Structure and Bonding in Sulphatobis(thiourea)tin(II)

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are orthorhombic, space group $P2_12_12$, with $Z = 4$ in a unit cell of dimensions: $a = 16{\cdot}98$, $b = 12{\cdot}86$, $c = 5{\cdot}22$ Å. The structure was refined by least-squares methods to R 0·083 for 1023 reflections. The tin atoms are in distorted pyramidal sites surrounded by two sulphate oxygen atoms at 2·41 and 2·24 Å and by two thiourea sulphur atoms at 2·62 and 2·86 Å. The thiourea groups are planar but not equivalent and are linked to the sulphate ions by hydrogen bonding.

MANY tin(II) compounds act as acceptor molecules towards suitable donor ligands. They act primarily as monofunctional acceptors but a number of materials containing additional ligands are known.[1] These additional ligands may either be bonded to the tin or be present for crystal packing purposes. Mössbauer and i.r. evidence have been found for both types of behaviour in multiligand tin(II) complexes [2] but the only material of this type of known structure is $SnCl_2,2H_2O$ [3] in which only one water molecule is bonded to the tin. The second molecule is held in its environment by hydrogen bonding.

The ^{119}Sn Mössbauer chemical isomer shifts [2] of the monothiourea complexes of the tin(II) halides are lower than those of the parent compounds and are consistent with the formation of strong tin–sulphur bonds. The polythiourea complexes, however, have slightly higher shifts than the corresponding monothiourea ones, suggesting that the additional ligand molecules are not bonded or are only weakly bonded to tin. None of these thiourea (tu) complexes show any quadrupole splitting in spite of the likely asymmetry of the tin co-ordination. $Sn(tu)_2(SO_4)$ (tu = thiourea) has Mössbauer data which are typical for thiourea complexes of tin(II) and also provides an opportunity to investigate the structural relationship between a tin(II) complex and its parent compound, tin(II) sulphate which is of known structure.[4]

EXPERIMENTAL

Preparation.—The material was prepared [2] by the addition of the stoicheiometric quantity of thiourea to a solution of tin(II) sulphate in sulphuric acid.

Crystal Data.—$C_2H_8N_4O_4S_3Sn$, $M = 367$, Orthorhombic, $a = 16{\cdot}98 \pm 0{\cdot}04$, $b = 12{\cdot}86 \pm 0{\cdot}03$, $c = 5{\cdot}22 \pm 0{\cdot}02$ Å, $U = 1139{\cdot}9$ Å^3, $D_m = ca.\ 2{\cdot}0$ (by displacement of monochlorobenzene), $Z = 4$, $D_c = 2{\cdot}14$, $F(000) = 680$. Space group $P2_12_12$ (D_2^3, No. 18) from systematic absences: $h00$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å (for cell data).

Intensity Data and Structure Refinement.—Diffraction intensity data were collected from a small crystal (mean diameter 0·077 mm) mounted up the *c* axis on a Hilger and Watts Y 190 linear diffractometer (manual equi-inclination Weissenberg setting). Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å) was used and reflections from four octants were collected and, neglecting anomalous dispersion, averaged to give 1088 independent reflections above background intensity for layers 0—6. Lorentz-polarisation corrections were applied but absorption effects were neglected ($\mu\bar{R} = 0{\cdot}271$).

The tin atom positions were obtained from a three-dimensional Patterson synthesis. The positions of the sulphur atoms were determined from a Fourier synthesis phased on the basis of the tin atoms. Least-squares refinement of layer scales, atomic positions, and isotropic temperature factors for the tin and sulphur atoms gave R 19·2%.

The positions of the remaining lighter atoms were determined from Fourier and difference syntheses. A final least-squares refinement using anisotropic temperature factors for the tin and sulphur atoms and isotropic ones for the others converged with R 0·098. A number of very weak reflections for which $|F_o| > 2|F_c|$ or $|F_c| > 2|F_o|$ were removed and the 1023 remaining reflections converged with R 0·083. The corresponding parameters are shown in Table 1, the interatomic distances and angles in Table 2 and the observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20724 (11 pp., 1 microfiche).†

