The Crystal Structure of $Tl(ZnSO_4Cl)$

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The crystal structure of $Tl(ZnSO_4Cl)$ has been determined from X-ray single crystal data. The crystals are monoclinic, space group $P2_1/c$ (No. 14) with four formula units in a unit cell with the dimensions $a = 7.278$, $b = 9.551$, $c = 8.092$ and $\beta = 93.97°$. X-Ray intensity data were collected with an integrating Weissenberg camera using Mo$K\alpha$ radiation. 656 independent reflections were observed in the layers $hk0 - hk7$.

The coordinates of the thallium atom were obtained from a three-dimensional Patterson function. The other atoms were located from three-dimensional electron density difference syntheses. A correction for the absorption was performed; the linear absorption coefficient was 340 cm^{-1}. A least-squares full matrix refinement was performed including anisotropic temperature factors for the thallium and zinc atoms, isotropic temperature factors for chlorine, sulphur, and oxygen atoms, and an overall scale factor. The discrepancy factor $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.073$ (656 reflections). The final positional and thermal parameters are given in Table 1 and selected interatomic distances and

Table 1. Final positional and thermal parameters with standard deviations (within brackets). The temperature factor expression used for the thallium and zinc atoms is $\exp-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})$. The point position of all atoms is 4(*e*).

	x	y	z	B (Å^2)
Tl	0.3690(2)	0.0894(2)	0.2099(2)	–
Zn	0.9037(5)	0.2014(4)	0.4612(5)	–
Cl	0.6232(11)	0.1853(9)	0.5418(12)	1.85(13)
S	0.1109(8)	0.4369(6)	0.2687(9)	0.71(9)
O1	0.1071(31)	0.3552(26)	0.1099(31)	2.00(38)
O2	−0.0294(36)	0.3826(28)	0.3655(35)	2.51(44)
O3	0.2903(40)	0.4155(36)	0.3525(41)	3.25(51)
O4	0.0591(27)	0.5823(24)	0.2386(29)	1.54(32)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl	0.0103(2)	0.0069(2)	0.0094(3)	−0.0013(2)	0.0007(2)	0.0023(2)
Zn	0.0060(5)	0.0021(3)	0.0023(6)	0.0005(3)	0.0014(4)	0.0012(3)

Table 2. Selected distances (Å) and bond angles (°) with standard deviations (within brackets) in the structure of $Tl(ZnSO_4Cl)$.

Tl–O3	2.91(3)	Zn–O1	1.92(2)
Tl–O3	3.06(3)	Zn–O2	1.97(3)
Tl–O4	3.17(2)	Zn–O4	2.01(2)
Tl–O2	3.19(3)	Zn–Cl	2.19(1)
Tl–Cl	3.20(1)		
Tl–O1	3.24(2)	S–O2	1.43(3)
Tl–Cl	3.28(1)	S–O3	1.44(3)
Tl–Cl	3.30(1)	S–O4	1.46(2)
Tl–O3	3.38(3)	S–O1	1.50(3)
∠O1–S–O2	108.0(1.5)	∠Cl–Zn–O1	119.2(0.8)
∠O1–S–O3	107.0(1.6)	∠Cl–Zn–O2	116.1(0.8)
∠O1–S–O4	111.3(1.4)	∠Cl–Zn–O4	112.3(0.6)
∠O2–S–O3	110.4(1.7)	∠O1–Zn–O2	107.0(1.0)
∠O2–S–O4	104.6(1.4)	∠O1–Zn–O4	101.8(1.0)
∠O3–S–O4	115.4(1.6)	∠O2–Zn–O4	97.5(1.1)

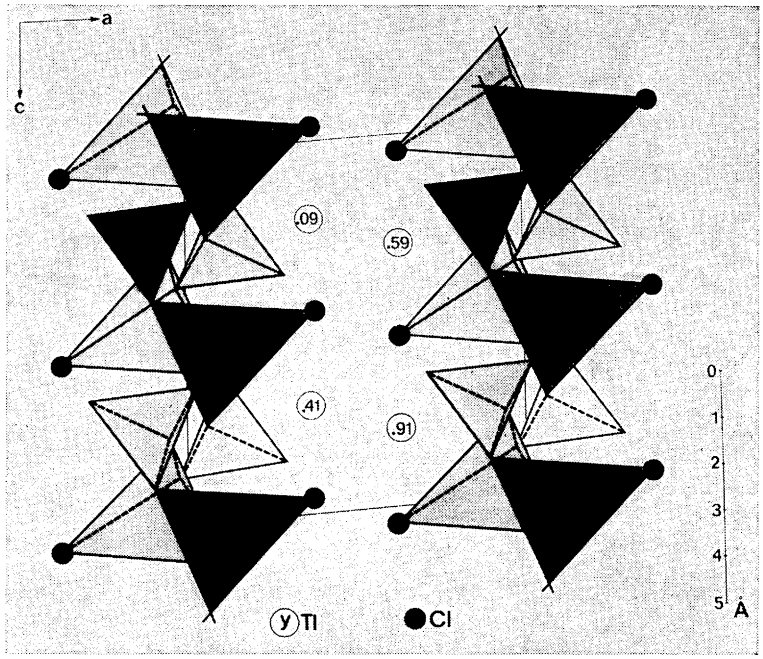

Fig. 1. Part of the infinite layers $(ZnSO_4Cl)_n^{n-}$ and the Tl^+ ions in the crystal structure of $Tl(ZnSO_4Cl)$, viewed along the *b*-axis. The small tetrahedra denote the sulphate groups and the larger ones the "ZnO_3Cl tetrahedra". The *y*-coordinates of the Tl^+ ions are given.

angles in Table 2.

The crystal structure of $Tl(ZnSO_4Cl)$ is built up of infinite layers of the composition $(ZnSO_4Cl)_n^{n-}$, held together by thallium ions, Tl^+. The thallium atoms are surrounded by three chlorine and six oxygen atoms in an irregular way. The Tl – Cl distances vary between 3.20(1) and 3.30(1) Å and five Tl – O distances range between 2.91(4) and 3.24(2) Å. The distances are normal as compared to the values 3.33 Å for Tl – Cl [1] and 2.57 to 3.19 Å for Tl – O.[2] The sixth Tl – O distance is 3.38(3) Å. A next nearest oxygen atom is then situated at the distance of 3.90(3) Å from the thallium atom. The architecture of the sheets can be described as follows. In a distorted tetrahedral arrangement the zinc atoms are each coordinated to one chlorine and to three oxygen atoms, the latter belonging to three different sulphate groups. In this way every "ZnO_3Cl tetrahedron" is linked by sharing three corners to sulphate tetrahedra and each of the sulphate tetrahedra is linked to three "ZnO_3Cl tetrahedra", forming the infinite layers of the composition $(ZnSO_4Cl)_n^{n-}$ (Fig. 1). The layers are parallel to the *bc* plane. The average bond distance S – O in the sulphate group is 1.46(2) Å and the mean distance O – O 2.38(2) Å. The Zn – O distances in the "ZnO_3Cl tetrahedra" are between 1.92(3) and 2.01(3) Å and the distance Zn – Cl is 2.19(1) Å. The distances are normal compared to those in Refs. 1 and 3.

In order to obtain more accurate values of the interatomic distances a diffractometer study has been started. A full report of this work will be published elsewhere.

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