

The Crystal Structures of $Tl_3[Hg(SO_4)_2][HgSO_4Cl]$ and $Rb_3[Hg(SO_4)_2][HgSO_4Cl]$

BENGT BOSSON

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology,
P.O. Box 740, S-220 07 Lund 7, Sweden

The crystal structures of $M_3[Hg(SO_4)_2][HgSO_4Cl]$, $M = Tl(I), Rb$ have been determined from single-crystal diffractometer data. The compounds are isostructural, crystallizing in the monoclinic space group $P2_1$, with $Z = 2$. The unit-cell dimensions are

$$a = 7.870(1), b = 9.752(1), c = 9.945(1) \text{ \AA}, \beta = 110.72(1)^\circ \text{ and} \\ a = 7.862(2), b = 9.790(4), c = 10.002(1) \text{ \AA}, \beta = 111.12(2)^\circ$$

for the thallium and rubidium compounds, respectively. The structures may be considered as ionic, made up of $Hg(SO_4)_2^{2-}, HgSO_4Cl^-$ and M^+ ions. There is no reason to assume the presence of a stereochemical inert electron pair for the Tl^+ ion in the present structure.

The present investigation was undertaken to study the coordination polyhedra of univalent thallium and rubidium. A study in the same field has been reported previously.¹ Work is in progress on $RbZnSO_4Cl, TlZnSO_4Cl$ (a refinement) and $Tl_2S_2O_3$.

EXPERIMENTAL

Preparation. Single crystals of $Tl_3[Hg(SO_4)_2][HgSO_4Cl]$ and $Rb_3[Hg(SO_4)_2][HgSO_4Cl]$ were prepared by melting MCl, M_2SO_4 ($M = Tl, Rb$) and anhydrous $HgSO_4$ in a mol ratio of 1:1:2 in a sealed gold tube at a temperature of 700 °C. The crystals are in the form of transparent thin plates. The homogeneity of the crystalline samples was checked by X-ray Guinier-Hägg powder photographs.

Crystal data and space group. Preliminary Weissenberg photographs showed that the present thallium and rubidium salts are isostructural. The compounds crystallize in the monoclinic system. The only systematic absences found were $0k0$ with $k = 2n + 1$, which are char-

acteristic of the space groups $P2_1$ (No. 4) and $P2_1/m$ (No. 11). An $N(z)$ test showed the structure to be noncentrosymmetric, thus indicating the space group $P2_1$.

The unit-cell dimensions were determined for $Tl_3[Hg(SO_4)_2][HgSO_4Cl]$ from powder photographs taken in a Guinier-Hägg focusing camera with $CuK\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$) and potassium chloride as an internal standard (cubic, $a = 6.2929$). Refinement of the cell parameters was performed by a least-squares program. The lattice constants for $Rb_3[Hg(SO_4)_2][HgSO_4Cl]$ were obtained from a least-squares analysis of the settings of 30 reflexions measured on a four-circle diffractometer with $MoK\alpha_1$ radiation ($\lambda = 0.70926 \text{ \AA}$).

The densities of the compounds were observed by measuring the loss of weight in benzene. Some crystal data are presented in Table 1.

Collection and reduction of intensity data

$Tl_3[Hg(SO_4)_2][HgSO_4Cl]$. A crystal with the dimensions $0.16 \times 0.03 \times 0.13 \text{ mm}^3$ along a, b

Table 1. Crystallographic data for $M_3[Hg(SO_4)_2][HgSO_4Cl]$ where $M = Tl$ or Rb .

	M = Tl	M = Rb
a (Å)	7.870(1)	7.862(2)
b (Å)	9.752(1)	9.790(4)
c (Å)	9.945(1)	10.002(1)
β (°)	110.72(1)	111.12(2)
V (Å ³)	713.9(1)	718.0(4)
Z	2	2
M (g mol ⁻¹)	1337.93	981.22
D_m (g cm ⁻³)	6.22	4.45
D_x (g cm ⁻³)	6.10	4.48
$\mu(MoK\alpha)$ (cm ⁻¹)	565	334

and *c*, respectively, was chosen for the data collection. The intensity data were recorded on a computer-controlled Enraf-Nonius four-circle diffractometer (CAD4) using graphite-monochromatized MoK α radiation ($\lambda=0.71069$ Å). The $\omega-2\theta$ scan technique was used with a scan interval $\Delta\omega^\circ$, of $0.9+0.5 \tan \theta$. One fourth of reciprocal space out to $(\sin \theta)/\lambda=0.985$ Å $^{-1}$ was examined. Instrumental stability and crystal setting were checked using two standard reflexions remeasured every 90 min. No significant variation in their intensities could be observed.

