References

Brown, P., Mahon, M. F. & Molloy, K. C. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3503–3509.

Enraf–Nonius (1992). *CAD-4/PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Mehrotra, S. K., Srivastava, G. & Mehrotra, R. C. (1974). *J. Organomet. Chem.* **65**, 361-366.

Murphy, D., Sheehan, J. P., Spalding, T. R., Ferguson, G., Lough, A. J. & Gallagher, J. F. (1993). *J. Mater. Chem.* **3**, 1275–1283.

Spek, A. L. (1994). *PLATON. Molecular Geometry Program*. Univ. of Utrecht, The Netherlands.

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Chlorobis(*N*,*N*-diethyldithiocarbamato)-(vinyl)tin(IV)

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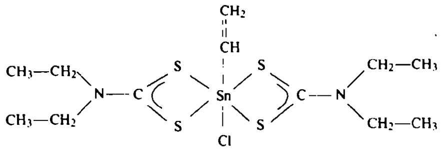
Abstract

The crystal structure of the title compound, $[SnCl(C_2H_3)(C_5H_{10}NS_2)_2]$, consists of relatively isolated complex molecules, the closest intermolecular contact [3.573 (6) Å] being between the methyl C atom C(3) and the S atom S(2) of neighbouring molecules. The Sn atom is hexacoordinated by the vinyl group, the Cl atom and the two bidentate dithiocarbamate ligands, resulting in a distorted octahedral geometry. The vinyl group and Cl atom both occupy *cis* positions with respects to the dithiocarbamate ligands.

Comment

Our current interest in a series of bis-dithiocarbamate (dtc) complexes of tin(IV) arises partly because of the variety of their coordination geometries around the Sn atom and partly because of their biological activity. The coordination geometry depends on the bonding mode (monodentate, bidentate or anisobidentate) of the dtc ligands (Lindley & Carr, 1974; Harrison & Mangia, 1976; Morris & Schlemper, 1979; Lockhart, Manders, Schlemper & Zuckerman, 1986; Jung, Jeong & Sohn, 1990; Vrábel, Lokaj, Kellö, Garaj, Batsanov & Struchkov, 1992). In this paper we report the structure of $[Cl(C_2H_3)Sn(S_2CNEt_2)_2]$, (I). One aim of this work was to further our understanding of the metal–ligand bonds in organotin–dtc complexes.



(I)

Single crystals of (I) were obtained by slow evaporation from a mixture of $CHCl_3$/ethanol at room temperature. The molecular geometry and atom-labeling scheme for the complex are shown in Fig. 1. The Sn^{IV} atom has sixfold coordination, with the two dithiocarbamate ligands, the vinyl group and the Cl atom occupying mutually *cis* positions. The coordination polyhedron around the Sn^{IV} atom may reasonably be described as a distorted tetragonal bipyramid: three S atoms [S(1), S(2), S(4)] and the Cl(1) atom occupy the equatorial plane; the Sn atom is located 0.223 (5) Å above this plane while the atoms S(3) and C(11) are axial. The angle between these axial groups, S(3)—Sn(1)—C(11), is 161.0 (2)°. The two dtc ligands in the present complex show a bidentate bonding mode; however, X-ray studies show that dtc ligands usually act in an anisobidentate manner in organotin(IV)–bis-dtc complexes, except for $[PhSnCl(S_2CNEt_2)_2]$ (Harrison & Mangia, 1976) and $[CH_3OOCCH_2CH_2SnCl(S_2CNMe_2)_2]$ (Jung, Jeong & Sohn, 1990) in which four Sn—S bond distances [Sn—S(1) 2.528 (6), Sn—S(2) 2.661 (7), Sn—S(3) 2.551 (5), Sn—S(4) 2.593 (4);

Sn—S(1) 2.535 (3), Sn—S(2) 2.635 (3), Sn—S(3) 2.540 (3), Sn—S(4) 2.599 (3) Å] are similar to those in the present complex [Sn(1)—S(1) 2.517 (2), Sn(1)—S(2) 2.610 (2), Sn(1)—S(3) 2.541 (4), Sn(1)—S(4) 2.569 (2) Å].

The crystal structure of (I) consists of relatively isolated molecules, all intermolecular distances being longer than 3.55 Å. The interplanar angle between the two dtc ligands is 88.7 (2)°.

