 (7). 10^{-6}. No attempt was made to locate the hydrogen atom.

Atomic coordinates and isotropic temperature factors are listed in Table I. Anisotropic thermal parameters of Tl atoms are reported in Table II. The F_{obs} and F_{calc} values are listed in Table III.[1]

TABLE I

REFINED POSITIONAL PARAMETERS ($\times$ 10^4) AND ISOTROPIC TEMPERATURE FACTORS (FOR S AND O) OR EQUIVALENT ISOTROPIC PARAMETERS FOR Tl ATOMS

Atom	x	y	z	B (or B_{eq})[a] (Å^2)
Tl(1)	−445(2)	1131(1)	2167(2)	1.70
Tl(2)	−330(2)	5206(1)	1911(2)	2.56
Tl(3)	2500	2467(1)	0	0.97
S(1)	−266(7)	3222(2)	2417(8)	1.04(6)
S(2)	4920(8)	4128(3)	2502(9)	1.18(6)
O(1)	−1281(22)	3638(9)	401(25)	1.55(23)
O(2)	4115(25)	3569(10)	688(28)	1.96(26)
O(3)	6285(25)	4643(10)	2290(28)	2.04(27)
O(4)	−1667(24)	2697(9)	2595(26)	1.82(25)
O(5)	1311(24)	2742(9)	2499(27)	1.74(25)
O(6)	3299(25)	4537(10)	2501(27)	1.90(26)
O(7)	515(22)	3739(9)	4205(24)	1.45(22)
O(8)	6051(26)	3688(10)	4529(28)	2.07(27)
O(9)	4853(20)	1959(7)	2821(21)	0.92(19)

[a] B_{eq}: equivalent isotropic temperature factors are computed according to the relation $B_{eq} = \frac{4}{3}\Sigma_{ij}\beta_{ij}a_i \cdot a_j$.

TABLE II

REFINED ANISOTROPIC THERMAL COEFFICIENTS FOR Tl ATOMS[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(1)	0.01007(19)	0.00128(2)	0.01214(22)	−0.00003(5)	0.00678(17)	−0.00020(6)
Tl(2)	0.01430(24)	0.00186(3)	0.1976(32)	0.00066(7)	0.01030(23)	0.00030(8)
Tl(3)	0.00459(12)	0.00081(2)	0.00568(14)	−0.00006(5)	0.00192(10)	0.00012(6)

[a] The anisotropic temperature factor is defined by $\exp(-\Sigma_{ij}\beta_{ij}h_ih_j)$.

Scattering factors for Tl^+, Tl^{3+}, S, and O were taken from Ref. (4). The anomalous dispersion corrections were made according to Cromer and Liberman (5). The full matrix least-squares refinements were performed with a local modification of ORFLS (6). A weight of unity was attributed to all reflections.

Description of the Structure

Building blocks of the structure are TlO_6 octahedra and SO_4 tetrahedra linked together to form sheets of composition $TlOH(SO_4)_2$ parallel to (0 1 0) plane (Fig. 1). In the |Ī 0 1| direction two TlO_6 octahedra are linked by one SO_4 tetrahedron in the same manner as InO_6 octahedra in $HIn(SO_4)_2$, $4H_2O$ (7). In the [1 0 1] direction, the linkage is more complex: two TlO_6 octahedra are joined not only by one SO_4 tetrahedron but also by OH bridge. Therefore, one TlO_6 octahedron is bound to four other octahedra. The cohesion between sheets is purely electrostatic via the Tl^+ ions (Fig. 2).

Discussion of the Structure

The Tl^{III} atom is surrounded by six oxygen atoms forming a distorted octahedron; four oxygen atoms also belong to sulfate groups and are in contact with only one thallium atom; the remaining two are hydroxyl oxygens and are in contact with two thallium atoms. Such OH bridges exist in $TlOHSO_4(H_2O)_{2.5}$ (8) in which the TlO_6 oc-

tahedra are completed by H_2O molecules and form infinite chains. In this compound there is no significant difference between the six Tl–O distances ranging from 2.16 to 2.26 Å (average value 2.22 Å). In $Tl_2TlOH(SO_4)_2$, the average Tl–O distance is 2.24 Å, which is in good agreement with

