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The Crystal Structures of RbZnSO₄Cl and TlZnSO₄Cl

BY BENGT BOSSON

Inorganic Chemistry 2, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden

From single-crystal X-ray diffractometer data the structure of RbZnSO₄Cl has been determined. A refinement of the structure of TlZnSO₄Cl, based on diffractometer data, is also given. The compounds are closely related, crystallizing in the monoclinic space group $P2_1/c$ with $Z=4$. The structure of the Rb compound may, however, be disordered. The cell dimensions are $a=7\cdot2610$ (3), $b=9\cdot6152$ (5), $c=8\cdot3086$ (6) Å, $\beta=95\cdot542$ (6)° and $a=7\cdot278$ (1), $b=9\cdot551$ (1), $c=8\cdot092$ (1) Å, $\beta=93\cdot97$ (1)° for the Rb and Tl compounds respectively. Fundamental building elements of the structures are infinite layers of formula $(ZnSO_4Cl)_n^{n-}$, parallel to the bc plane. The layers are held together by Rb^+ or Tl^+ ions. There seems to be no reason to assume the presence of a stereochemical inert pair for Tl^+.

Introduction

The present investigation was undertaken to study the coordination polyhedra of univalent Tl and Rb. A preliminary study of TlZnSO₄Cl has been published (Bosson, 1973). Work is in progress on the structures of Tl₃[Hg(SO₄)₂] [HgSO₄Cl], Rb₃[Hg(SO₄)₂] [HgSO₄Cl] and Tl₂S₂O₃.

Experimental

Single crystals of RbZnSO₄Cl and TlZnSO₄Cl were prepared by melting MCl (M = Rb or Tl) and anhydrous ZnSO₄ in the mole ratio 1:1 at 440°C in porcelain crucibles (Luzhnaya & Vereshchetine, 1956). The preparations consisted of colourless, transparent thin plates. The homogeneities of the samples were checked by Guinier–Hägg powder photographs.

RbZnSO₄Cl

Weissenberg photographs indicated the space group $P2_1/c$ as the following spectra were systematically absent: $h0l$, $l\neq2n$; $0k0$, $k\neq2n$. However, horizontal streaks occurred in the photographs. A few very weak $h0l$ reflexions for $l=2n+1$ were recorded on the diffractometer. They are most probably due to parasites but a disordering cannot be excluded.

The lattice constants were obtained from a least-squares analysis of the settings of 40 reflexions measured on the diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1\cdot54051$ Å). The density was determined by displacement in benzene. Some crystal data are given in Table 1.

A single crystal, $0\cdot04 \times 0\cdot22 \times 0\cdot23$ mm along **a**, **b** and **c**, respectively, was selected and mounted so that a crystallographic axis did not coincide with the goniometer φ-axis.

Table 1. Crystal data

RbZnSO$_4$Cl
F.W. 282·4; monoclinic; space group $P2_1/c$
$a = 7·2610$ (3), $b = 9·6152$ (5), $c = 8·3086$ (6) Å
$\beta = 95·542$ (6)°, $V = 577·42$ (6) Å^3, $Z = 4$
$D_m = 3·37$, $D_x = 3·25$ g cm^{-3}
μ(Cu $K\alpha$) = 247 cm^{-1}

TlZnSO$_4$Cl
F.W. 401·3; monoclinic; space group $P2_1/c$
$a = 7·278$ (1), $b = 9·551$ (1), $c = 8·092$ (1) Å
$\beta = 93·97$ (1)°, $V = 561·0$ (2) Å^3, $Z = 4$
$D_m = 4·90$, $D_x = 4·75$ g cm^{-3}
μ(Mo $K\alpha$) = 340 cm^{-1}

The intensities were recorded at room temperature on a computer-controlled Enraf–Nonius four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The ω–2θ scan technique was employed, with a scan interval $\Delta\omega = (0·9 + 0·5 \tan \theta)°$. Instrumental stability and crystal setting were checked with two standard reflexions remeasured every 90 min. No significant variation in their intensities was observed.

The number of reflexions was 1127, of which 82 were considered unobserved with $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics. 14 very weak $h0l$ reflexions with $l = 2n + 1$ were considered to be probably due to parasites and were excluded. The remaining 1031 intensities were corrected for Lorentz, polarization and absorption effects. The polarization factor used was the one for ideally mosaic crystals. The crystal was described by nine planes, and the evaluated transmission factors were in the range 0·063 to 0·372.

TlZnSO$_4$Cl

The observed space group for TlZnSO$_4$Cl is $P2_1/c$. The lattice constants were improved by least squares based on the powder pattern obtained at room temperature with a Guinier–Hägg camera. Cu $K\alpha_1$ radiation ($\lambda = 1·5405$ Å) was used and KCl was added as an internal standard. The density was determined by displacement.