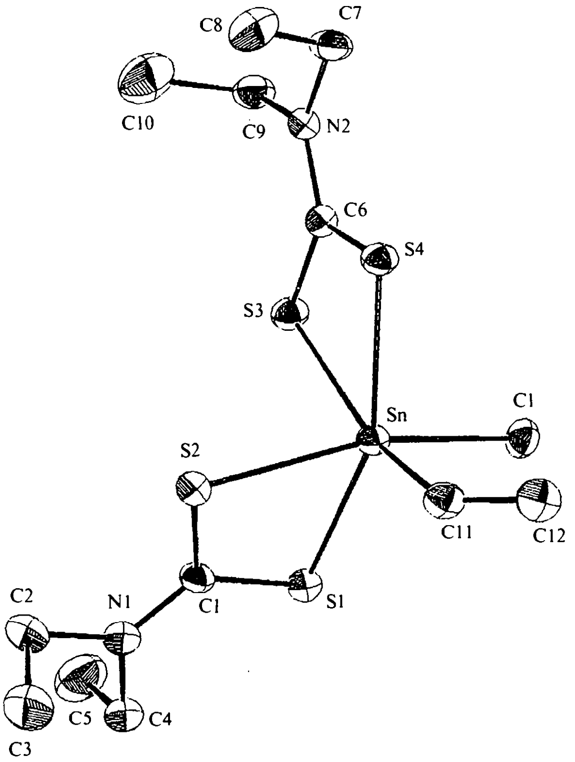


Fig. 1. Perspective view of the title molecule with atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

Crystal data

$[SnCl(C_2H_3)(C_5H_{10}NS_2)_2]$
$M_r = 477.71$
Triclinic
$P\bar{1}$
$a = 7.082\ (10)$ Å
$b = 10.065\ (8)$ Å
$c = 14.559\ (10)$ Å
$\alpha = 96.03\ (6)°$
$\beta = 94.13\ (9)°$
$\gamma = 107.59\ (9)°$
$V = 978\ (2)$ Å^3
$Z = 2$
$D_x = 1.62$ Mg m^{-3}
$D_m = 1.64\ (3)$ Mg m^{-3}
D_m measured by flotation in $ZnSO_4$ solution

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 3$–$14°$
$\mu = 1.85$ mm^{-1}
$T = 293$ K
Prismatic
0.2 × 0.2 × 0.1 mm
Colourless

Data collection

$XP2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4694 measured reflections
4515 independent reflections
3078 observed reflections [$I > 1.96\sigma(I)$]
$R_{int} = 0.012$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 98 reflections
intensity variation: <5%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.046$
$S = 0.93$
3078 reflections
181 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + (0.02F_o)^2]$

$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Sn(1)	0.07713 (3)	0.26090 (2)	0.24037 (1)	3.82 (1)
Cl(1)	0.11691 (12)	0.09551 (7)	0.34379 (5)	5.04 (3)
S(1)	0.20396 (11)	0.13253 (7)	0.11334 (5)	4.30 (2)
S(2)	0.10054 (13)	0.38878 (8)	0.09266 (5)	4.78 (2)
S(3)	0.42934 (10)	0.41847 (7)	0.29727 (5)	4.30 (2)
S(4)	0.06994 (11)	0.46720 (7)	0.35851 (5)	4.38 (2)
N(1)	0.2443 (4)	0.2558 (3)	−0.0376 (2)	4.99 (7)
N(2)	0.4349 (3)	0.6246 (2)	0.4274 (1)	4.03 (6)
C(1)	0.1882 (4)	0.2594 (3)	0.0455 (2)	4.17 (8)
C(2)	0.2354 (5)	0.3637 (4)	−0.0979 (2)	6.88 (15)
C(3)	0.0592 (7)	0.3144 (5)	−0.1606 (3)	8.54 (17)
C(4)	0.3212 (5)	0.1463 (3)	−0.0783 (2)	5.47 (11)
C(5)	0.5402 (6)	0.1871 (5)	−0.0631 (3)	8.28 (16)
C(6)	0.3217 (4)	0.5170 (3)	0.3673 (2)	3.74 (7)
C(7)	0.3438 (5)	0.7094 (3)	0.4875 (2)	5.54 (10)
C(8)	0.2973 (5)	0.8211 (4)	0.4424 (3)	7.82 (15)
C(9)	0.6529 (5)	0.6672 (3)	0.4348 (2)	5.37 (10)
C(10)	0.7381 (6)	0.7788 (5)	0.3803 (4)	9.01 (17)
C(11)	−0.2392 (4)	0.1839 (3)	0.2193 (2)	5.04 (9)
C(12)	−0.3502 (5)	0.1086 (4)	0.2718 (3)	6.25 (12)

Table 2. *Selected geometric parameters* (Å, °)