TABLE IIII

PRINCIPAL DISTANCES (Å) AND ANGLES (°) IN $Tl_2TlOH(SO_4)_2$

Tl(1) polyhedron			
Tl–O(1)ⁱᵛ	2.93(1)	Tl–O(5)ⁱ	3.10(2)
Tl–O(2)ⁱᵛ₁₀₀	2.83(2)	Tl–O(6)ⁱⁱ₁₁₀	3.02(2)
Tl–O(3)ⁱⁱ₁₁₀	2.92(2)	Tl–O(6)ⁱᵛ₁₀₁̄	3.28(2)
Tl–O(4)ⁱ	2.98(2)	Tl–O(7)ⁱᵛ₁₀₁̄	2.80(1)
		Tl–O(8)ⁱᵛ₁₀₁̄	2.73(2)
Tl(2) polyhedron			
Tl–O(1)ⁱ	2.93(2)	Tl–O(7)ⁱⁱ	2.97(2)
Tl–O(3)ⁱ₁₀₀	2.95(2)	Tl–O(7)ⁱⁱⁱ₀₁₁̄	3.02(2)
Tl–O(3)ⁱⁱⁱ₁₁₁̄	3.10(2)	Tl–O(8)ⁱⁱ₁₁₁̄	3.14(2)
Tl–O(6)ⁱ	2.88(2)	Tl–O(9)ⁱⁱ₁₀	3.14(1)
Tl(3) octahedron			
Tl–O(2)ⁱ	2.22(2)	Tl–O(8)ⁱᵛ₊₀₁̄	2.26(2)
Tl–O(4)ⁱᵛ₀₀₁̄	2.18(2)	Tl–O(9)ⁱ	2.16(1)
Tl–O(5)ⁱ	2.48(2)	Tl–O(9)ⁱᵛ₁₀₁̄	2.13(1)
Tl–O(9)–Tl	124.3(8)		
Sulfate tetrahedra			
S(1)–O(1)	1.48(2)	S(2)–O(2)	1.52(2)
S(1)–O(4)	1.48(2)	S(2)–O(3)	1.46(2)
S(1)–O(5)	1.46(2)	S(2)–O(6)	1.45(2)
S(1)–O(7)	1.46(2)	S(2)–O(8)	1.51(2)
O(1)–S(1)–O(4)	11(2)	O(2)–S(2)–O(3)	108(2)
O(1)–S(1)–O(5)	110(2)	O(2)–S(2)–O(6)	110(3)
O(1)–S(1)–O(7)	112(2)	O(2)–S(2)–O(8)	109(2)
O(4)–S(1)–O(5)	106(2)	O(3)–S(2)–O(6)	112(3)
O(4)–S(1)–O(7)	108(2)	O(3)–S(2)–O(8)	109(3)
O(5)–S(1)–O(7)	111(2)	O(6)–S(2)–O(8)	109(2)

Note. For Tl polyhedra 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) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $x,\bar{y}, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.
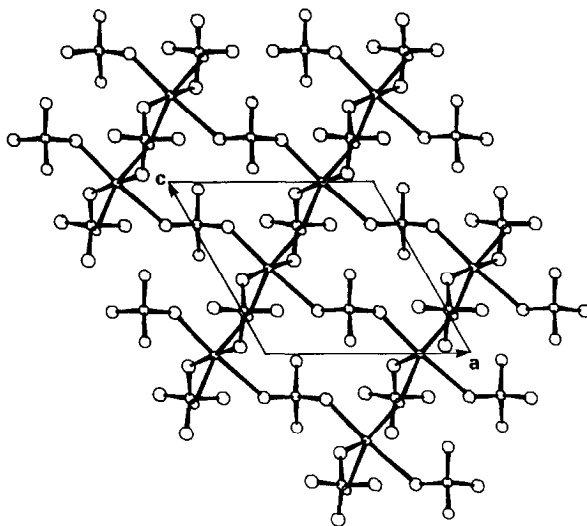
FIG. 1. A sheet Tl^{III}OH(SO$_4$)$_2$, view along the [010] direction.

the previously reported values (2.26 Å in Tl$_2$O$_3$), but there are significant differences between the six Tl–O distances: the Tl–OH distances are shorter (2.16 and 2.13 Å) while the Tl–O(5) separation is abnormally high (2.48 Å).