The total number of reflexions was 1544, of which 79 were considered unobserved, being weaker than $3\sigma(I)$, where *I* is the intensity and $\sigma(I)$ its standard deviation based on counting statistics. The remaining 1465 intensities were corrected for Lorentz, polarization and absorption effects. The polarization factor used was that for ideally mosaic crystals. The crystal could be described by eight planes and the transmission factors, evaluated by numerical integration, were in the range 0.018–0.121.

Rb₂[Hg(SO₄)₂][HgSO₄Cl]. A crystal with the dimensions $0.17 \times 0.22 \times 0.09$ along *a*, *b* and *c*, respectively, was used for the data collection on the diffractometer with the same experimental conditions as described above. Of the 2046 independent reflexions recorded, 75 were excluded as $I < 3\sigma(I)$. The remaining 1971 reflexions were treated as mentioned above. For calculating the absorption corrections, the crystal was described by seven planes. The transmission factors were in the range 0.025–0.113.

STRUCTURE DETERMINATION

Tl₂[Hg(SO₄)₂][HgSO₄Cl]. The positions of the heavy metal atoms were found from a combination of a three-dimensional Patterson function and direct methods. The chlorine, sulfur and oxygen atoms were located from a three-dimensional electron density difference synthesis. All atoms occupy the general point position $2(a)$ in the space group $P2_1$.

A full-matrix least-squares refinement minimizing $\sum w_i(|F_o| - |F_c|)^2$ was performed with weights $w_i^{-1} = \sigma^2(F_o^2)/4F_o^2 + aF_o^2 + b$. In the last cycle of refinement, the values $a=0.0003$ and $b=2.0$ were used. The convergency was followed by the agreement indices *R* and *R_w*, defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}$. A refinement of the atomic coordinates with anisotropic temperature factors for thallium and mercury converged to $R=0.051$ and $R_w=0.052$. In this refinement the effect of anomalous dispersion was included, moreover a correction for extinction was applied. The value of the isotropic extinction parameters *g* was 2.2×10^5 .

Rb₂[Hg(SO₄)₂][HgSO₄Cl]. The positional and thermal parameters for the thallium compound were used as preliminary parameters for the rubidium salt. An exactly similar refinement was employed here as for *Tl₂[Hg(SO₄)₂][HgSO₄Cl]*. Weights used in the last cycle of the refinement were $w_i^{-1} = \sigma^2(F_o^2)/4F_o^2 +$

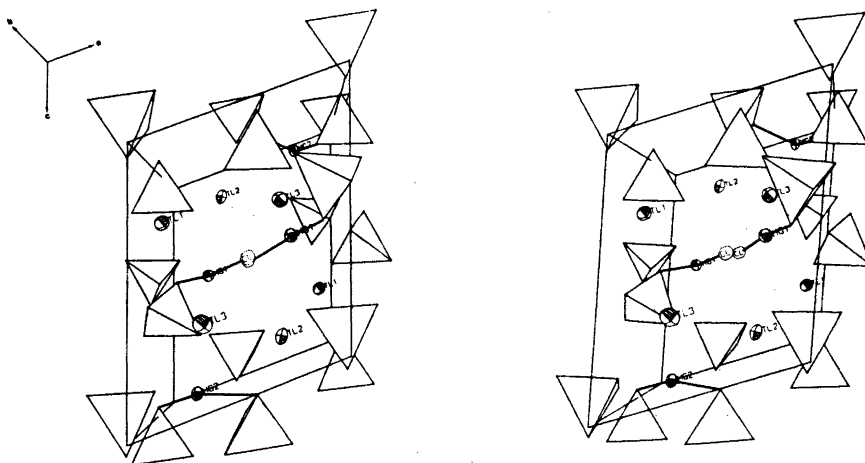


Fig. 1. A stereoscopic pair of drawings showing the ions $\text{Hg}(\text{SO}_4)_2^{2-}$, HgSO_4Cl^- and Tl^+ . The tetrahedra denote the sulfate groups.

