Acta Cryst. (1976). B32, 941

Tin(IV) Tetrakis-(*N*,*N*-dimethyldithiocarbarmate)

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(*Received* 18 *September* 1975; *accepted* 20 *November* 1975)

Abstract. Triclinic, $P\bar{1}$, $a=9{\cdot}357$ (1), $b=9{\cdot}618$ (2), $c=13{\cdot}640$ (2) Å, $\alpha=95{\cdot}95$ (1), $\beta=80{\cdot}95$ (1), $\gamma=102{\cdot}06$ (1)°, formula $Sn[S_2CN(CH_3)_2]_4$, $Z=2$, $D_o=1{\cdot}688$ (9), $D_c=1{\cdot}684$ g cm^{-3}. The distorted octahedral complex contains two *cis* bidentate and two monodentate ligands; each bidentate ligand shows a long [2·595 (4), 2·707 (5) Å] and a short [2·510 (4), 2·515 (4) Å] Sn–S distance. Short S···S distances suggest weak intramolecular interactions between mono and bidentate ligands.

Introduction. Suitable crystals were grown by diffusion (Johnson, 1972). Dimethylamine (0·05 mol) and $SnCl_4$ (0·005 mol) were dissolved in 150 ml of acetone; in another flask, 25 ml of CS_2 were dissolved in 125 ml of acetone. The solutions were poured into either end of a U-tube containing a fine sintered glass porous partition. After three days, needle-shaped crystals were recovered from the $SnCl_4$ side. A crystal measuring 0·15 × 0·07 × 0·07 mm was mounted in a sealed glass capillary. Preliminary Weissenberg photographs revealed a triclinic lattice with no systematic extinctions. Space group $P\bar{1}$ was assumed, and, with $Z=2$, the observed (flotation) and calculated densities agreed well. Intensity data were collected at room temperature (21 ± 2°C) with an Enraf–Nonius CAD-3 automated diffractometer (θ–2θ scan, $4<2\theta<60°$) using graphite monochromated Mo $K\alpha$ radiation. Of the 5403 unique reflections recorded, 1908 with $F^2 \geq 3\sigma$ (counting statistics) were considered observed, Lp corrected, and used in the structure solution and refinement. Absorption corrections were not applied (μ for Mo $K\alpha=17{\cdot}9$ cm^{-1}).

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques using programs described previously (Potenza, Giordano, Mastropaolo & Efraty, 1974). Atomic scattering factors were those of Cromer & Waber (1965) and all atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion correction were applied to Sn (*International Tables for X-ray Crystallography*, 1962). Weights, $w=1/\sigma^2$, were chosen by an analysis of variance to make $\Delta F/\sigma$ independent of F_o. This led to the following assignments: $\sigma(F_o)=0{\cdot}345+0{\cdot}055|F_o|$ for $|F_o|<6{\cdot}2$, $\sigma(F_o)=1{\cdot}154–0{\cdot}0783|F_o|$ for $6{\cdot}2\leq|F_o|\leq10{\cdot}4$ and $\sigma(F_o)=-0{\cdot}018+0{\cdot}0345|F_o|$ for $|F_o|>10{\cdot}4$. The quantity $R_{wF}=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}$ was minimized. Using anisotropic thermal parameters for Sn and S, several cycles of refinement reduced $R_F=\sum||F_o|-|F_c||/\sum|F_o|$ to 0·067 and R_{wF} to 0·072. For the final cycle, all calculated parameter changes were less than their estimated standard deviation obtained from the inverse matrix. A final difference map showed no significant features. No attempt was made to locate H atoms. Atomic parameters* are listed in Table 1 while a view of the complex, showing the numbering scheme, is given in Fig. 1. Table 2 lists selected bond distances and angles.

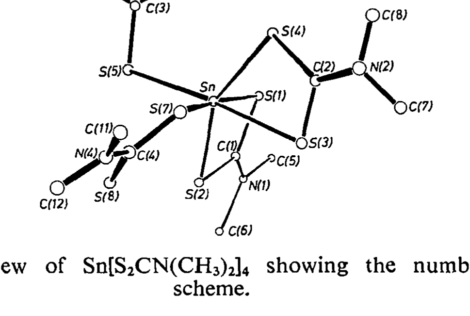

Fig. 1. View of $Sn[S_2CN(CH_3)_2]_4$ showing the numbering scheme.

