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Crystal and Molecular Structure of Bis-(*N*,*N*-diethyldithiocarbamato)tin(II)

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The crystal structure of bis-(*N*,*N*-diethyldithiocarbamato)tin(II), $Sn[S_2CN(C_2H_5)_2]_2$, has been determined by a single-crystal three-dimensional X-ray diffraction study. The compound crystallizes in space group $P2_1/a$ with four formula units in each unit cell of dimensions $a=17\cdot294$ (6), $b=8\cdot492$ (2), $c=11\cdot503$ (8) Å, and $\beta=103\cdot42$ (5)°. Calculated and observed densities are 1·682 (2) and 1·67 (1) g cm^{-3}, respectively. Intensity data were obtained using an Enraf–Nonius automated diffractometer (Mo $K\alpha$ radiation, $\lambda=0\cdot71069$ Å). The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to a conventional R value of 7·6% for 2285 independent reflections. The structure consists of monomers with each Sn atom coordinated to four S atoms by two bidentate ligands. The four S atoms and the Sn(II) lone pair form a distorted pyramidal valence polyhedron (square pyramid or trigonal bipyramid) which resembles those of yellow PbO and several Pb(II) dithioalkyl derivatives. Each bidentate ligand forms a four-membered SnS_2C ring with a short [2·574 (2), 2·592 (3) Å] and a long [2·765 (3), 2·819 (3) Å] Sn–S distance. Long and short M–S distances for bidentate ligands are shown to be characteristic of complexes containing MS_2X rings when M contains a lone pair of electrons.

Introduction

Recently, a large number of metal dithiocarbamate and related dithioalkyl compounds have been examined structurally. Interest in these compounds has centered on their practical applications (Hagihara & Yamashita, 1966; Klug, 1966) and in the nature of the metal–ligand bonding. In general, the coordination geometries of dithiocarbamate complexes have been found to be irregular. Distortions from idealized geometries have been attributed to the steric requirements of four-membered MS_2X rings and to the limited dithiocarbamate ligand bite (Ricci, Eggers & Bernal, 1972).

With Pb(II), several structures containing PbS_2X (X=C,P) rings have been determined (lead ethylxanthate, Hagihara & Yamashita, 1966; lead isopropylxanthate, Hagihara, Yoshida & Watanabe, 1969; lead n-butylxanthate, Hagihara, Watanabe & Yamashita, 1968; lead diethyldithiocarbamate, Iwasaki & Hagihara, 1972; lead diethyldithiophosphate, Ito, 1972; and lead diisopropyldithiophosphate, Lawton & Kokotailo, 1969). Except for the latter, all have the following common features: Pb is coordinated to four S atoms, the ligands are bidentate, Pb–S bond lengths for a given ligand are unequal, and all may be considered to be derived from the coordination in yellow PbO (Kay, 1961). For lead diisopropyldithiophosphate, unequal Pb–S bond lengths were found for a given ligand, but the ligands are bridging and the structure is polymeric.

Our interest in bis-(*N*,*N*-diethyldithiocarbamato)-tin(II) began with a Mössbauer study (Herber, 1973) which indicated that Sn was in a non-symmetric, four-coordinate environment. A structural study was undertaken to establish the molecular geometry for spectroscopic analysis and to determine the extent to which the structural features found for Pb(II) would be present in Sn(II) compounds.

Experimental section

A sample consisting of white needles was supplied to us by Professor R. Herber and Dr J. L. De Vries of Rutgers University.

Crystal and X-ray data

$Sn[S_2CN(C_2H_5)_2]_2$, $M=415\cdot23$, monoclinic, $P2_1/a$, $a=17\cdot294$ (6), $b=8\cdot492$ (2), $c=11\cdot503$ (8) Å, $\beta=103\cdot42$ (5)°, $U=1641\cdot4$ Å^3, $D_o=1\cdot67$ (1), $D_c=1\cdot682$ (2) g/cm^3, $Z=4$, $\mu=23\cdot7$ cm^{-1} for Mo $K\alpha$ radiation.

