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X-Ray Crystal Structure Determinations of Two Thiourea Tin(II) Complexes: Diacetatobis(thiourea)tin(II) and Ditin(II)tetrabromopenta(thiourea)dihydrate

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The crystal structures of diacetatobis(thiourea)-tin(II) (I) and ditin(II)tetrabromopenta(thiourea)-dihydrate (II) have been determined by X-ray diffraction analysis. The compound I crystallizes in the monoclinic space group Pc with $a = 11.932(6)$, $b = 10.937(5)$, $c = 21.919(8)$ Å, $\beta = 96.5(1)$, $Z = 8$. *The compound II crystallizes in the orthorhombic space group Pnma with* $a = 27.83(3)$, $b = 16.13(4)$, $c = 6.11(6)$ Å, $Z = 4$. *In compound I the tin atom has a square pyramidal environment. It is bonded to two thiourea sulphur atoms and to two carboxylate oxygens. In the compound II there are two tin sites both with trigonal pyramidal coordination. The* ^{119}*Sn Mössbauer data for thiourea tin(II) compounds are discussed, in terms of their crystal structures.*

Introduction

Many tin(II) compounds act as acceptor molecules towards suitable donor ligands. Because of the presence of an empty p-orbital of similar energy to those used in bonding, covalent SnX_2 compounds 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 lattice-packing purposes. The only crystal structures of materials of this type that are known include tin(II) chloride dihydrate [2], the 1.4 dioxan derivatives of tin(II) chloride [3] and tin(II) bromide [4], and the sulphatobis-(thiourea)tin(II) complex [5]. In tin(II) chloride dihydrate, the tin environment is in the most commonly distorted form, that of a trigonal pyramid with two short bonds to chlorine and one longer than average Sn–O bond to the oxygen atom of a water molecule; the second water molecule is simply held in the lattice by hydrogen bonding. The two 1,4 dioxan complexes of $SnCl_2$ and $SnBr_2$ have tin lying in the less common distorted four-coordinate environment with two short bonds to the halogens and two longer than average bonds [6] to the two oxygen atoms of two bridging dioxan molecules. The tin environment in sulphatobis(thiourea)tin(II) may also be described in terms of a square pyramidal distribution of ligands about the tin atom, although its coordination is unusual and could be discussed as being intermediate between trigonal and square pyramidal environments. Bonds to the two oxygens of bridging sulphate groups and to a sulphur atom, at 2.62 Å distant, form the usual trigonal pyramidal arrangement, but there is an additional significantly longer Sn–S distance of 2.86 Å to complete a second trigonal pyramid, creating what is best described as an overall square-pyramidal environment.

There are a number of polythiourea tin(II) complexes known [7] and we now report the crystal structure determination of two of them *viz.* Sn(acetate)$_2$·2tu and $Sn_2Br_4 \cdot 5tu \cdot 2H_2O$ (tu = thiourea) and identify their tin environments as one of those described above.

Experimental

Preparation

Single crystals of diacetatotin(II)dithiourea and ditin(II)tetrabromopentathioureadihydrate were pre-

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pared by the literature method [7]. The unit cell data were determined, for each, from Weissenberg and single crystal precession photographs (Mo-K_α radiation $\lambda = 0.7107$ Å).

Crystal Data

$C_6H_{14}N_4O_4S_2Sn$, $M = 388.7$, monoclinic $a = 11.932(6)$, $b = 10.937(7)$, $c = 21.919(8)$ Å, $\beta = 96.5(1)°$, $U = 2841.7(4)$ Å^3, $D_m = 1.32$ gcm^{-3}, $Z = 8$, $D_c = 1.33$ gcm^{-3}, F(000) = 1536. Space group Pc(C_s^2, No. 7) from systematic absences *h0l*: when *l* is odd.