Discussion. From infrared and n.m.r. spectroscopy, it was suggested (Bonati, Minghetti & Cenini, 1968) that $Sn[S_2CNR_2]_4$ contained eight-coordinated Sn. The structure of $Sn[S_2CN(C_2H_5)_2]_4$ (Harreld & Schlemper, 1971) clearly revealed six coordination with two mono and two bidentate ligands. However, alkyl substitution can affect the geometry of complexes containing four-membered MS_2X rings. For example, $Pb[S_2P(O–i–C_3H_7)_2]_2$ has been described as distorted pentagonal bipyramidal (Lawton & Kokotailo, 1969) and $Pb[S_2P(O–C_2H_5)_2]_2$ as distorted tetragonal pyramidal (Ito, 1972). The present study was undertaken to examine the coordination geometry in detail and to investigate the effect of alkyl substitution.

The structure consists of discrete monomers with no unusually short intermolecular contacts. Each $Sn[S_2CN(CH_3)_2]_4$ complex contains two essentially bidentate and two monodentate ligands which provide a distorted octahedral environment about Sn. The

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* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31526 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* (× 10⁴) *and thermal parameters for* $Sn[S_2CN(CH_3)_2]_4$

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses.

	x	*y*	*z*	*B* (Å²)
Sn	2304 (1)	−1935 (1)	2261 (1)	–
S(1)	3954 (5)	−1752 (4)	544 (3)	–
S(2)	1971 (5)	−4342 (4)	1323 (3)	–
S(3)	4589 (5)	−2593 (4)	2990 (3)	–
S(4)	3922 (5)	251 (4)	2960 (3)	–
S(5)	36 (5)	−1562 (5)	1654 (4)	–
S(6)	1903 (6)	1359 (5)	1709 (4)	–
S(7)	953 (6)	−2181 (8)	4017 (4)	–
S(8)	−973 (7)	−4596 (6)	3009 (4)	–
N(1)	3571 (14)	−4267 (13)	−503 (9)	3·4 (3)
N(2)	6207 (16)	−223 (15)	3734 (10)	4·1 (3)
N(3)	−840 (14)	702 (13)	1313 (9)	3·2 (3)
N(4)	−1445 (19)	−3713 (17)	4938 (12)	6·0 (4)
C(1)	3219 (16)	−3529 (15)	373 (11)	2·7 (3)
C(2)	5018 (18)	−814 (16)	3281 (12)	3·3 (3)
C(3)	280 (17)	259 (16)	1540 (11)	3·0 (3)
C(4)	−562 (20)	−3536 (18)	4018 (13)	4·2 (4)
C(5)	4585 (21)	−3600 (18)	−1366 (13)	4·6 (4)
C(6)	2887 (20)	−5803 (18)	−673 (13)	4·3 (4)
C(7)	7204 (25)	−1089 (23)	4031 (16)	6·3 (5)
C(8)	6565 (24)	1298 (21)	3970 (15)	5·7 (5)
C(9)	−2281 (19)	−271 (18)	1087 (12)	4·1 (4)
C(10)	−780 (19)	2276 (17)	1234 (12)	4·0 (4)
C(11)	−1168 (27)	−2850 (24)	5834 (17)	7·1 (6)
C(12)	−2888 (32)	−4754 (28)	5044 (21)	8·9 (7)

Anisotropic thermal parameters (× 10⁴). The expression for the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	81 (2)	86 (2)	33 (1)	7 (1)	−11 (1)	−16 (1)
S(1)	94 (6)	54 (5)	42 (3)	−6 (5)	−6 (4)	1 (3)
S(2)	107 (6)	53 (5)	46 (3)	−3 (5)	5 (4)	−1 (3)
S(3)	102 (6)	80 (5)	51 (3)	25 (5)	−14 (4)	5 (3)
S(4)	109 (6)	75 (5)	52 (3)	13 (5)	−36 (3)	−15 (3)
S(5)	122 (7)	69 (6)	95 (4)	17 (5)	−43 (5)	10 (4)
S(6)	131 (7)	111 (7)	109 (5)	−5 (6)	−65 (5)	−3 (4)
S(7)	100 (8)	326 (12)	38 (3)	−14 (8)	−7 (4)	−24 (5)
S(8)	213 (10)	121 (7)	70 (4)	−12 (7)	17 (5)	−7 (4)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Ligand 1		Ligand 2	
Sn—S(1)	2·595 (4)	Sn—S(3)	2·707 (5)
Sn—S(2)	2·510 (4)	Sn—S(4)	2·515 (4)
S(1)–C(1)	1·71 (1)	S(3)–C(2)	1·69 (2)
S(2)–C(1)	1·73 (1)	S(4)–C(2)	1·72 (2)
C(1)–N(1)	1·36 (2)	C(2)–N(2)	1·35 (2)
N(1)–C(5)	1·50 (2)	N(2)–C(7)	1·50 (3)
N(1)–C(6)	1·49(2)	N(2)–C(8)	1·44 (2)