Table 2. Final positional parameters and isotropic temperature factors in Ti₃[Hg(SO₄)₂][HgSO₄Cl] and Rb₃[Hg(SO₄)₂][HgSO₄Cl]. Standard deviations are given in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Ti ₃ [Hg(SO ₄) ₂][HgSO ₄ Cl]				
Ti(1)	0.9036(2)	0.2500(0)	0.7300(2)	—
Ti(2)	0.3166(2)	0.1183(2)	0.1422(2)	—
Ti(3)	0.6761(2)	0.4415(3)	0.3016(2)	—
Hg(1)	0.2688(2)	0.3516(3)	0.4966(2)	—
Hg(2)	0.7600(2)	0.0711(2)	0.0445(2)	—
Cl	0.484(1)	0.208(1)	0.488(1)	2.7(2)
S(1)	0.912(1)	0.116(1)	0.391(1)	1.7(2)
S(2)	0.014(1)	0.415(1)	0.110(1)	1.6(2)
S(3)	0.443(1)	0.301(1)	0.859(1)	1.8(2)
O(1A)	0.972(3)	0.256(3)	0.446(3)	1.6(4)
O(1B)	0.737(3)	0.122(3)	0.266(3)	1.8(4)
O(1C)	0.873(3)	0.049(3)	0.513(3)	2.3(5)
O(1D)	0.046(3)	0.045(3)	0.352(3)	2.3(4)
O(2A)	0.016(3)	0.461(3)	0.960(3)	1.9(5)
O(2B)	0.121(4)	-0.003(4)	0.862(4)	3.9(7)
O(2C)	0.967(4)	0.266(4)	0.092(3)	3.5(6)
O(2D)	0.199(3)	0.438(3)	0.214(3)	2.5(5)
O(3A)	0.580(4)	0.364(4)	0.816(3)	3.7(6)
O(3B)	0.264(3)	0.290(3)	0.746(3)	3.0(5)
O(3C)	0.504(4)	0.153(3)	0.912(4)	3.7(6)
O(3D)	0.426(4)	0.370(4)	0.981(3)	3.4(6)
Rb ₃ [Hg(SO ₄) ₂][HgSO ₄ Cl]				
Rb(1)	0.8986(3)	0.7500(0)	0.7314(3)	—
Rb(2)	0.3188(3)	0.8787(4)	0.1328(3)	—
Rb(3)	0.6734(4)	0.5539(4)	0.3035(4)	—
Hg(1)	0.2653(1)	0.6507(3)	0.4983(1)	—
Hg(2)	0.7635(1)	0.9290(3)	0.0512(1)	—
Cl	0.481(1)	0.805(1)	0.481(1)	2.6(1)
S(1)	0.907(1)	0.892(1)	0.391(1)	1.3(1)
S(2)	0.028(1)	0.596(1)	0.110(1)	1.3(1)
S(3)	0.451(1)	0.710(1)	0.859(1)	1.4(1)
O(1A)	0.964(3)	0.754(2)	0.449(2)	1.9(3)
O(1B)	0.734(3)	0.883(2)	0.267(2)	1.9(3)
O(1C)	0.869(3)	0.963(2)	0.513(2)	2.0(3)
O(1D)	0.040(2)	0.963(2)	0.352(2)	1.7(2)
O(2A)	0.027(3)	0.554(2)	0.965(2)	2.2(3)
O(2B)	0.104(3)	0.016(3)	0.855(3)	3.0(4)
O(2C)	0.981(4)	0.742(3)	0.088(3)	3.4(4)
O(2D)	0.216(3)	0.577(2)	0.213(2)	2.5(3)
O(3A)	0.590(3)	0.655(2)	0.810(2)	2.8(3)
O(3B)	0.270(3)	0.719(2)	0.740(2)	2.1(3)
O(3C)	0.501(3)	0.854(2)	0.913(3)	3.0(4)
O(3D)	0.436(3)	0.634(2)	0.979(3)	2.7(3)

0.008*F*_o². This gave *R* = 0.077, *R*_w = 0.089, and a smooth weighting scheme. The extinction parameter *g* was 4.4 × 10⁵.

Because of the space group a determination of the absolute configuration was possible for the crystal used.³ The refinement of a structure with an absolute configuration opposite in the

y-direction to the one chosen for Ti₃[Hg(SO₄)₂]-[HgSO₄Cl] converged for the single crystal used for Rb₃[Hg(SO₄)₂][HgSO₄Cl]. Hamilton's *R*-test³ indicates the absolute configuration for the rubidium crystal actually investigated up to a 0.005 significance level.