Crystal Data

$C_5H_{24}N_{10}O_2S_5Sn_2Br_4$, $M = 973$, orthorhombic, $a = 27.83(3)$, $b = 16.13(4)$, $c = 6.11(6)$ Å, $U = 2724.4$ Å^3, $Z = 4$, $D_c = 2.37$ gcm^{-3}, F(000) = 1456. Space group centrosymmetric Pnma (D_{2h}^{16}; No. 62) from systematic absences 0*kl*: where $k + l$ is odd, 0*k*0: where *k* is odd *hk*0: where *h* is odd. It is interesting to observe that the same cell parameters are shown by the chloride homologue.

The calculations were carried out using SHELX-76 [8] and BONDLA from 'X-RAY' 72' [9]. Stereographic projections of the unit cell were obtained using CELLPLOT. The stereochemical arrangement of $Sn(CH_3CO_2)_2 \cdot 2tu$ and $Sn_2Br_4 \cdot 5tu \cdot 2H_2O$ are shown in Figs. 1, 2 and 3, 4 respectively. The observed and calculated structure factors may be obtained on request.

Structure Refinement

The unit cell data for each material were determined from Weissenberg and single crystal precession photographs.

The tin atom positions in both structures and the bromine atom positions in the bromide complex were obtained from three dimensional Patterson syntheses. The positions of the sulphur atoms in $Sn(CH_3CO_2)_2 \cdot 2tu$ were determined from a Fourier synthesis phased on the basis of the tin atoms and those in $Sn_2Br_4 \cdot 5tu \cdot 2H_2O$ were located from a three dimensional difference Fourier map with phasing based on the refined tin and bromine positions. Least squares refinement of layer scales, atomic positions and isotropic temperature factors for tin and sulphur atoms in the acetate gave a residual of 17%. A residual of 19% was achieved after location of the tin, bromine and sulphur atom positions in the bromide. The positions of the remaining lighter atoms were determined from Fourier and difference syntheses. The hydrogen atoms in $Sn(CH_3CO_2)_2 \cdot 2tu$ were found but not refined. The final least-squares refinement in $Sn(CH_3CO_2)_2 \cdot 2tu$ converged with $R = 0.060$ and in $Sn_2Br_4 \cdot 5tu \cdot 2H_2O$ converged with $R = 0.077$. The corresponding parameters for the acetate and bromide derivatives are shown in Tables I and II respectively, and the interatomic distances and angles are presented in Tables III and IV respectively.

Results and Discussion

This discussion is confined to an identification of the tin environment in the two materials, and a description of the type of environment found for each.

The structure of the acetate complex consists of discrete $Sn(CH_3CO_2)_2 \cdot 2tu$ moieties. The arrangement

TABLE I. Fractional Coordinates and Thermal Parameters for $Sn(CH_3CO_2)_2 \cdot 2tu$.