TABLE 1

Final parameters

Atom	*x*	*y*	*z*	B/Å^2
Sn	0·2063(1)	0·0669(1)	0·1571(4)	*
S(1)	0·1148(4)	0·2282(5)	0·2303(13)	*
S(2)	0·3272(4)	0·1185(5)	0·6986(12)	*
S(3)	0·1136(4)	0·0420(5)	0·7039(14)	*
O(1)	0·2917(14)	0·1531(13)	0·4576(35)	2·7(4)
O(2)	0·2846(13)	0·1643(13)	0·9095(35)	2·6(4)
O(3)	0·3249(11)	0·0041(15)	0·7136(44)	3·5(4)
O(4)	0·4059(12)	0·1599(15)	0·7127(46)	3·9(5)
C(1)	0·1253(14)	0·9136(15)	0·6536(49)	1·7(4)
C(2)	0·1088(17)	0·3036(18)	0·9508(50)	2·1(5)
N(1)	0·1946(14)	0·8655(16)	0·6859(51)	3·1(5)
N(2)	0·0610(17)	0·8546(21)	0·5706(64)	4·7(7)
N(3)	0·0381(14)	0·3530(18)	0·9211(54)	3·5(6)
N(4)	0·1665(14)	0·3199(16)	0·8033(52)	3·2(5)

* Anisotropic temperature factors, of the form exp $-[b_{11}h^2 + b_{22}k^2 + b_{33}k^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl]$, with the corresponding standard deviations in parentheses, are as follows:

	10^4b_{11}	10^4b_{22}	10^3b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}
Sn	16(1)	41(1)	23(4)	−1(1)	4(2)	2(2)
S(1)	13(3)	57(5)	18(5)	12(3)	1(7)	−1(8)
S(2)	4(3)	37(3)	17(5)	1(2)	6(6)	11(7)
S(3)	17(3)	39(4)	25(5)	3(3)	−16(7)	−13(8)

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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[2] J. E. Cassidy, W. Moser, J. D. Donaldson, A. Jelen, and D. G. Nicholson, *J. Chem. Soc.* (*A*), 1970, 173.

[3] B. Kamenar and D. Grdenić, *J. Chem. Soc.*, 1961, 3954.

[4] J. D. Donaldson and D. C. Puxley, *Acta Cryst.*, 1972, **B28**, 864.

TABLE 2

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Tin co-ordination			
Sn–S(1)	2·62(1)	Sn–O(1)	2·41(2)
Sn–S(3)	2·86(1)	Sn–O(2)	2·24(2)
S(1)–Sn–S(3)	83·2(0·2)	S(3)–Sn–O(1)	157·3(0·4)
S(1)–Sn–O(1)	84·1(0·5)	S(3)–Sn–O(2)	85·0(0·6)
S(1)–Sn–O(2)	89·6(0·5)	O(1)–Sn–O(2)	76·2(0·6)
(*b*) Thiourea groups			
S(1)–C(2)	1·75(3)	C(2)–N(4)	1·26(3)
C(2)–N(3)	1·37(3)		
S(1)–C(2)–N(3)	114(2)	N(3)–C(2)–N(4)	122(2)
S(1)–C(2)–N(4)	124(2)		
Sum of angles about C(2) 360			
Sn–S(1)–C(2)	111(1)		
Dihedral angle between planes [S(1), N(3), N(4)] and [Sn, S(1), C(2)] 35(1)			
S(3)–C(1)	1·68(2)	C(1)–N(2)	1·40(3)
C(1)–N(1)	1·34(3)		
S(3)–C(1)–N(1)	122(2)	N(1)–C(1)–N(2)	118(2)
S(3)–C(1)–N(2)	119(2)		
Sum of angles about C(1) 360			
Sn–S(3)–C(1)	100(1)		
Dihedral angle between planes [S(3), N(1), N(2)] and [Sn, S(3), C(1)] 40(4)			
(*c*) Sulphate groups			
S(2)–O(1)	1·46(2)	S(2)–O(3)	1·47(2)
S(2)–O(2)	1·44(2)	S(2)–O(4)	1·44(2)
O(1)–S(2)–O(2)	109(1)	O(2)–S(2)–O(3)	111(1)
O(1)–S(2)–O(3)	110(1)	O(2)–S(2)–O(4)	106(1)
O(1)–S(2)–O(4)	108(1)	O(3)–S(2)–O(4)	113(1)

DISCUSSION

The complex contains tin atoms linked by sulphate groups to form chains along [001] (see Figure 1); Sn–O distances are 2·24 and 2·41 Å. The thiourea groups, which are planar, have sulphur atoms at 2·62 and 2·86 Å from the tin. The sulphate group is linked to both thiourea groups by N–H ··· O hydrogen bonds.