In all refinements, the atomic scattering

Table 3. Final anisotropic temperature factors for the heavy atoms in $Tl_3[Hg(SO_4)_2][HgSO_4Cl]$ and $Rb_3[Hg(SO_4)_2][HgSO_4Cl]$. The form of the anisotropic temperature factor is: $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. Standard deviations are given in parentheses.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$Tl_3[Hg(SO_4)_2][HgSO_4Cl]$						
Tl(1)	0.01088(29)	0.00620(19)	0.00716(21)	-0.00048(19)	0.00293(19)	-0.00078(18)
Tl(2)	0.00889(26)	0.00574(18)	0.00857(24)	0.00028(18)	0.00154(20)	-0.00028(18)
Tl(3)	0.01592(35)	0.00771(22)	0.01062(28)	0.00304(23)	0.00603(26)	0.00279(21)
Hg(1)	0.00832(26)	0.00662(18)	0.00612(20)	0.00160(19)	0.00300(19)	0.00043(18)
Hg(2)	0.00626(24)	0.00511(17)	0.00718(21)	0.00056(16)	0.00220(18)	-0.00042(17)
$Rb_3[Hg(SO_4)_2][HgSO_4Cl]$						
Rb(1)	0.00755(36)	0.00583(21)	0.00469(21)	-0.00073(22)	0.00183(22)	-0.00104(18)
Rb(2)	0.00674(37)	0.00642(21)	0.00648(25)	0.00018(24)	-0.00001(24)	-0.00030(22)
Rb(3)	0.01332(51)	0.00737(26)	0.00813(30)	0.00278(30)	0.00407(32)	0.00291(25)
Hg(1)	0.00630(15)	0.00622(10)	0.00471(11)	0.00143(9)	0.00171(9)	0.00005(7)
Hg(2)	0.00484(14)	0.00532(8)	0.00447(10)	0.00061(8)	0.00127(8)	-0.00022(7)

Table 4. Selected distances (Å) and bond angles (°) with standard deviations in parentheses in the structures of $M_3[Hg(SO_4)_2][HgSO_4Cl]$, where M = Tl or Rb.

	M = Tl	M = Rb
Distances		
M(1)-O(3B)	2.80(3)	2.91(2)
M(1)-O(1C)	2.90(3)	2.97(2)
M(1)-O(2A)	2.96(3)	2.91(2)
M(1)-O(2B)	3.03(4)	3.08(3)
M(1)-O(1D)	3.03(3)	3.02(2)
M(1)-O(1A)	3.08(3)	3.05(2)
M(1)-O(3A)	3.14(4)	2.96(2)
M(1)-O(2D)	3.25(3)	3.43(2)
M(1)-Cl	3.35(1)	3.38(1)
M(1)-O(2C)	3.45(4)	3.39(3)
M(2)-O(3A)	2.60(4)	2.81(2)
M(2)-O(2A)	2.87(3)	3.06(2)
M(2)-O(2B)	2.94(4)	3.00(3)
M(2)-O(2C)	3.00(4)	2.86(3)
M(2)-O(1B)	3.09(3)	3.05(2)
M(2)-O(3C)	3.14(4)	3.03(2)
M(2)-O(3D)	3.21(4)	3.16(2)
M(2)-Cl	3.34(1)	3.32(1)
M(2)-O(2D)	3.40(3)	3.24(2)
M(3)-O(2B)	2.68(4)	2.78(3)
M(3)-O(1A)	2.89(3)	2.96(2)
M(3)-O(3C)	2.95(4)	2.87(2)
M(3)-O(3D)	3.16(4)	3.20(2)
M(3)-O(1B)	3.20(3)	3.30(2)
M(3)-O(3B)	3.44(4)	3.36(2)
M(3)-O(1C)	3.54(3)	3.52(2)
M(3)-O(1D)	3.53(3)	3.49(2)
M(3)-O(2D)	3.55(3)	3.38(2)
M(3)-Cl	3.60(1)	3.66(1)

Table 4. Continued.