A crystal of dimensions 0·35 × 0·17 × 0·17 mm was mounted in a sealed capillary parallel to the long axis (b). Data were collected with an Enraf–Nonius CAD-3 automated diffractometer using Mo $K\alpha$ radiation and a graphite monochromator. A θ–2θ scan was used to a maximum of $\theta=30°$. At the end of data collection, the crystal surface was slightly orange. However, standard reflections, measured at fifty-reflection intervals, were consistent to $\pm 2\%$ and did not decrease noticeably with time. It was assumed that decomposition was not significant. The usual Lorentz and polarization factors were applied to the 5200 measured diffraction maxima. Of these, 2285 with $F^2 \geq 2\sigma(F^2)$ where $\sigma(F^2)$ is the standard deviation as estimated from counting statistics, were used in the structure solution and refinement. Systematic absences of $0k0$ with k odd and of $h0l$ with h odd fixed the space group as $P2_1/a$. Absorption corrections were not made; for a cylindrical crystal ($\mu R=0\cdot2$), the maximum effect of absorption was estimated to be less than 1% (*International Tables for X-ray Crystallography*, 1959).

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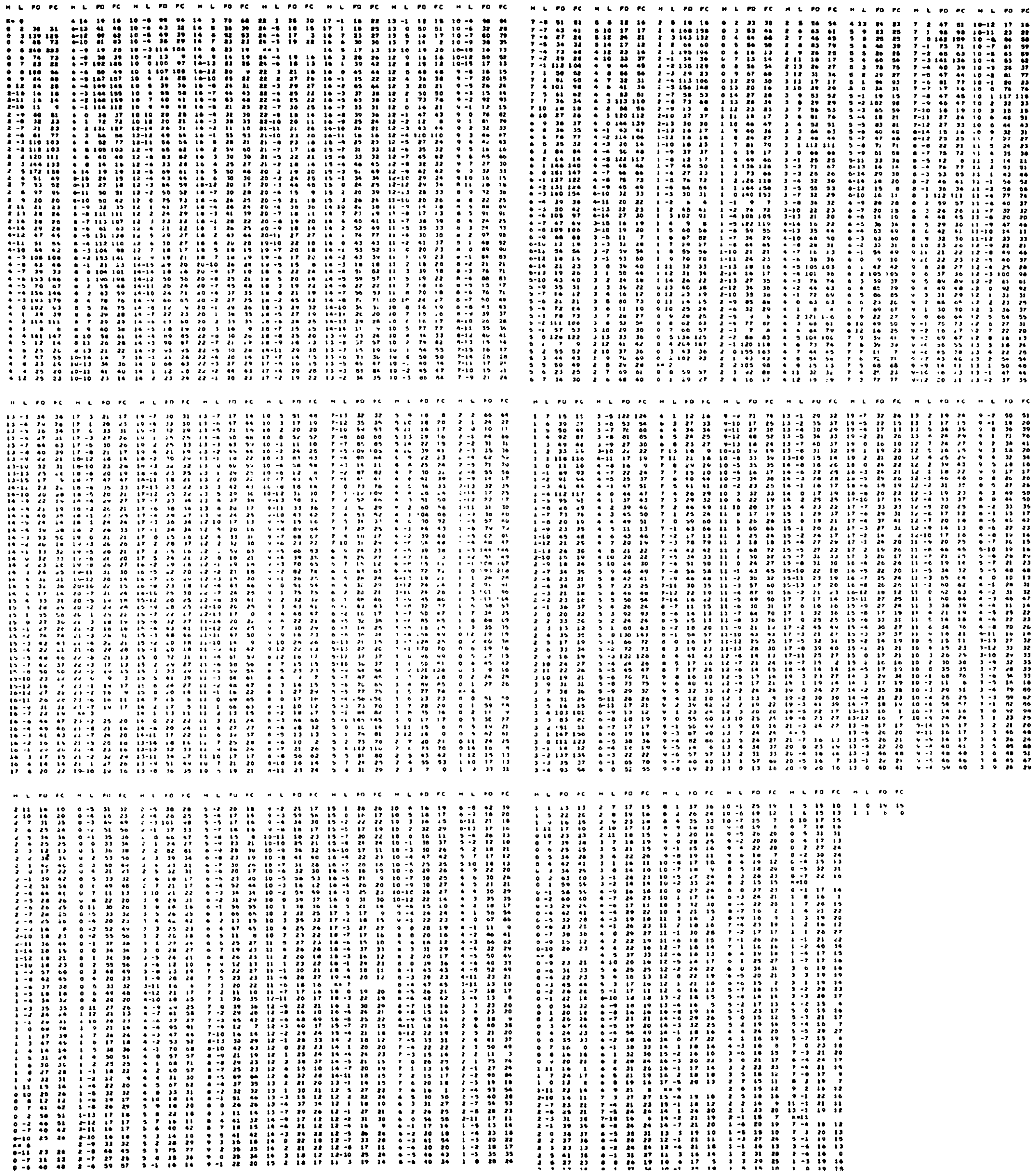
Solution of the structure