Tin Co-ordination.—The tin co-ordination is shown in Figure 2. Bonds to O(1) (2·41 Å), O(2) (2·24 Å), and S(1) (2·62 Å) form the usual trigonal pyramidal arrangement [1] but there is an additional significantly longer Sn–S distance of 2·86 Å to complete a second trigonal pyramid [Sn, S(3), O(1), and O(2)] which shares the [Sn, O(2), and S(1)] face with the first. All four ligand atoms lie on one side of the tin because of the stereochemical effect of the lone-pair [1] (Figure 2). A similar geometrical arrangement is found for the tin co-ordination in potassium trifluorostannate hemihydrate [5] and for that of lead in both lead(II) diethyl dithiocarbamate [6] and diethyl dithiophosphate.[7] The bond lengths Sn–O(2) (2·24 Å) and Sn–S(1) (2·62 Å) are similar to the corresponding ones found in $SnSO_4$ [4] and Sn_2S_3.[8] The Sn–S(3) distance (2·86 Å) is, however, significantly longer than usual and Sn–O(1) (2·41 Å) is also lengthened. It appears that it is **not** possible to form a fourth bond to Sn^{II} without lengthening at least one of the three bonds in the usual trigonal pyramidal tin environment (*cf.* $KSnF_3,\frac{1}{2}H_2O$ [5] where the tin forms four bonds to fluorine of 2·01, 2·04, 2·27, and 2·27 Å). Tin(II) materials should [1] act as monofunctional acceptors since they have vacant 5*p* orbitals and 1 : 1 complexes between tin(II) acceptors and various unidentate donors are well known. To form a complex with a second donor molecule requires the use of the tin 5*d* orbitals. Although this is less likely, because of the energy separation between the tin 5*p* and 5*d* orbitals,[1] it probably occurs in tetragonal tin(II) oxide [9] and may occur in $KSnF_3,\frac{1}{2}H_2O$ and $Sn(tu)_2(SO_4)$.

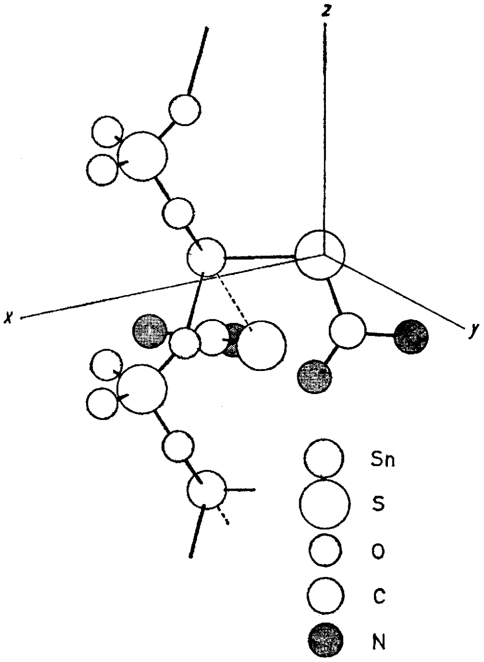

FIGURE 1 A view of the structure

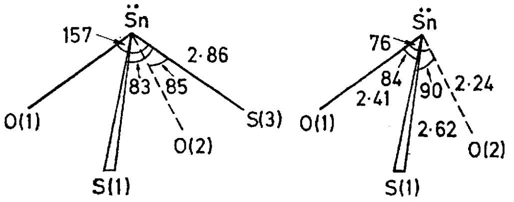

FIGURE 2 The environment of Sn atoms; distances (Å), angles (°)

Thiourea Groups.—*X*-ray [10,11] and neutron [12] diffraction studies of thiourea have shown the molecules to be

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[9] W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392.

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planar to within 0·01 Å excluding those hydrogen atoms involved in hydrogen bonding. This would be expected of a system with delocalised π molecular orbitals involving the nitrogen atoms. The molecules are linked by almost linear N–H ··· S hydrogen bonds (N–S 3·35—3·43 Å and N–H ··· S 169—171°).