A single crystal, 0·05 × 0·35 × 0·32 along **a**, **b** and **c**, respectively, was used for the data collection on a Pailred linear diffractometer with Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å). The crystal was mounted along **b**. The reflexions of the layer lines $h0l$–$h9l$ were measured with the equi-inclination and ω-scan technique and a scan rate of 1·0° min^{-1}. As a check on the crystal stability and the electronics the intensities of two standard reflexions were measured at regular intervals. No significant variation was observed.

1716 independent reflexions were recorded. 486 were omitted as the two measured background values differed by more than 3·09 times the e.s.d. of their difference or as their intensities had $I \leq 3\sigma(I)$, where $\sigma(I)$ was based on counting statistics. The remaining 1230 reflexions were corrected for Lorentz, polarization and absorption effects. The crystal was described by

six planes and the transmission factors, evaluated by numerical integration, varied from 0·046 to 0·211.

Structure determination and refinement

RbZnSO$_4$Cl

The refinement of the structure was performed in the space group $P2_1/c$. The positional parameters of the atoms in the Tl compound (Bosson, 1973) were used as preliminary parameters for the Rb salt. 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 $a = 0·0025$ and $b = 5·0$ were used. The convergence was followed 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 with anisotropic thermal parameters and the scattering factors corrected for anomalous dispersion for Rb and Zn and isotropic thermal parameters for Cl, S and O converged to $R = 0·080$, $R_w = 0·112$ and $S = 1·75$ (a smooth weighting scheme with $S = [\sum w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m

Table 2. Final positional parameters and isotropic temperature factors in RbZnSO$_4$Cl and TlZnSO$_4$Cl

Standard deviations are given in parentheses.

RbZnSO$_4$Cl

	x	y	z	B (Å^2)
Rb	0·36208 (14)	0·08233 (12)	0·19976 (13)	—
Zn	0·9049 (2)	0·1977 (1)	0·4566 (2)	—
Cl	0·6242 (4)	0·1844 (3)	0·5316 (3)	2·39 (5)
S	0·1071 (3)	0·4305 (2)	0·2666 (3)	1·32 (5)
O(1)	0·1103 (10)	0·3401 (8)	0·1232 (8)	2·06 (12)
O(2)	−0·0320 (10)	0·3774 (8)	0·3705 (9)	2·30 (12)
O(3)	0·2912 (12)	0·4373 (9)	0·3512 (11)	3·15 (15)
O(4)	0·0360 (11)	0·5689 (8)	0·2158 (10)	2·57 (14)

TlZnSO$_4$Cl

	x	y	z	B (Å^2)
Tl	0·36931 (9)	0·08903 (7)	0·20980 (7)	—
Zn	0·9034 (2)	0·2014 (2)	0·4607 (1)	—
Cl	0·6219 (5)	0·1841 (4)	0·5415 (4)	2·26 (5)
S	0·1111 (4)	0·4365 (3)	0·2693 (3)	1·27 (4)
O(1)	0·1103 (14)	0·3568 (12)	0·1122 (12)	2·10 (14)
O(2)	−0·0365 (15)	0·3825 (11)	0·3692 (12)	2·11 (14)
O(3)	0·2896 (17)	0·4252 (12)	0·3554 (14)	2·57 (14)
O(4)	0·0597 (17)	0·5843 (11)	0·2364 (14)	2·47 (17)

Table 3. Final anisotropic temperature factors ($\times 10^4$) for thallium, rubidium and zinc in TlZnSO$_4$Cl and RbZnSO$_4$Cl

The expression used is
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
Standard deviations are given in parentheses.

RbZnSO$_4$Cl

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb	120 (3)	77 (2)	102 (2)	−3 (1)	18 (2)	21 (1)
Zn	116 (3)	23 (2)	64 (2)	−1 (1)	30 (2)	2 (1)

TlZnSO$_4$Cl

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl	124 (2)	90 (1)	101 (1)	−13 (1)	1 (1)	22 (1)
Zn	94 (2)	39 (2)	50 (2)	2 (1)	16 (2)	5 (1)

denotes the number of observations and n the number of parameters varied).

TlZnSO$_4$Cl

The positional parameters of the atoms were taken from Bosson (1973). An exactly similar refinement was employed as for RbZnSO$_4$Cl except that a secondary extinction correction was added. Weights used in the last cycle were $w_i^{-1} = \sigma^2(F_o^2)/4F_o^2 + 0.0055F_o^2 + 5.0$. The values $R = 0.070$, $R_w = 0.098$ and $S = 1.15$ were obtained. The final isotropic extinction parameter g was 1.14×10^4.

In all refinements the scattering factors as well as the anomalous dispersion terms were those given by Cromer & Liberman (1970).