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	0.2491(1)	0.2084(1)	0.1227(1)	0.0340(4)	0.0329(4)	0.0315(4)	0.0010(4)	0.0148(3)	0.0001(4)
S(1)	0.4869(3)	0.1760(3)	0.1573(1)	0.032(1)	0.055(2)	0.044(1)	0.007(1)	0.009(1)	−0.008(1)
S(2)	0.0137(3)	0.1635(3)	0.1150(2)	0.032(1)	0.044(2)	0.061(2)	−0.002(1)	0.016(1)	−0.001(1)
O(1)	0.2389(7)	0.0412(8)	0.0673(4)	0.043(5)	0.045(5)	0.046(5)	−0.005(4)	0.027(4)	−0.005(4)
O(2)	0.3476(7)	0.1270(9)	0.0043(4)	0.045(5)	0.063(6)	0.037(5)	−0.003(4)	0.021(4)	−0.015(5)
O(3)	0.2606(6)	0.0618(7)	0.1907(4)	0.029(4)	0.034(4)	0.036(4)	−0.003(4)	0.016(3)	0.004(3)
O(4)	0.2183(8)	0.2188(9)	0.2473(4)	0.073(7)	0.044(6)	0.040(5)	−0.002(4)	0.023(4)	0.002(5)
N(1)	0.499(1)	0.317(1)	0.0582(6)	0.060(8)	0.064(9)	0.051(7)	0.001(7)	0.006(6)	−0.010(7)
N(2)	0.637(1)	0.342(1)	0.1385(6)	0.045(7)	0.081(9)	0.071(8)	0.016(7)	0.003(6)	−0.026(7)
N(3)	0.0120(9)	0.403(1)	0.0926(5)	0.038(6)	0.045(7)	0.053(6)	0.006(5)	0.025(5)	0.004(5)
N(4)	−0.0855(8)	0.344(1)	0.1710(5)	0.033(6)	0.050(7)	0.063(7)	0.011(6)	0.030(5)	0.013(5)
C(1)	0.290(1)	0.040(1)	0.0181(5)	0.039(7)	0.044(7)	0.036(7)	−0.004(6)	0.011(5)	0.004(6)
C(2)	0.273(1)	−0.072(1)	−0.0202(7)	0.057(9)	0.084(7)	0.050(8)	−0.035(7)	0.018(6)	−0.031(7)
C(3)	0.546(1)	0.285(1)	0.1151(6)	0.029(6)	0.045(7)	0.054(8)	−0.008(6)	0.010(5)	−0.006(5)
C(4)	0.238(1)	0.106(1)	0.2420(5)	0.039(7)	0.041(8)	0.030(6)	0.001(5)	0.007(5)	0.001(5)
C(5)	−0.0215(9)	0.312(1)	0.1266(5)	0.018(5)	0.050(7)	0.039(6)	−0.001(6)	0.009(4)	0.002(5)
C(6)	0.227(1)	0.016(1)	0.2923(7)	0.090(1)	0.059(9)	0.049(8)	0.018(8)	0.035(7)	0.012(8)

TABLE II. Fractional Coordinates and Thermal Parameters for Sn$_2$Br$_4$·5tu·2H$_2$O.

Atom	X/A	Y/B	Z/C	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
Sn(1)[a]	0.1015(2)	0.2500	0.6137(7)	0.042(3)	0.027(2)	0.02(2)	0.00	0.003(2)	0.00
Sn(2)[a]	0.2474(2)	0.2500	0.7095(6)	0.028(2)	0.037(2)	0.01(2)	0.00	0.002(2)	0.00
Br(1)[a]	0.2592(3)	0.2500	0.277(1)	0.044(4)	0.040(4)	0.021(3)	0.00	0.004(3)	0.00
Br(2)[a]	0.1217(3)	0.2500	0.038(1)	0.057(4)	0.038(4)	0.014(3)	0.00	−0.001(3)	0.00
Br(3)[a]	0.3282(2)	0.1290(3)	0.7599(8)	0.068(3)	0.042(2)	0.027(2)	−0.004(2)	−0.002(3)	0.015(3)
S(1)	0.0359(4)	0.1302(7)	0.707(2)	0.43(7)	0.035(6)	0.038(7)	0.001(6)	−0.002(6)	−0.002(5)
S(2)	0.1853(4)	0.1102(7)	0.578(1)	0.059(8)	0.029(6)	0.010(4)	0.002(4)	0.009(5)	−0.006(5)
S(3)	0.4718(7)	0.2500	0.379(3)	0.04(1)	0.06(1)	0.029(9)	0.00	−0.005(9)	0.00
N(1)[b]	0.049(1)	0.083(2)	0.290(6)	0.037(9)					
N(2)[b]	0.065(1)	−0.011(2)	0.546(6)	0.040(9)					
N(3)[b]	0.198(2)	−0.035(3)	0.759(8)	0.07(1)					
N(4)[b]	0.188(1)	0.069(2)	0.007(7)	0.06(1)					
N(5)[b]	0.377(2)	0.2500	0.26(1)	0.17(2)					
N(6)[b]	0.433(3)	0.2500	−0.04(1)	0.07(2)					
C(1)[b]	0.050(1)	0.067(2)	0.493(7)	0.03(1)					
C(2)[b]	0.192(1)	0.046(2)	0.791(7)	0.024(9)					
C(3)[b]	0.424(3)	0.2500	0.17(1)	0.17(3)					
O(H)[b]	−0.071(1)	0.438(2)	0.977(5)	0.040(8)					

[a] Occupancy 0.5. [b] Isotropical thermal parameter.