The two SO$_4$ tetrahedra are different: S(1)O$_4$ is nearly regular with S(1)–O dis-

FIG. 2. Linkage of the sheets Tl^{III}OH(SO$_4$)$_2$ by Tl^I atoms, view along [101] direction.

tances ranging from 1.46 to 1.48 Å (average value 1.47 Å), while the S(2)O$_4$ tetrahedron is highly distorted with two long bonds (1.52 and 1.51 Å) with O atoms linked to Tl(3), and two shorter bonds (1.45 and 1.46 Å) with O not bonded to Tl(3); such a deformation has already been found, for example, in the two forms of (NH$_4$)$_3$ In(SO$_4$)$_3$ (9, 10). The regularity of S(1)O$_4$ tetrahedron precludes the possibility of a misplacement of the O(5) atom.

In this compound the s^2 lone pairs of Tl$^+$ atoms exhibit no marked stereochemical activity. Indeed, around the Tl(1) atom there are nine oxygen atoms with distances Tl–O ranging from 2.73 to 3.28 Å (Fig. 3); around the Tl(2) atom, there are eight oxygen atoms with distances ranging from 2.88 to 3.14 Å. The average Tl–O values are 2.95 and 3.02 Å, respectively.

The heavy Tl atoms and the small deviations from a centrosymmetric arrangement might lead to errors in the light atom positions not reflected by the standard deviations.

An unusual phenomenon was observed during the second-order harmonic test: at 20°C the signal was strong (about the inten-
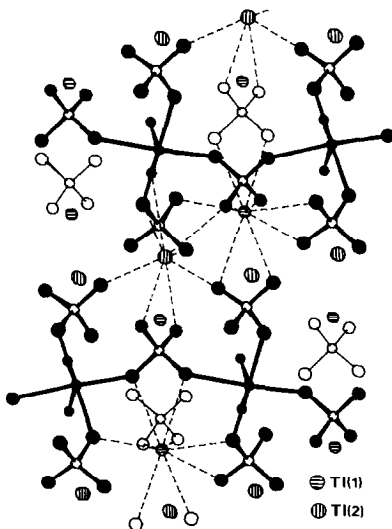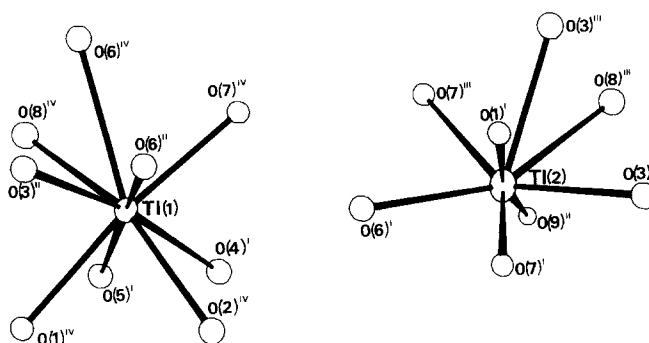
FIG. 3. Thallium I coordination polyhedra.

sity obtained with KDP samples) and indicated noncentrosymmetry of the compound. On heating, the signal disappeared at about 100°C and did not return on cooling. Thermal study of $Tl_2TlOH(SO_4)_2$ by DTA, TGA, and high temperature X-ray powder diffraction does not show any transition before the decomposition (which begins at 220°C). However, micro-DSC obtained with a Perkin Elmer DSC2 apparatus displays a slight nonreversible thermal phenomenon at 104°C. These facts seem to point to a nonreversible transition from a noncentrosymetric space group (Cc) to a centrosymmetric one ($C2/c$). Indeed the arrangement of the $Tl^{III}OH(SO_4)_2$ sheets is almost centrosymmetric and the greatest movement involves the Tl^+ ions. An attempt was made to measure the intensities diffracted by a single crystal which was heated to 110°C and cooled to ambient temperature: no significant differences were found in the intensities nor in the subsequent Patterson map. It seems that the transition is reversible but slow in the reverse direction, so that the crystal tested either had not undergone the transformation or had time enough to revert to the low tem-

perature form. This transition is presently under intense study.

Acknowledgments

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