In dithiourea tin(II) sulphate, $\mathrm{Sn(tu)_2(SO_4)}$, the non-hydrogen atoms of the thiourea groups are coplanar (the sums of the angles about both carbon atoms are 360°). The hydrogen bonding in the structure (*vide infra*) suggests that the hydrogen atoms are also approximately in the same plane as the other atoms of the thiourea molecule rather than completing a pyramidal arrangement at the nitrogen atoms. Bond distances and angles within the thiourea molecules in $\mathrm{Sn(tu)_2(SO_4)}$ fall within the previously observed range for thiourea complexes and are not significantly different from those in thiourea itself. The two thiourea groups in $\mathrm{Sn(tu)_2(SO_4)}$ are however, not equivalent. The S–C bond lengths (1·68 and 1·75 Å) match the corresponding differences in the Sn–S distances (2·86 and 2·62 Å). Thus the S(1)⁚C(2)[N(3), N(4)] group is much more strongly bonded to the tin atom than is the other thiourea, an observation which is consistent with the i.r. data.[2]

It has been suggested that thiourea forms both σ and π donating complexes [13] and that both types of bonding may occur in the same compound.[13-15] The Sn–S–C bond angles in $\mathrm{Sn(tu)_2(SO_4)}$ are 100 and 111°. This compares with the range (106—116°) usually found [16] for metal–sulphur–carbon angles in transition-metal–thiourea complexes which are thought to contain σ bonds formed by sulphur atoms donating electrons from the non-bonding sp^2 lobes. The tin atoms in $\mathrm{Sn(tu)_2(SO_4)}$ are considerably removed from the planes of both thiourea groups. The dihedral angles between the Sn–S–C planes and the thiourea molecular planes (S–N–N) are 35 and 40° instead of 0° as would be expected for a pure σ bonded system or *ca.* 90° for a π complex. Corresponding dihedral angles for transition-metal complexes are generally in the range 14—35°.[16] It has been argued [16] that, although hydrogen bonding, van der Waal's forces, and packing considerations do play a role in the precise orientation of the thiourea ligand in such complexes, the observed angles are fundamentally a consequence of the metal–thiourea interaction.

The structures of various thiourea complexes of the related $\mathrm{Pb^{2+}}$ ion [17-20] show a considerably wider variation of metal–sulphur–carbon bond angle than do the transition-metal complexes [90—120 in $\mathrm{Pb(tu)_2Cl_2}$,[17] 103—115 in $\mathrm{Pb(tu)_6(ClO_4)_2}$,[18] and 99—124° in $\mathrm{Pb(tu)(AcO)_2}$ [20]]. In $\mathrm{Pb(tu)_6(ClO_4)_2}$ [18] the dihedral angles between the Pb–S–C planes and the thiourea planes are 14, 31, and 54°. The authors have nevertheless suggested that the orientation of the thiourea groups is again primarily controlled by the metal–thiourea interaction.

In view of the extensive hydrogen bonding network found (*vide infra*) in $\mathrm{Sn(tu)_2(SO_4)}$ it appears more likely that, as for $\mathrm{Cd(tu)_2(HCO_2)_2}$,[21] hydrogen bonding is the dominant factor in determining the orientation of the thiourea molecules.

Hydrogen Bonding.—Hydrogen bonding of the types N–H ··· Cl,[16,17] N–H ··· Br,[20,22,] and N–H ··· S [12,18] has been reported for thiourea and its complexes.