TABLE III. Bond Distances and Bond Angles for Sn(CH$_3$CO$_2$)$_2$·2tu.

Bond distances (Å)		Bond angles (°)	
Sn–O(1)	2.191(9)	S(1)–Sn–S(2)	159.2(1)
Sn–O(3)	2.182(8)	S(1)–Sn–O(3)	75.3(2)
Sn–S(1)	2.875(3)	S(2)–Sn–O(3)	84.2(2)
Sn–S(2)	2.837(3)	S(1)–Sn–O(1)	91.9(2)
S(1)–C(3)	1.72(1)	S(2)–Sn–O(1)	80.3(2)
C(3)–N(1)	1.35(2)	O(1)–Sn–O(3)	76.1(3)
C(3)–N(2)	1.30(2)	S(1)–C(3)–N(1)	122(1)
S(2)–C(5)	1.70(1)	S(1)–C(3)–N(2)	120(1)
C(5)–N(3)	1.33(1)	N(1)–C(3)–N(2)	119(1)
C(5)–N(4)	1.35(1)	S(2)–C(5)–N(3)	122.4(9)
O(3)–C(4)	1.28(1)	S(2)–C(5)–N(4)	121.8(9)
C(4)–O(4)	1.26(1)	N(3)–C(5)–N(4)	116(1)
C(4)–C(6)	1.49(2)	S(4)–O(3)–C(4)	108.3(7)
O(1)–C(1)	1.30(1)	Sn–O(1)–C(1)	117.6(8)
C(1)–O(2)	1.23(1)	O(3)–C(4)–C(6)	116(1)
C(1)–C(2)	1.49(2)	O(3)–C(4)–O(4)	121(1)
		O(4)–C(4)–C(6)	123(1)
		O(1)–C(1)–O(2)	122(1)
		O(1)–C(1)–C(2)	115(1)
		C(2)–C(1)–O(2)	123(1)

TABLE IV. Bond Distances and Bond Angles for Sn$_2$Br$_4$·5tu·2H$_2$O.

Bond distances (Å)		Bond angles (°)	
Sn(1)–Br(2)	2.649(7)	S(1)–Sn(1)–Br(2)	86.2(3)
Sn(1)–S(1)	2.709(13)	S(2)–Sn(1)–Br(2)	85.2(2)
Sn(1)–S(1)	2.709(13)	S(2)–Sn(1)–S(1)	89.8(3)
Sn(1)–S(2)	3.243(12)	Br(1)–Sn(2)–Br(3)	90.6(2)
Sn(1)–S(2)	3.243(12)	S(2)–Sn(2)–Br(1)	78.5(2)
Sn(2)–Br(1)	2.657(7)	S(2)–Sn(2)–Br(3)	87.9(3)
Sn(2)–Br(3)	2.982(6)	C(1)–S(1)–Sn(1)	96(1)
Sn(2)–Br(3)	2.982(6)	C(2)–S(2)–Sn(1)	117(1)
Sn(2)–S(2)	2.948(11)	Sn(1)–S(2)–Sn(2)	82.2(3)
Sn(2)–S(2)	2.948(11)	C(2)–S(2)–Sn(2)	101(4)
S(1)–C(1)	1.70(4)	N(1)–C(1)–S(1)	128(3)
C(1)–N(1)	1.27(5)	N(2)–C(1)–S(1)	116(3)
C(1)–N(2)	1.37(5)	N(1)–C(2)–S(2)	115(4)
S(2)–C(2)	1.67(4)	N(3)–C(2)–S(2)	120(4)
C(2)–N(3)	1.34(5)	N(4)–C(2)–S(2)	125(3)
C(2)–N(4)	1.37(6)	N(4)–C(2)–N(3)	114(4)
S(3)–C(3)	1.82(8)	N(5)–C(3)–S(3)	115(5)
C(3)–N(5)	1.40(9)	N(6)–C(3)–S(3)	122(6)
C(3)–N(6)	1.34(9)	N(6)–C(3)–N(5)	123(7)
N(1)–H··O	2.92(2)		
N(2)–H··O	3.03(2)		
O–H···Br(3)	3.31(3)		
O–H···S(3)	3.38(3)		