Approximate Sn and S coordinates were obtained from a normal sharpened Patterson map while the C and N atom positions were deduced from a difference synthesis based on the Sn and S phases. A modified version of *ORFLS* (Busing, Martin & Levy, 1962) was used for the structure factor calculations and full-matrix least-squares refinement. $R_{wF2}=[\sum w(F_o^2-F_c^2)^2/$

Table 1. *Observed and calculated structure factors for* Sn(II)$[S_2CN(C_2H_5)_2]_2$

The final scale factor by which F_c is multiplied to place it on the observed scale is 0·363.



$\sum wF_o^4]^{1/2}$ was the function minimized. Weights were set according to $w=1/\sigma^2(F^2)$. Atomic scattering factors for Sn, S, C and N were those of Cromer & Waber (1965), while those for H were obtained from *International Tables for X-ray Crystallography* (1962). All atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion corrections were applied to Sn (*International Tables for X-ray Crystallography*, 1962).

Four cycles of refinement of all Sn, S, C and N atoms using isotropic thermal parameters reduced $R_F=\sum ||F_o|-|F_c||/\sum|F_o|$ to 0·14, $R_{F^2}=[\sum(F_o^2-F_c^2)^2/\sum F_o^4]^{1/2}$ to 0·19 and R_{wF^2} to 0·21. Six cycles of refinement using anisotropic temperature factors for Sn and S gave R_F = 0·093, R_{F^2} = 0·14 and R_{wF^2} = 0·16. A difference synthesis at this stage revealed broad, diffuse maxima of height 0·5–0·6 eÅ^{-3} near the ethyl group C atoms. H atoms were placed at these positions; however, some H coordinates were adjusted slightly to give more nearly the expected C–H bond lengths and tetrahedral angles. Bond distances thus determined varied from 0·97 to 1·10 Å while the H–C–H angles varied from 102 to 117°. H atoms were included for further refinement with isotropic temperature factors equal to those of the C atom to which they are bonded. Inclusion of H atoms reduced R_F to 0·090. After three refinement cycles of all nonhydrogen parameters, all parameter changes were less than their estimated standard deviation. Final values of R_{wF^2}, R_{F^2} and R_F were 0·125, 0·106 and 0·076, respectively.

Observed and calculated structure factors are shown in Table 1. Since calculated values of F for intense, low-order reflections were not systematically larger than observed values, no correction was made for secondary extinction. Final atomic parameters and estimated standard deviations from the least-squares refinement are shown in Table 2.

Description of the structure

Line drawings of the molecule, showing the numbering scheme and giving bond distances and angles, are shown in Fig. 1. Fig. 2 shows half the unit-cell contents viewed along **b**.