Ligand 3		Ligand 4	
Sn——S(5)	2·500 (6)	Sn——S(7)	2·536 (5)
Sn····S(6)	3·439 (6)	Sn····S(8)	3·643 (6)
S(5)—C(3)	1·74 (2)	S(7)—C(4)	1·71 (2)
S(6)—C(3)	1·69 (2)	S(8)—C(4)	1·67 (2)
C(3)—N(3)	1·30 (2)	C(4)—N(4)	1·40(2)
N(3)—C(9)	1·53 (2)	N(4)—C(11)	1·43 (3)
N(3)—C(10)	1·52 (2)	N(4)—C(12)	1·50 (3)
S(1)···S(3)	3·678 (7)	S(3)···S(7)	3·556 (7)
S(1)···S(4)	3·639 (6)	S(4)···S(5)	4·263 (7)
S(1)···S(5)	3·774 (6)	S(4)···S(6)	3·138 (8)
S(2)···S(3)	3·638 (6)	S(4)···S(7)	3·463 (7)
S(2)···S(5)	3·486 (7)	S(5)···S(7)	3·599 (8)
S(2)···S(7)	4·107 (7)	S(5)···S(8)	3·499 (8)
S(2)···S(8)	3·284 (7)		

S(1)–Sn—S(2)	70·9 (1)	S(2)–Sn—S(7)	109·0 (2)
S(1)–Sn—S(3)	87·8 (1)	S(3)–Sn—S(4)	68·3 (1)
S(1)–Sn—S(4)	90·8 (1)	S(3)–Sn—S(7)	85·3 (2)
S(1)–Sn—S(5)	95·6 (2)	S(4)–Sn—S(5)	116·4 (2)
S(2)–Sn—S(3)	88·3 (2)	S(4)–Sn—S(7)	86·6 (2)
S(2)–Sn—S(5)	88·2 (2)	S(5)–Sn—S(7)	91·2 (2)
S(1)–C(1)–S(2)	118·6 (8)	S(5)–C(3)–S(6)	120·7 (11)
S(3)–C(2)–S(4)	118·5 (10)	S(7)–C(4)–S(8)	123·6 (10)

monodentate ligands are *cis*. Overall, this geometry is similar to that found for the ethyl analog. Each bidentate ligand shows significantly different Sn–S distances; ligand 1, with Sn–S distances of 2·510 (4) and 2·595 (4) Å, is nearly 'isobidentate', while ligand 2, with corresponding distances of 2·515 (4) and 2·707 (6) Å, is decidedly 'anisobidentate'. The long Sn–S distance contrasts sharply with corresponding distances in $Sn[S_2CN(C_2H_5)_2]_4$ [2·529 (7), 2·554 (7) Å] and is the most unusual feature of the structure. Previously, structures with MS_2X rings showed large differences in M–S distances only when the central atom contained a lone electron pair or when the ligand was bridging (Potenza & Mastropaolo, 1973). In the present structure, these differences may arise from weak intramolecular interactions or from packing distortions. In either case, when compared with $Sn[S_2CN(C_2H_5)_2]_4$, they indicate the extent to which bond distances in the primary coordination sphere can vary when the ligand is a weak donor.