of the atoms in the cell is shown in Fig. 1 and the details of the tin environment are given in Fig. 2. The tin atom lies in a square-pyramidal environment bonded to the two sulphur atoms of the nearest-neighbour thiourea moieties and to two unidentate acetate groups via the oxygen atoms. The two bonds to the carboxylate oxygens are slightly longer than average [6] at 2.18 Å compared to 2.14 Å whilst the Sn–S bonds of 2.85 Å are long compared to the average [6] Sn–S bond of 2.67 Å. Two longer tin–oxygen bonds (2.80, 3.09 Å) to oxygen atoms from surrounding acetate groups, complete a distorted octahedral environment about the tin atom.

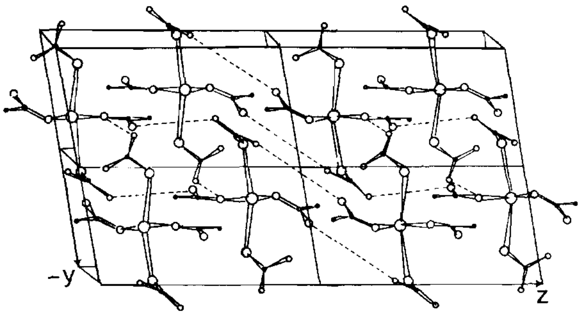

Fig. 1. Cell projection of diacetatobis(thiourea)tin(II).

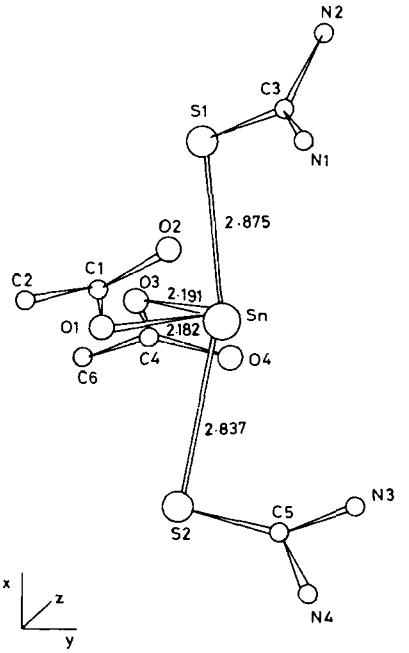

Fig. 2. Tin(II) environment in $Sn(CH_3CO_2)_2$•2tu.

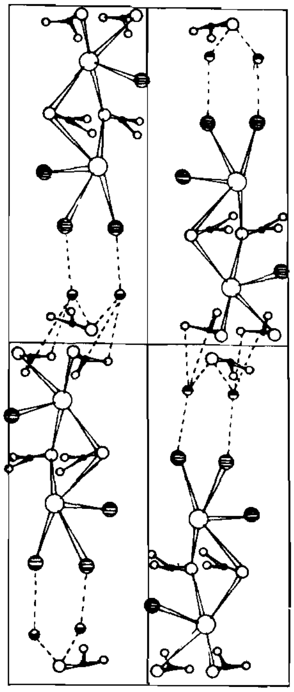

Fig. 3. Cell projection of ditin(II)tetrabromopenta(thiourea)-dihydrate.

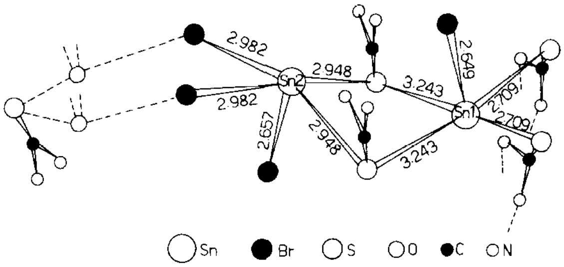

Fig. 4. Tin(II) environments in Sn_2Br_4•5tu•$2H_2O$.