In $Sn[S_2CN(C_2H_5)_2]_2$, Sn is coordinated to four S atoms by two bidentate ligands. Three of the four interligand S–S distances [S(1)–S(3), S(1)–S(4) and S(2)–S(3)] lie between 3·63 and 3·84 Å, and are close to the S–S van der Waals separation (3·7 Å). Each ligand forms a four-membered SnS_2C ring with a short [2·574 (2), 2·592 (3) Å] and a long [2·765 (3), 2·819 (3) Å] Sn–S distance. Metal–sulfur bond distances to ligand 2 are longer than those to ligand 1 by approximately 0·03 Å. Using Cruickshank's criterion for comparison of bond lengths (Lipson & Cochran, 1966), this difference is significant. The S atoms with long Sn–S bonds are far apart [S(2)–Sn–S(4) angle 139·6°] while those with short Sn–S bonds are close together [S(1)–Sn–S(3) angle 96·2°]. The valence polyhedron can be described as distorted square pyramidal with the Sn(II) lone pair apical or distorted trigonal bipyramidal with the lone pair equatorial. A trigonal bipyramidal description

Table 2. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^2) *for* $Sn[S_2CN(C_2H_5)_2]_2$

Estimated standard deviations are given in parentheses.

	x	y	z	B
Sn	4612·7 (3)	1807·8 (7)	−1748·6 (5)	–
S(1)	3256·8 (12)	770·3 (29)	−1523·6 (17)	–
S(2)	4407·6 (12)	2137·7 (27)	552·2 (18)	–
S(3)	4178·7 (13)	4722·2 (27)	−2718·3 (17)	–
S(4)	3803·3 (14)	2464·0 (30)	−4121·0 (19)	–
N(1)	2997 (3)	923 (7)	669 (5)	297 (12)
N(2)	3608 (4)	5572 (8)	−4312 (5)	388 (14)
C(1)	3510 (4)	1225 (8)	23 (6)	285 (15)
C(2)	3835 (4)	4326 (9)	−3613 (7)	347 (16)
C(3)	3600 (6)	7206 (12)	−3986 (8)	593 (23)
C(4)	3303 (5)	5315 (11)	−5699 (8)	484 (21)
C(5)	4392 (6)	8078 (13)	−3956 (9)	740 (27)
C(6)	3965 (5)	5353 (11)	−6359 (8)	548 (22)
C(7)	2206 (4)	189 (9)	157 (6)	344 (16)
C(8)	3143 (4)	1386 (9)	1944 (7)	376 (17)
C(9)	1575 (4)	1407 (9)	−298 (7)	383 (17)
C(10)	3354 (5)	−2 (11)	2769 (8)	502 (20)
H3–1	3484	7182	−3103	593
H3–2	3187	7887	−4473	593
H4–1	2925	6250	−6000	484
H4–2	2922	4379	−5814	484
H5–1	4450	9064	−3416	740
H5–2	4900	7287	−3489	740
H5–3	4414	8241	4781	740
H6–1	4083	6499	−6440	548
H6–2	3751	5000	−7252	548
H6–3	4334	4500	−6038	548
H7–1	2055	−500	760	344
H7–2	2250	−375	−562	344
H8–1	2703	2001	2147	376
H8–2	3599	2178	2149	376
H9–1	1734	2500	−45	383
H9–2	1382	1500	−1164	383
H9–3	1120	1400	134	383
H10–1	3875	−500	2599	502
H10–2	3500	499	3625	502
H10–3	2784	−677	2639	502

Table 2 (*cont.*)

Anisotropic thermal parameters (× 10^5).

Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	274 (2)	1497 (9)	769 (4)	−5 (5)	153 (2)	59 (7)
S(1)	269 (8)	1657 (41)	317 (16)	−234 (17)	117 (9)	−11 (24)
S(2)	252 (8)	1567 (49)	500 (18)	−166 (17)	30 (10)	37 (24)
S(3)	422 (9)	1252 (41)	391 (17)	48 (17)	163 (10)	−78 (21)
S(4)	473 (34)	1473 (19)	527 (67)	−219 (6)	178 (54)	−128 (17)

might be favored because of the non-equivalence of the Sn–S distances. If S(1), S(3) and the lone pair are equatorial, S(2) and S(4), with long Sn–S distances, are axial. This arrangement seems reasonable in terms of a simple electron-pair repulsion model (Sidgwick & Powell, 1940; Gillespie & Nyholm, 1957; Gillespie, 1961) and has the advantage of accounting for long and short Sn–S distances. However, in view of the highly distorted geometry about Sn, any attempt to describe the valence polyhedron in detail would involve an admixture of ideal geometries.

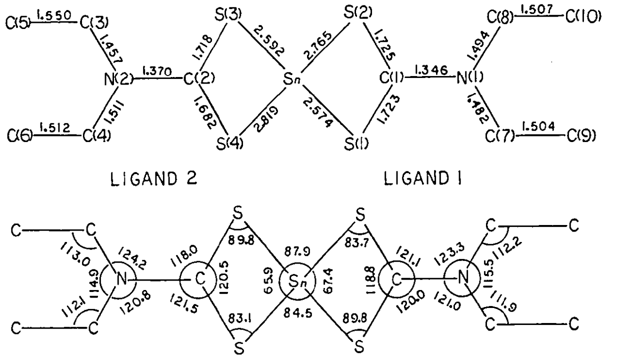


Fig. 1. Bond distances and angles in $Sn[S_2CN(C_2H_5)_2]_2$. Distances and angles were calculated using a modified version of *ORFFE* (Busing, Martin & Levy, 1964). Average e.s.d.'s are: Sn–S (±0·003 Å); S–S (±0·004 Å); S–C (±0·009 Å); N–C (±0·012 Å); C–C (±0·014 Å); S–Sn–S (±0·2°); Sn–S–C (±0·3°); S–C–S (±0·4°); S–C–N (±0·5°); C–N–C (±0·6°); N–C–C (±0·6°). The following distances and angles are not given in the figure: S(1)–S(2), 2·970; S(1)–S(3), 3·844; S(1)–S(4), 3·633; S(3)–S(4), 2·952; S(2)–S(4), 5·240; S(2)–S(3), 3·721 Å; S(1)–Sn–S(3), 96·2; S(2)–Sn–S(4) 139·6°.

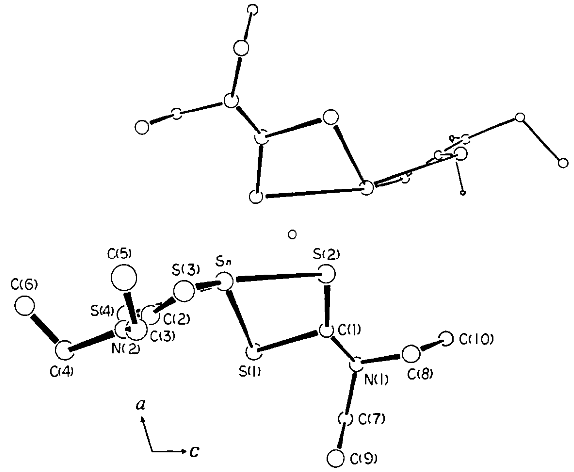


Fig. 2. The structure viewed along **b**. For clarity, only molecules related by the center of symmetry are shown.

There is little evidence to indicate that the lone pair is involved in intermolecular bonding to any appreciable extent. The shortest intermolecular contacts involving Sn are Sn–S(2′) [3·862 (3) Å] and Sn–C(9′) [3·738 (9) Å]. The remaining intermolecular contacts are not unusually short (Table 3), and the structure consists essentially of discrete monomers.