Hg(1)-O(1C)	2.17(3)	2.10(2)
Hg(1)-Cl	2.24(1)	2.32(1)
Hg(1)-O(1A)	2.40(2)	2.46(2)
Hg(1)-O(3B)	2.58(3)	2.50(2)
Hg(1)-O(2D)	2.80(3)	2.83(2)
Hg(2)-O(2A)	2.09(3)	2.10(2)
Hg(2)-O(3C)	2.16(4)	2.16(2)
Hg(2)-O(1B)	2.34(3)	2.30(2)
Hg(2)-O(2C)	2.42(4)	2.44(3)
Hg(2)-O(3D)	2.42(4)	2.50(2)
Angles		
Cl-Hg(1)-O(1A)	116.2(0.8)	113.2(0.5)
Cl-Hg(1)-O(1C)	158.6(0.7)	158.6(0.6)
Cl-Hg(1)-O(2D)	92.1(0.7)	85.9(0.5)
Cl-Hg(1)-O(3B)	98.3(0.8)	98.2(0.5)
O(1A)-Hg(1)-O(1C)	83.6(1.03)	85.3(0.7)
O(1A)-Hg(1)-O(2D)	93.8(0.9)	97.5(0.6)
O(1A)-Hg(1)-O(3B)	76.5(0.9)	76.2(0.6)
O(1C)-Hg(1)-O(2D)	77.9(1.1)	80.9(0.7)
O(1C)-Hg(1)-O(3B)	94.1(1.1)	96.7(0.7)
O(2D)-Hg(1)-O(3B)	168.1(0.9)	173.5(0.6)
O(1B)-Hg(2)-O(2A)	118.4(1.0)	122.3(0.7)
O(1B)-Hg(2)-O(2C)	85.9(1.1)	90.9(0.8)
O(1B)-Hg(2)-O(3C)	97.2(1.1)	97.8(0.8)
O(1B)-Hg(2)-O(3D)	91.3(1.1)	89.9(0.7)
O(2A)-Hg(2)-O(2C)	83.7(1.2)	85.5(0.8)
O(2A)-Hg(2)-O(3C)	144.2(1.2)	138.0(0.9)
O(2A)-Hg(2)-O(3D)	94.3(1.2)	90.0(0.8)
O(2C)-Hg(2)-O(3C)	103.8(1.3)	107.4(0.9)
O(2C)-Hg(2)-O(3D)	175.2(1.2)	175.1(0.8)
O(3C)-Hg(2)-O(3D)	80.4(1.3)	77.3(0.8)

factors as well as the real ($\Delta f'$) and imaginary ($\Delta f''$) anomalous dispersion terms were those given by Cromer *et al.*^{4,5}

The final positional parameters and isotropic temperature factors for both structures are given in Table 2. Anisotropic temperature factors for the thallium, mercury and rubidium atoms are presented in Table 3. In Table 4 selected interatomic distances and angles are given. Observed and calculated structure amplitudes are available on request.

All computations were made on the UNIVAC 1108 computer in Lund. A short account of the program system used has been given.⁶

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Tl₃[Hg(SO₄)₂][HgSO₄Cl]. The structure may be considered as ionic, made up of Hg(SO₄)₂²⁻, HgSO₄Cl⁻ and Tl⁺ ions. The group Hg(SO₄)₂²⁻ has previously been reported to exist in solution.⁷ A stereoscopic view of the structure is presented in Fig. 1.

The sum of the ionic radii of Tl⁺ and O²⁻ for eight-coordination is 3.00 Å and of Tl⁺ and Cl⁻ 3.41 Å according to a summary.⁸ A value of 3.33 Å is also reported⁹ for Tl⁺ to Cl⁻. In the structure there are three kinds of thallium(I) atoms, denoted Tl(1), Tl(2) and Tl(3) in Fig. 1. The shortest thallium to oxygen distances, 2.80, 2.60 and 2.68 Å, and thallium to chlorine distances, 3.35, 3.34 and 3.60 Å, for Tl(1), Tl(2) and Tl(3), respectively, may indicate that they are mainly ionic in character.

All thallium atoms have irregular environments. The Tl(1) atom is surrounded by eight oxygen atoms at distances between 2.80 and 3.25 Å (mean value 3.02 Å), and by one chlorine atom at 3.35 Å. A ninth oxygen atom is situated at a distance of 3.45 Å (Fig. 2a). Tl(2) has seven oxygen neighbours at distances between 2.60 and 3.21 Å (mean value 2.98 Å) and one chlorine atom at 3.34 Å. An eighth oxygen atom is situated at a distance of 3.40 Å (Fig. 2b). Tl(3) is surrounded by five oxygen atoms, the distances ranging from 2.68 to 3.20 Å (mean value 2.98 Å) and by an addi-