The final positional and thermal parameters are given in Tables 2 and 3.* In Table 4 selected interatomic distances and angles are presented.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31607 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

All computations were made on the Univac 1108 Computer in Lund (Stålhandske, 1974).

Description and discussion of the structures

RbZnSO$_4$Cl

A stereoscopic view of the structure of the corresponding Tl salt is shown in Fig. 1. The structure can be described as consisting of infinite layers of the composition $(ZnSO_4Cl)_n^{n-}$ and Rb$^+$ ions.

The Zn atom is surrounded by one Cl and three O atoms, forming a distorted tetrahedron. Zn–O are 1.94, 1.97 and 1.97 Å and Zn–Cl 2.19 Å, close to the reported values for ionic bonds 2.02 (5) (*International Tables for X-ray Crystallography*, 1962) and 2.23 (1) Å (Follner & Brehler, 1970), respectively. The layers are parallel to the bc plane and are held together by Rb$^+$ ions.

The average S–O in the sulphate group is 1.473 (4) Å. The distance is normal compared to the value 1.49 Å (*International Tables for X-ray Crystallography*, 1962).

The Rb atom is surrounded by five O atoms at distances between 2.90 and 3.11 Å (mean value 3.02 Å)
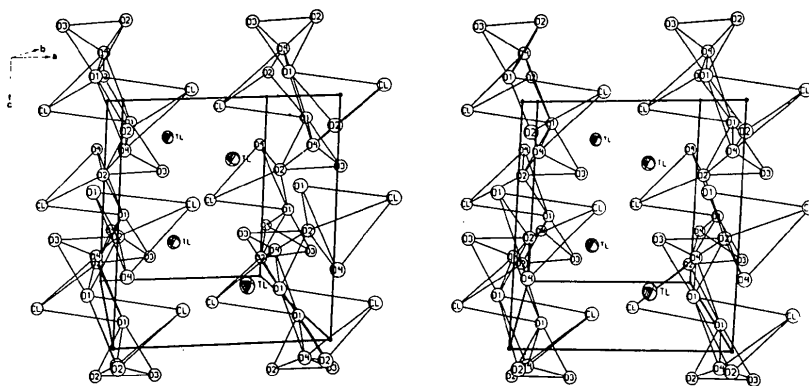

Fig. 1. A stereoscopic pair of drawings showing the infinite layers $(ZnSO_4Cl)_n^{n-}$ parallel to (100) and the Tl$^+$ ions in the crystal structure of TlZnSO$_4$Cl. The small tetrahedra denote the sulphate groups and the larger ones the 'ZnO$_3$Cl tetrahedra'.
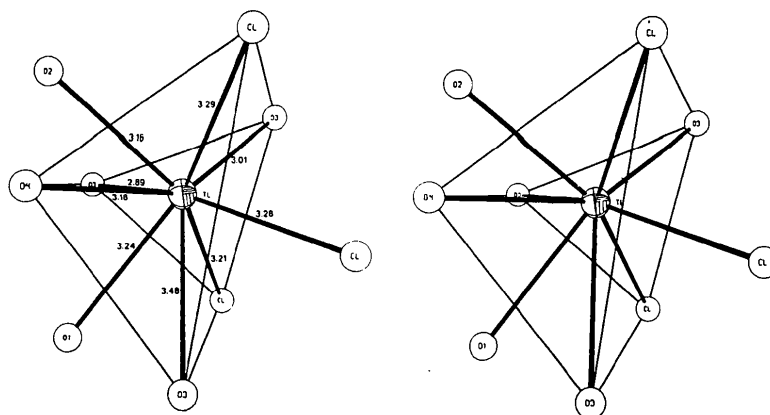

Fig. 2. Stereoscopic illustration of the environment of the thallium atom.

Table 4. *Selected distances (Å) and bond angles (°) with
standard deviations in parentheses*

Notations of the atoms, *cf.* Table 2.