Table 3. *Intermolecular contacts less than* 4 Å

C(1)–C(7)	3·58 (1) Å	C(9)–C(7)	3·82 (1) Å
S(3)–C(9)	3·63 (1)	C(6)–C(9)	3·84 (1)
S(3)–C(7)	3·67 (1)	Sn—S(2)	3·862 (3)
C(4)–S(1)	3·69 (1)	C(9)–N(1)	3·95 (1)
Sn—C(9)	3·738 (9)	S(2)–C(5)	3·98 (1)
N(1)–C(7)	3·74 (1)	C(8)–C(7)	3·99 (1)
S(2)–C(7)	3·76 (1)	C(5)–C(9)	3·99 (1)

Ignoring terminal methyl groups, both ligands are planar to ±0·02 Å; equations for the least-squares planes (weighted according to atomic number) and distances of atoms from the planes are given in Table 4. The Sn atom is 0·033 Å removed from the plane of ligand 1 and 0·360 Å from that of ligand 2. Ligand 1 has more symmetric and longer C–S bond lengths [1·725 (8), 1·723 (9) Å] than ligand 2 [1·718 (9), 1·682 (9) Å]. All of these distances lie between those expected for single and double carbon–sulfur bonds. The C–S asymmetry in ligand 2 is significant and suggests greater double bond character for the C(2)–S(4) bond as compared with the remaining three. Increased double bond character for C(2)–S(4) may be related to the Sn–S distances [Sn–S(4) is the longest] and to the planarity of the ligands [S(4) is on ligand 2 which is least coplanar with Sn]. Average bond distances and angles in the ligands compare favorably with those reported for

Table 4. *Equations of least-squares planes*

Equations are expressed in the form $AX+BY+CZ=D$ where X, Y and Z refer to the crystallographic axes.

Plane	A	B	C	D	Atoms defining the plane
1	0·3752	−0·8986	0·1344	1·3099	S(1), S(2), C(1), N(1), C(7), C(8)
2	−0·9873	−0·0979	0·3506	−8·3709	S(3), S(4), C(2), N(2), C(3), C(4)

Deviations of atoms from the planes (Å)

Plane	Sn	S(1)	S(2)	S(3)	S(4)	C(1)	C(2)	N(1)	N(2)
1	0·033	0·004	−0·020			0·029		0·034	
2	0·390			−0·011	0·011		0·007		−0·015

Plane	C(5)	C(6)	C(7)	C(8)
1			0·001	−0·028
2	0·018	−0·008		

other dithiocarbamate structures (Ricci, Eggers & Bernal, 1972).

Comparison with PbS_2X structures

As indicated by the data in Table 5 (for numbering scheme, see Fig. 3), the valence polyhedron in $Sn[S_2CN(C_2H_5)_2]_2$ resembles those which have been reported for yellow PbO and several Pb(II) dithioalkyl derivatives; black SnO is not comparable directly since it is isostructural with the red (tetragonal) form of PbO. All the PbS_4 compounds show long (axial) and short (equatorial) Pb–S distances within a given PbS_2X ring. These differences are significant for all compounds except $Pb[S_2CO{-}nC_4H_9]_2$ where bond length standard deviations are very large. Values of the S–M–S angles in $Sn[S_2CN(C_2H_5)_2]_2$ are particularly striking when compared with those for the lead ethyl derivatives $Pb[S_2CN(C_2H_5)_2]_2$, $Pb[S_2COC_2H_5]_2$ and $Pb[S_2P(OC_2H_5)_2]_2$; to a first approximation, the valence polyhedron for the ethyl compounds is independent of the metal and the ligand. MS_2X rings in the lead ethyl compounds are considerably less coplanar than those in $Sn[S_2CN(C_2H_5)_2]_2$ as indicated by the distances of metal atoms from the ligand planes (Table 5). Deviations of the metal atoms from the ligand planes do not appear to be related in any simple way to the structural details of the valence polyhedra. For the lead ethyl derivatives, it has been suggested (Iwasaki & Hagihara, 1972) that the characteristic polyhedron observed results from a distortion of the yellow PbO structure until at least one interligand S–S contact attains the van der Waals separation. A similar interpretation seems reasonable for $Sn[S_2CN(C_2H_5)_2]_2$ and lone-pair bonding-pair repulsions could account in part for this feature.