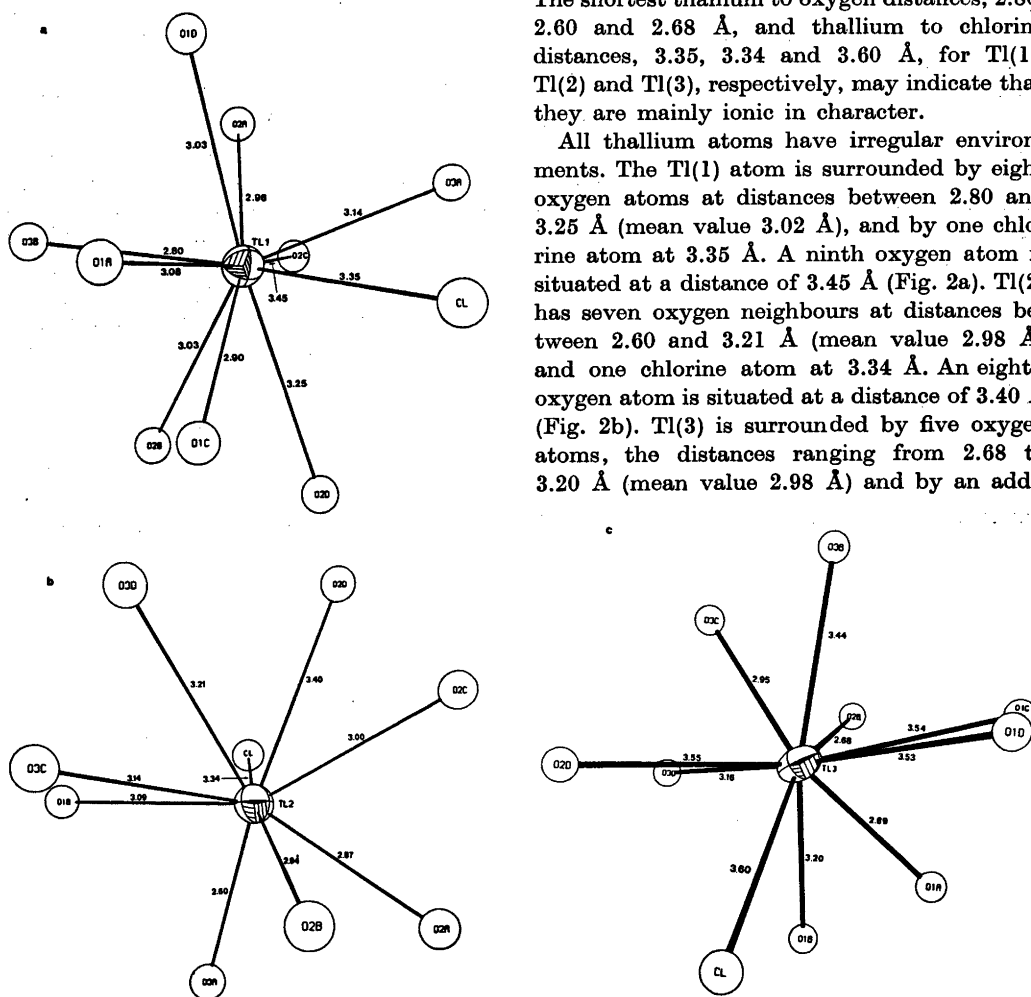


Fig. 2a-c. The environments of the Tl(1), Tl(2) and Tl(3) atoms.

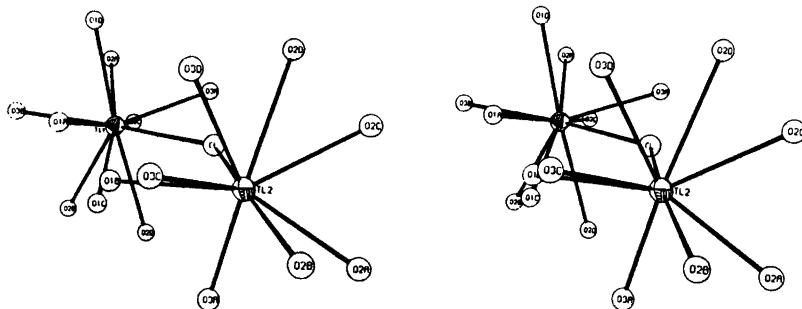


Fig. 3. Stereoscopic illustration showing the environments of the Tl(1) and Tl(2) atoms.

tional four, at distances varying between 3.44 to 3.55 Å. The chlorine–thallium distance is 3.60 Å. (Fig. 2c). Several thallium to oxygen distances are reported for different structures in the literature, *e.g.* 2.91–3.24 Å¹ for eight-coordination and 2.82–3.04 Å¹⁰ for seven-coordination. In all of these structures, additional oxygen atoms are situated 3.4–3.5 Å from thallium. The environments of the Tl(1) and Tl(2) atoms are shown in a stereo view (Fig. 3).

In the structure there are two kinds of mercury atoms, denoted Hg(1) and Hg(2) in Fig. 1. The Hg(1) atom has two close ligands, in a nearly linear geometry, one oxygen atom at the distance 2.17 Å and one chlorine atom at 2.24 Å, the angle O–Hg–Cl being 158.6°. Thus a HgSO₄Cl[−] ion is formed. Three additional oxygen atoms from three other sulfate

tetrahedra at the distances 2.40, 2.58 and 2.80 Å complete a distorted trigonal bipyramid (Fig. 4a).