RbZnSO₄Cl		TlZnSO₄Cl	
Rb–O(3)	2·90 (1)	Tl–O(3)	2·89 (1)
–O(3)	2·94 (1)	–O(3)	3·01 (1)
–O(4)	3·04 (1)	–O(4)	3·18 (1)
–O(1)	3·11 (1)	–O(1)	3·24 (1)
–O(2)	3·11 (1)	–O(2)	3·16 (1)
–Cl	3·334 (3)	–Cl	3·206 (4)
–Cl	3·342 (3)	–Cl	3·275 (3)
–Cl	3·396 (3)	–Cl	3·293 (4)
–O(3)	3·69 (1)	–O(3)	3·48 (1)
Zn–O(2)	1·94 (1)	Zn–O(2)	1·94 (1)
–O(1)	1·97 (1)	–O(1)	1·96 (1)
–O(4)	1·97 (1)	–O(4)	1·98 (1)
–Cl	2·192 (3)	–Cl	2·200 (4)
S—O(3)	1·45 (1)	S—O(3)	1·44 (1)
–O(4)	1·48 (1)	–O(4)	1·48 (1)
–O(1)	1·48 (1)	–O(1)	1·48 (1)
–O(2)	1·48 (1)	–O(2)	1·48 (1)
O(1)–S—O(2)	109·4 (4)	O(1)–S—O(2)	109·3 (6)
O(1)–S—O(3)	109·4 (5)	O(1)–S—O(3)	109·1 (6)
O(1)–S—O(4)	109·4 (4)	O(1)–S—O(4)	110·5 (6)
O(2)–S—O(3)	112·4 (5)	O(2)–S—O(3)	112·0 (6)
O(2)–S—O(4)	103·8 (5)	O(2)–S—O(4)	104·3 (6)
O(3)–S—O(4)	112·3 (5)	O(3)–S—O(4)	111·6 (7)
Cl—Zn–O(1)	116·9 (2)	Cl—Zn–O(1)	119·0 (3)
Cl—Zn–O(2)	114·5 (2)	Cl—Zn–O(2)	114·8 (3)
Cl—Zn–O(4)	116·3 (3)	Cl—Zn–O(4)	112·2 (4)
O(1)–Zn–O(2)	103·5 (3)	O(1)–Zn–O(2)	107·9 (5)
O(1)–Zn–O(4)	101·1 (3)	O(1)–Zn–O(4)	101·7 (5)
O(2)–Zn–O(4)	102·5 (3)	O(2)–Zn–O(4)	98·6 (4)

and by three Cl atoms ranging from 3·33 to 3·40 Å (mean value 3·36 Å). A sixth O atom is situated 3·69 Å away.

Rb–O distances 2·88 to 3·24 and 2·91 to 3·33 Å ($\sigma\sim0\cdot01$ Å) for nine and ten-coordination, respectively, have been reported (Nord, 1974). The Rb⁺ ion in RbH₃(SeO₃)₂ is surrounded by eight O atoms, the Rb–O distances being between 2·94 (1) and 3·19 (1) Å (Liminga, Tellgren & Ahmad, 1973). The Rb–Cl distance for six-coordination is 3·29 Å (*International Tables for X-ray Crystallography*, 1962). The sum of the ionic radii for Rb⁺ and O²⁻ for eight-coordination is 3·00 and for Rb⁺ and Cl⁻ 3·41 Å (Shannon & Prewitt, 1969).

The Rb atom in RbZnSO₄Cl is thus bonded by mainly ionic bonds to the five closest O and the three Cl atoms.

TlZnSO₄Cl

TlZnSO₄Cl is closely related to the Rb compound (Fig. 1), though slight differences in the distances are found (Table 4).

The coordination around Zn is distorted tetrahedral. In the 'ZnO₃Cl tetrahedron' Zn–O are 1·94, 1·96 and 1·98 Å and Zn–Cl 2·20 Å. The Zn–O and Zn–Cl distances are 2·02 (5) (*International Tables for X-ray*

Crystallography, 1962) and 2·23 (1) Å (Follner & Brehler, 1970), respectively, for ionic bonds.

The average S–O in the sulphate group is normal, 1·472 (6) Å.

Tl is surrounded by three Cl at 3·206 to 3·293 Å and five O atoms at 2·89 and 3·24 Å. A sixth Tl–O distance is 3·48 Å. The five nearest O atoms have a mean Tl–O of 3·10 Å. This is close to the sum of the ionic radii of Tl⁺ and O²⁻, 3·00 Å (Shannon & Prewitt, 1969) for eight-coordination. The sum of the ionic radii for Tl⁺ and Cl⁻ with the same coordination numbers is 3·41 Å (Shannon & Prewitt, 1969). The mean value for the three Tl–Cl distances is 3·26 Å. These distances suggest that the bonding of Tl is mainly ionic. The O atom situated at 3·48 Å has only weak interactions with the Tl atom.

A stereoscopic pair of drawings showing the environment of the Tl⁺ ion is given in Fig. 2. The coordination polyhedron may be described as a distorted three-capped trigonal prism, with Tl⁺ surrounded by three Cl and six O atoms.

Though Fig. 1, showing the cell content of TlZnSO₄Cl, may give the impression that Tl⁺ is coordinated to one side and though the distributions of and distances to the nearest and next-nearest neighbours do not contradict this impression there seems to be no necessity to assume the presence of a stereochemical inert pair for the Tl⁺ ion. This is because approximately the same coordination is obtained for the noble gas shell ion Rb⁺ in the closely related RbZnSO₄Cl.

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