A different PbS_4 geometry might be expected for $Pb[S_2CO{-}iC_3H_7]_2.C_5H_5N$ since, unlike the ethyl derivatives, the structure must accomodate a pyridine molecule. In $Pb[S_2CO{-}iC_3H_7]_2.C_5H_5N$, there is a relatively short Pb–N distance [2·55 (4) Å; Hagihara, Yoshida & Watanabe, 1969] and this could account for the small S(2)–Pb–S(4) angle. In $Pb[S_2P(O{-}iC_3H_7)_2]_2$, the ligands are bridging and the valence polyhedron has been described as distorted pentagonal bipyramidal. However, the two equatorial Pb–S distances nearest the nominal location of the lone pair are long [3·221 (9), 3·211 (9) Å; Lawton & Kokotailo, 1969]. The remaining four Pb–S distances are close to those found for $Pb[S_2P(OC_2H_5)_2]_2$ and the arrangement of these atoms about Pb crudely approximates those of the other compounds in Table 5: the two S atoms with

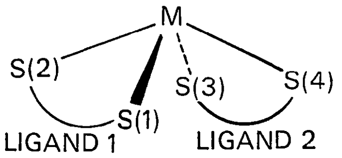


Fig. 3. Numbering scheme for Table 5.

Table 5. *Comparison of* Pb(II) *and* Sn(II) *compounds containing* MS_2X *rings*

The numbering scheme is shown in Fig. 3. All compounds are distorted pyramidal except for $Pb[S_2P(O{-}iC_3H_7)_2]_2$ which is distorted pentagonal bipyramidal. Bond distances are in Å, angles in degrees and e.s.d.'s in parentheses. Missing information was not supplied by the authors. For S_2CNR_2, the planar portion of the ligand is S_2CNC_2, for S_2COR it is S_2CO and for $S_2P(OR)_2$ it is S_2P. Entries under 'Planarity ligand 1,2' give the distance of the metal atom from the ligand plane. Values followed by a * were calculated by the present authors using coordinates in the literature cited.

	Ligand 1				Ligand 2			
Compound	M–S(1)	M–S(2)	S(1)–X	S(2)–X	M–S(3)	M–S(4)	S(3)–X	S(4)–X
$Sn[S_2CN(C_2H_5)_2]_2$	2·574 (2)	2·765 (3)	1·723 (8)	1·725 (8)	2·592 (3)	2·819 (3)	1·718 (9)	1·682 (9)
$Pb[S_2CN(C_2H_5)_2]_2$	2·744 (9)	2·885 (11)	1·724 (24)	1·709 (31)	2·786 (9)	2·940 (10)	1·745 (27)	1·635 (27)
$Pb[S_2COC_2H_5]_2$	2·742 (25)	2·838 (25)	1·70 (11)	1·68 (11)	2·785 (30)	2·950 (30)	1·78 (10)	1·66 (10)
$Pb[S_2P(OC_2H_5)_2]_2$	2·754 (6)	2·996 (5)	1·995 (8)	1·969 (7)	2·790 (6)	3·022 (6)	1·991 (9)	1·968 (7)
$Pb[S_2CO{-}iC_3H_7]_2.C_5H_5N$	2·833 (18)	2·896 (13)	1·57 (5)	1·74 (4)	2·722 (19)	3·057 (16)	1·73 (5)	1·60 (5)
$Pb[S_2CO{-}nC_4H_9]_2$	2·83 (4)	2·77 (9)	1·86 (19)	1·62 (20)	2·76 (6)	3·03 (8)	1·66 (19)	1·58 (20)
PbO	2·214 (23)	2·487 (6)			2·223 (15)	2·487 (6)		
$Pb[S_2P(O{-}iC_3H_7)_2]_2$								
equatorial	2·756	3·211			2·772	3·221		
axial	3·042	2·979						