The mercury atom Hg(2) has also two close ligands, one oxygen atom belonging to the S(2) sulfate group at 2.09 Å and another oxygen atom belonging to the S(3) sulfate group at 2.16 Å. The bond angle is 149°. In this way a Hg(SO₄)₂^{2−} ion is formed. Three additional oxygen atoms are situated at the larger distances of 2.34 and 2.42 (× 2) Å. The polyhedron thus formed may be described as a deformed trigonal bipyramid (Fig. 4b). Both mercury atoms of the asymmetric part of the unit cell thus occur as discrete complexes HgSO₄Cl[−] and Hg(SO₄)₂^{2−}. To our knowledge, only one discrete mercury sulfate complex has previously been found in the solid state, namely the finite Hg₂(OH)₂(SO₄)₂ chain in the crystal structure

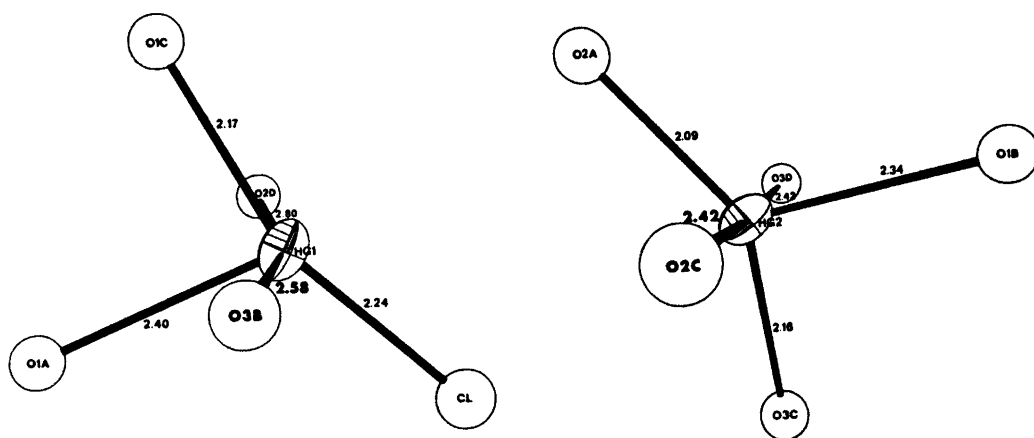


Fig. 4 a–b. The environments of the Hg(1) and Hg(2) atoms.

of Hg₃(OH)₂(SO₄)₂·H₂O.^{11,12} It may be noted that all chlorine atoms of the unit cell are bonded to mercury. The tendency of mercury to coordinate a chlorine atom is thus larger than to coordinate a sulfate oxygen atom in the solid state. The fact that the present compound has been synthesized under water-free conditions, and the presence of large cations as Tl⁺ or Rb⁺ may have contributed to the occurrence of discrete mercury complexes in the crystal structure.

Twofold coordination is prevalent among mercury(II) compounds. As an example, in Hg₂OCl₄¹³ the mercury atom forms two nearly colinear bonds to one oxygen and one chlorine atom, the distances Hg—O and Hg—Cl being 2.06(3) and 2.30(2) Å, respectively. The structures of HgCrO₄·½H₂O¹⁴ and Hg₃(OH)₂·(SO₄)₂·H₂O¹¹ have recently been refined to a high degree of accuracy, the calculations being based on neutron diffraction data.^{12,15} In HgCrO₄·½H₂O the mercury atom has two close oxygen neighbours belonging to two different chromate tetrahedra at the distances 2.055(1) and 2.064(1) Å, the O—Hg—O angle being 179.95(5)°. In the finite complex Hg₃(OH)₂(SO₄)₂ in the structure of Hg₃(OH)₂·(SO₄)₂·H₂O the distances mercury to a sulfate oxygen atom and an hydroxide oxygen atom are 2.058(2) and 2.087(2) Å, respectively, the angle O—Hg—O being 168.79(4)°. The complex formation of mercury is thus less pronounced in the compounds now investigated, also containing the big cations Tl⁺ or Rb⁺ than in compounds where the metals atoms are only mercury.

The dimensions of the three different sulfate groups are in good agreement with those reported (1.44–1.53 Å).⁹ The mean S—O distances are 1.47, 1.48 and 1.51 Å. The S—O distances for the oxygen atoms bonded to mercury seem to be somewhat elongated (Table 4).