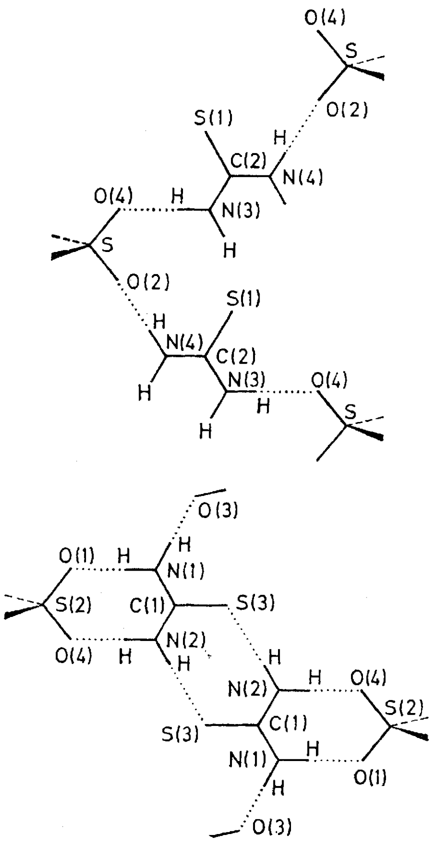

FIGURE 3 The hydrogen bonding network

The present structure contains a complex hydrogen bonding network, which consists principally of N–H ··· O bonds but also some N–H ··· S bonds. This is shown diagrammatically in Figure **3** with the relevant bond parameters in Table **3**. The oxygen atoms involved in N–H ··· O hydrogen bonds are approximately in the same plane as the thiourea groups concerned, and the N–H ··· O distances and C–N ··· O angles are within

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the accepted ranges.[23] Two N · · · S interactions also comply with the N–H · · · S distance and C–N · · · S angle criteria for hydrogen bonding[24] [N(2) · · · S(3′) and N(4) · · · S(1′)], but since the S(1) atom is not coplanar with the thiourea molecule containing the N(4) atom, the N(4) · · · S(1′) interaction probably does not constitute a hydrogen bond.

TABLE 3

Hydrogen bonding in $Sn(tu)_2(SO_4)$

(*a*) N(1) atom			
N(1) · · · O(1)	2·84	C(1)–N(1) · · · O(1)	118·8
N · · O(1) ·(2)	2·84	C(1)–N(1) · · · O(3)	113·6
		O(1) · · · N(1) · · · O(3)	123·5
		Sum of angles about N(1)	356
(*b*) N(2) atom			
N(2) · · · O(4)	2·96	C(1)–N(2) · · · O(4)	117·7
N(2) · · · S(3)	3·32	C(1)–N(2) · · · S(3)	114·5
		O(4) · · · N(2) · · · S(3)	127·7
		Sum of angles about N(2)	360
(*c*) N(3) atom			
N(3) · · · O(4)	2·95	C(2)–N(3) · · · O(4)	124·6
(*d*) N(4) atom			
N(4) · · · O(2)	2·89	C(2)–N(4) · · · O(2)	107·9
N(4) · · · S(1)	3·33	C(2)–N(4) · · · S(1)	106·5
		O(2) · · · N(4) · · · S(1)	96·3
		Sum of angles about N(4)	311

Sulphate Groups.—The sulphate groups have S–O bond lengths of 1·44—1·47 Å and the O–S–O bond angles are 106—113°, values not significantly different from those found in tin(II) sulphate.[4] (S–O 1·457—1·505 Å, and O–S–O 107·6—112·8°.) The errors are too great to draw any conclusions concerning deformations from regular tetrahedral symmetry.

I.r. and ^{119}Sn *Mössbauer Spectral Data*.—The i.r. spectrum[2] of $Sn(tu)_2(SO_4)$ shows two peaks at 725 and 710 cm^{-1} corresponding to the C=S stretching frequencies. This is consistent with the notably different Sn–S and S=C bonds for the two thiourea groups. The C=S stretching frequency in thiourea itself is 730 cm^{-1}. Hence the C=S stretching frequencies of the complex may probably be assigned as follows: 710 C(2)=S(1) (1·75 Å), and 725 cm^{-1} C(1)=S(3) (1·68 Å).

The ^{119}Sn Mössbauer parameters[2] of $Sn(tu)_2(SO_4)$ are of considerable interest. The chemical isomer shift of 1·20 mm s^{-1} (relative to α-Sn) compares with 1·90 mm s^{-1} for $SnSO_4$[1] showing that the sulphur of the thiourea group causes much greater *s* electron withdrawal from the tin than the oxygen atoms in the parent compound. Like most other thiourea complexes of tin(II), $Sn(tu)_2(SO_4)$ has an undetectably small quadrupole splitting in spite of the asymmetry of the tin environment. It is possible that the thiourea ligands, by acting as electron sinks, may reduce any imbalance in the *p* electrons on the tin atom. This study illustrates the necessity for care in the inference of stereochemistry from Mössbauer data.

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