For the monodentate ligands, bonding Sn–S distances are close to that reported for $Sn[S_2CN(C_2H_5)_2]_4$ [2·502 (7) Å] and somewhat longer than the 'normal' Sn–S single bond distance in the four-coordinated complex $(CH_3)_3SnS_2CN(CH_3)_2$ [2·47 (1) Å, Sheldrick & Sheldrick (1970)]. The monodentate Sn···S distances in the present structure [3·439 (6), 3·643 (6) Å] lie between those reported for $Sn[S_2CN(C_2H_5)_2]_4$ (3·89 Å, non-bonding) and $(CH_3)_3SnS_2CN(CH_3)_2$ (3·33, 3·16 Å, weak interaction). Lastly, the S(4)···S(6) and S(2)···S(8) distances, which occur between mono and bidentate ligands, are considerably shorter than a normal van der Waals contact (*ca* 3·7Å) and suggest a weak interaction between the two ligand types. Short S···S distances have also been reported for the ethyl analog as well as for a variety of inorganic and organic (Flippen, 1973) compounds. In the present structure, these distances vary with the angle between the S_2CN ligand planes. The planes of ligands 2 and 3, which contain S(4) and S(6), intersect at 19°, while those of ligands 1 and 4, which contain S(2) and S(8), intersect at 26°. Therefore, it would appear that the short S···S contacts are a consequence of this tendency towards coplanarity. Structural parameters for the dithiocarbamate ligands appear typical.

We thank the Center for Computer and Information Services, Rutgers University, for computer time.

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Acta Cryst. (1976). B**32**, 943

Dichloro-3,4 Isobutyranilide

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(*Reçu le* 19 *novembre* 1975, *accepté le* 20 *novembre* 1975)

Abstract. 3,4-Dichloroisobutyranilide is a weed-killer product with antiandrogenic activity. It crystallizes in the monoclinic system, space group $P2_1/c$; $a=6{\cdot}003$, $b=20{\cdot}023$, $c=9{\cdot}676$ Å, $\beta=110{\cdot}0°$, $Z=4$. The structure was solved by direct methods. The conformation is that expected for such a molecule. The ordering of the crystal is due to hydrogen bonding (2·84 Å) in the **c** direction and to charge transfer in the **b** direction.

Introduction. Le dichloro-3,4 isobutyranilide (RU 21270) (Topliss, Konzelman & Shapiro, 1963) appartient à une famille chimique connue, d'une part pour ses propriétés herbicides (Good, 1961) et d'autre part pour ses propriétés antiandrogènes (Bonne, 1975). L'analyse radiocristallographique d'un représentant de cette famille nous a semblé intéressante en ce sens qu'elle permet d'étudier sa conformation et aussi les possibilités d'interactions moléculaires que sa structure suggère. La formule chimique est représentée sur la Fig. 1.

Le RU 21270 cristallise par lente évaporation d'une solution alcoolique (méthanol ou éthanol) dans le système monoclinique du groupe de symétrie $P2_1/c$. La maille cristalline a été mesurée sur diffractomètre automatique en utilisant la radiation $K\alpha$ du cuivre. Les paramètres sont les suivants: $a=6{,}003$ (5), $b=20{,}023$ (9), $c=9{,}676$ (6) Å, $\beta=110{,}0$ (1)°. 1540 réflexions indépendantes ont été mesurées sur diffractomètre automatique. La structure a été résolue par la méthode de la multisolution en utilisant le programme *MULTAN* (Main, Germain & Woolfson, 1971) appliqué aux 270 réflexions ayant un facteur normalisé supérieur à 1,40. Les sections de densité électronique faites en utilisant les signes de la meilleure des deux solutions étudiées permettent de placer sans difficultés les 14 atomes lourds de la molécule cherchée.

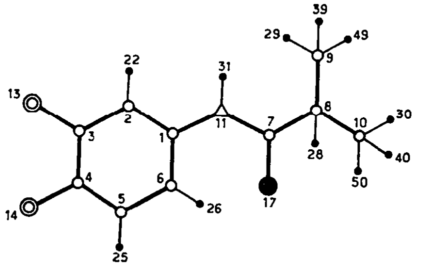

Fig. 1. Dichloro-3,4 isobutyranilide.

Les paramètres atomiques ont alors été affinés par moindres carrés et par blocs diagonaux en attribuant un facteur d'agitation thermique isotrope pour chaque atome. Les atomes d'hydrogène ont été placés sur des sections de différences de densité électronique, une fois le facteur R bloqué à 0,120. L'affinement a alors été poursuivi en utilisant un facteur d'agitation thermique anisotrope pour l'ensemble des atomes lourds. Le facteur R en fin d'affinement est égal à 0,064. Les coordonnées atomiques et les facteurs d'agitation thermique sont indiqués sur les Tableaux 1 et 2.*

Discussion. Les distances interatomiques et angles de valence sont représentés sur la Fig. 2. En général, toutes les valeurs observées ne diffèrent pas de façon significative des valeurs théoriques; on notera toute-

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* La liste des facteurs de structure a été déposée au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 31522: 17 pp., 1 microfiche). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.