Rb₃[Hg(SO₄)₂][HgSO₄Cl]. In Rb₃[Hg(SO₄)₂][HgSO₄Cl], isostructural with the thallium compound, the rubidium ions have the same coordinations as the thallium ions in the structure described above. The sum of the ionic radii for Rb⁺ and O²⁻ and for Rb⁺ and Cl⁻ are 3.00 and 3.41 Å,⁸ respectively, the same radii sum as for the corresponding thallium salt. The distance Rb—Cl of 3.29 Å is reported

for six-coordination.⁹ If the rubidium salt is compared with the corresponding thallium salt, slight differences in the distances and angles are found (Table 4). The Rb(1) atom is surrounded by seven oxygen atoms at distances between 2.91 and 3.08 Å (mean value 2.99 Å) and by one chlorine atom at 3.38 Å. An eighth and a ninth oxygen atom are situated 3.39 and 3.43 Å apart, respectively. Rb(2) is surrounded by eight oxygen atoms at distances between 2.81 and 3.24 Å (mean value 3.03 Å) and by one chlorine atom at 3.32 Å. Rb(3) has an environment of nine oxygen atoms ranging from 2.78 to 3.52 Å and one chlorine atom at 3.66 Å.

In the compound Rb₂SO₄¹⁶ there are two different sites of Rb atoms, denoted Rb(1) and Rb(2), both of them having irregular environments of oxygen atoms. The Rb(1) atom has ten oxygen atoms within the range 2.91 to 3.31 (σ≈0.01) Å, and Rb(2) has nine oxygen atoms at distances ranging from 2.88 to 3.24 (σ≈0.01) Å. The rubidium ion in RbH₂(SeO₃)₂¹⁷ is surrounded by eight oxygen atoms forming a distorted cube. The Rb—O distances are between 2.939(6) and 3.192(5) Å.

The two mercury atoms, Hg(1) and Hg(2), in the rubidium salt have the same surroundings as in the thallium salt (Table 4). The mean S—O distances for the three different sulfate groups in the rubidium compound are 1.47, 1.48 and 1.48 Å, respectively.

Only a few structures of chlorides and sulfates containing thallium(I) or rubidium ions have so far been investigated. Large coordination numbers and varying bonding distances are common for the metal ions in these systems. The lone electron pair of thallium(I) is stereochemically inactive in the compounds Tl₂[Cu(SO₃)₂]¹⁰ and TlZnSO₄Cl.¹ In the compound Tl₃[Hg(SO₄)₂][HgSO₄Cl] the inert pair of electrons of thallium(I) may also be stereochemically inactive. This is supported by the fact that the rubidium ion, with the noble gas electron configuration, has the same surroundings as the thallium ions in the isotypical compound.

Acknowledgements. I wish to express my sincere thanks to Professor Bengt Aurivillius for his valuable advice and stimulating interest. I also thank Dr. Karin Aurivillius for much valuable help. The work forms part of a pro-

gram supported by the Swedish Natural Science Research Council.

REFERENCES

1. Bosson, B. *Acta Chem. Scand.* 27 (1973) 2230.
2. Ibers, J. A. and Hamilton, W. C. *Acta Crystallogr.* 17 (1969) 781.
3. Hamilton, W. C. *Acta Crystallogr.* 18 (1965) 502.
4. Cromer, D. T. and Libermann, D. J. *Chem. Phys.* 53 (1970) 1891.
5. Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
6. Stålhandske, C. *Acta Crystallogr. B* 30 (1974) 1586.
7. Infeldt, G. and Sillén, L. G. *Sven. Kem. Tidskr.* 58 (1946) 104.
8. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr. B* 25 (1969) 925.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1965, Vol. III.
10. Hjertén, I. and Nyberg, B. *Acta Chem. Scand.* 27 (1973) 345.
11. Björnlund, G. *Acta Chem. Scand. A* 28 (1974) 169.
12. Aurivillius, K. and Stålhandske, C. *Z. Kristallogr.* To be published.
13. Aurivillius, K. *Ark. Kemi* 22 (1964) 537.
14. Aurivillius, K. *Acta Chem. Scand.* 26 (1972) 2113.
15. Aurivillius, K. and Stålhandske, C. *Z. Kristallogr.* To be published.
16. Nord, A. G. *Acta Crystallogr. B* 30 (1974) 1640.
17. Tellgren, R., Ahmad, D. and Liminga, R. J. *Solid State Chem.* 6 (1973) 250.

Received November 13, 1975.