The structure of the bromide consists of Sn_2Br_4-tu_4 groupings that contain both bridging and terminal thiourea groups. The fifth thiourea molecule and the two water molecules are not bonded to the tin atoms but lie between the terminal thiourea groups of one grouping and the Br atoms of an adjacent grouping (Fig. 3). In view of the long tin to weakly-bridging S-atoms, both types of tin atoms in the structure are best described as having trigonal pyramidal coordination (Fig. 4).

There are two tin sites present in Sn_2Br_4•5tu•$2H_2O$, both of which have trigonal pyramidal coordination. The tin atom, Sn(1), has one very short bond to bromine Br(2) of 2.65 Å and two bonds to sulphur atoms S(1) and S(2) at 2.71 Å, which is a distance typical of a Sn–S bond. The tin atom Sn(2), on the other hand, only has bonds to bromine atoms in its trigonal pyramidal coordination. Like Sn(1), it too has an unusually short Sn(2)–Br bond of 2.66 Å. Completing the trigonal environment about Sn(2) are two bromine atoms at distances of 2.98 Å from the tin, which are slightly longer than average, compared to 2.83 Å typical [6] for a tin–bromine bond. In addition to their trigonal pyramidal arrangement of nearest neighbours the two tin atoms are bridged by symmetry related sulphur atoms S(2) and S(2)′ at distances of Sn(1)–S(2) = 3.24 Å and Sn(2)–S(2) = 2.95 Å. A complex network of hydrogen bonds contributes to the cohesion of the structure. The crystal packing is mainly determined by the water oxygen atom in O–H···Br(3), O–H···S(3) and by the noncentral thiourea nitrogen in N(1)–H···O, N(2)–H···O (see Fig. 3 and Table IV).

^{119}*Sn Mössbauer Spectral Data*

The ^{119}Sn Mössbauer parameters [7] of these thioureatin(II) complexes of known structure are of considerable interest (Table V). The reduced isomer shift value of the known sulphato-complex compared

TABLE V. ^{119}Sn Mössbauer Data for Some Thiourea Complexes of Tin(II) Compounds [7].

Compound	δ mms^{-1}	Δ mms^{-1}
$SnSO_4$	3.95	1.00
$SnSO_4$•2tu	3.25	0
$Sn(CH_3CO_2)_2$	3.26	1.77
$Sn(CH_3CO_2)_2$•2tu	3.35	0
$SnBr_2$	3.98	0
Sn_2Br_4•5tu•$2H_2O$	3.67	0

to that of tin(II) sulphate must be associated with the formation of one short Sn--S bond (2.62 Å). In the absence of any structural information, it is tempting to interpret the shift values of the acetato- and bromo-complexes in the same way. In other words if the two structures were like that of the sulphato-complex, then the Mössbauer data of only the bromo-complex could be interpreted in the same way, as there is a reduction in its shift value on complex formation compared to that of its parent compound. As a result of the present study, however, the slight increase in chemical shift for the acetate complex from that of its parent compound, is consistent with the fact that there is no shortening of the Sn–O bonds to the acetate moieties or formation of short Sn–S bonds to the thiourea ligands on complexation. The singlet resonance line ($\delta = 3.67$ mms^{-1} $\Delta = 0$ mms^{-1}) observed for the bromo-complex is surprising since there are two tin sites with apparently different environments. Although the symmetry of the two tin atoms is different, the two sites must involve similar distribution of the available tin electron density, and the lowering in shift from that of tin(II) bromide must be due to a considerable shortening of the tin–bromine bonds (of average 2.65 Å) and not due to the formation of short Sn–S bonds as in the sulphatobisthiourea tin(II) complex. This study illustrates that structural predictions based on Mössbauer parameters alone could lead to wrong assumptions being made.

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