Compound	S(1)–M–S(3)	S(2)–M–S(4)	Planarity ligand 1	Planarity ligand 2	Reference
$Sn[S_2CN(C_2H_5)_2]_2$	96·2 (2)	139·6 (2)	0·03	0·36	This work
$Pb[S_2C(NC_2H_5)_2]_2$	96·2 (2)	133·2 (4)	0·29	0·80	Iwasaki & Hagihara (1972)
$Pb[S_2COC_2H_5]_2$	98·2 (9)	137·2 (10)	0·42	0·79	Hagihara & Yamashita (1966)
$Pb[S_2P(OC_2H_5)_2]_2$	94·1 (2)	138·2 (2)	–	–	Ito (1972)
$Pb[S_2CO{-}iC_3H_7]_2.C_5H_5N$	95·0 (6)	127·7 (5)	1·00*	0·03	Hagihara, Yoshida & Watanabe (1969)
$Pb[S_2CO{-}nC_4H_9]_2$	91·7 (15)	141·2 (26)	0·78*	0·26*	Hagihara, Watanabe & Yamashita (1968)
PbO	90·4 (10)	147·5 (10)	–	–	Kay (1961)
$Pb[S_2P(O{-}iC_3H_7)_2]_2$					
equatorial					Lawton & Kokotailo (1969)
axial					

long Pb–S distances are axial while the S(1)–Pb–S(3) angle is reduced to 75·3 (3)°, possibly as a result of steric crowding. Thus, some of the structural features found for the Sn and Pb ethyl compounds are also present in $Pb[S_2P(O\text{–}iC_3H_7)_2]_2$.

Lead atoms in the compounds listed in Table 5 show a tendency to coordinate additional atoms in contrast to Sn in $Sn[S_2CN(C_2H_5)_2]_2$. The presence of a short Pb–N contact in $Pb[S_2CO\text{–}iC_3H_7]_2.C_5H_5N$ and of two short Pb–S contacts in $Pb[S_2P(O\text{–}iC_3H_7)_2]_2$ has been noted above. There are two short intermolecular Pb–S distances in $Pb[S_2CN(C_2H_5)_2]_2$ (3·445, 3·554 Å) and in $Pb[S_2P(OC_2H_5)_2]_2$ (3·469, 3·478 Å), while in $Pb[S_2COC_2H_5]_2$, there are three such distances (3·32, 3·37 and 3·50 Å). The lack of such short distances in $Sn[S_2CN(C_2H_5)_2]_2$ may be related to the smaller size of Sn as compared with Pb.

Comparison with other MS_2X compounds

For the Sn(II) and Pb(II) compounds above, M–S distances within a given MS_2X ring differ typically by more than 0·1 Å. Larger differences (*ca.* 0·4–0·6 Å) have been reported for other compounds where the central atom contains a lone pair. Some examples are $As(III)[S_2CN(C_2H_5)_2]_3$ (Colapietro, Domenicano, Scaramuzza & Vaciago, 1968), $Se(II)[S_2CN(C_2H_5)_2]_2$ (Huesbye & Helland-Madsen, 1970) and $Te(II)[S_2COC_2H_5]_2$ (Huesbye, 1967). Where the central element has no lone pair and the ligands are not bridging, as with $Co(III)[S_2CN(C_2H_5)_2]_3$ (Merlino, 1968), $Ni(II)[S_2P(OCH_3)_2]_2$ (Jones, Ansell & Katz, 1969) and $Sn(IV)[S_2CN(C_2H_5)_2]_4$ (Harreld & Schlemper, 1971), M–S distances within a given MS_2X ring differ by no more than 0·04 Å. The available evidence indicates that long and short M–S distances within four-membered MS_2X rings are characteristic of complexes where the central atom contains a lone pair of electrons.

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