Sn(1)—Cl(1)	2.422 (2)	N(1)—C(2)	1.479 (5)
Sn(1)—S(1)	2.517 (2)	N(1)—C(4)	1.461 (5)
Sn(1)—S(2)	2.610 (2)	N(2)—C(6)	1.326 (3)
Sn(1)—S(3)	2.541 (4)	N(2)—C(7)	1.472 (5)
Sn(1)—S(4)	2.569 (2)	N(2)—C(9)	1.465 (5)
Sn(1)—C(11)	2.125 (4)	C(11)—C(12)	1.274 (5)
N(1)—C(1)	1.302 (4)		
S(4)—Sn(1)—C(11)	91.5 (2)	Cl(1)—Sn(1)—S(4)	100.6 (1)
S(3)—Sn(1)—C(11)	161.0 (2)	Cl(1)—Sn(1)—S(3)	89.7 (1)
S(3)—Sn(1)—S(4)	69.6 (2)	Cl(1)—Sn(1)—S(2)	159.3 (2)
S(2)—Sn(1)—C(11)	92.9 (2)	Cl(1)—Sn(1)—S(1)	90.0 (1)
S(2)—Sn(1)—S(4)	97.8 (1)	S(2)—C(1)—N(1)	122.5 (4)
S(2)—Sn(1)—S(3)	87.9 (1)	S(1)—C(1)—N(1)	120.3 (4)
S(1)—Sn(1)—C(11)	107.2 (2)	S(1)—C(1)—S(2)	117.3 (2)
S(1)—Sn(1)—S(4)	157.5 (2)	S(4)—C(6)—N(2)	122.3 (4)
S(1)—Sn(1)—S(3)	90.9 (2)	S(3)—C(6)—N(2)	120.2 (5)
S(1)—Sn(1)—S(2)	69.5 (1)	S(3)—C(6)—S(4)	117.5 (3)
Cl(1)—Sn(1)—C(11)	96.1 (2)		

Data reduction was performed with the *XP*2_1 program (Pavelčík, 1987). The structure was solved by the Patterson method and refined by block-diagonal least-squares methods. H atoms were placed at calculated positions and their coordinates and displacement parameters were fixed. Calculations were performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *J. Appl. Cryst.* **6**, 309–346.
Harrison, P. G. & Mangia, A. (1976). *J. Organomet. Chem.* **120**, 211–216.
Jung, O. S., Jeong, J. H. & Sohn, Y. S. (1990). *Acta Cryst.* C**46**, 31–33.
Lindley, P. F. & Carr, P. (1974). *J. Cryst. Mol. Struct.* **4**, 173–185.
Lockhart, T. P., Manders, W. F., Schlemper, E. O. & Zuckerman, J. J. (1986). *J. Am. Chem. Soc.* **108**, 4074–4078.
Morris, J. S. & Schlemper, E. O. (1979). *J. Cryst. Mol. Struct.* **9**, 13–31.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Pavelčík, F. (1987). *XP*2_1. Comenius Univ., Bratislava, Slovakia.
Vrábel, V., Lokaj, J., Kellö, E., Garaj, J., Batsanov, A. C. & Struchkov, Yu. T. (1992). *Acta Cryst.* C**48**, 633–635.

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2,4′-Bithiazole and Bis(2,4′-bithiazole)bis(dimethyl sulfoxide)copper(II) Diperchlorate

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Abstract

The synthesis and crystal structure of 2,4′-bithiazole, $C_6H_4N_2S_2$ (I), and its copper complex $[Cu(C_6H_4N_2S_2)_2(C_2H_6OS)_2](ClO_4)_2$ (II) are presented. The bithiazole molecules are planar in both compounds. The 2,4′-bithiazole (I) molecule is located on a symmetry center and the structure was solved by the introduction of disorder between the S atom and its neighbour S/C2, which caused a small deviation in the S—C and C—C bond distances. Other bond distances and angles are as expected. In the copper complex (II), the Cu atom is hexacoordinated and the 2,4′-bithiazole moiety again presents statistical disorder giving the ligand a local mirror symmetry.

Comment

2,4′-Bithiazole was isolated for the first time by Erlenmeyer, Weber, Schmidt, Kung, Zinsstay & Prijs (1948) from a Hantzsch cyclization. This molecule is of great interest because it is the chromophoric group of bleomycine which causes the degradation of DNA in a process that requires iron(II) and dioxygen (Riordan & Sakai, 1981; Zeen-Cheen & Cheng, 1970; Riordan, Glickson & Sakai, 1982; Aogagi, Suguna, Murugesa, Ehernfeld, Chang, Ohgi, Shekhani, Kirkup & Hecht, 1982; Levin, Subrahananion, Katz, Smith, Burlett & Hecht, 1980). In fact, it is only derivatives of 2,4′-bithiazole that have been studied by X-ray diffraction (Trowitzsch, Höfle & Sheldrick, 1981; Koyama, Nakamura, Muraoku, Takita, Maeda & Umezawa, 1968). More recently, π-accepting ligands such as bithiazole have been of considerable interest because they tend to stabilize a particular electronic configuration of the associated metal (Cu, Rh, Ni, Pd). This interaction generates metal–ligand excited transfer states which can be studied through their photoluminescent properties (Krause, Krause & Lamtruong, 1988). We prepared 2,4′-bithiazole as a model compound in order to obtain precise intercycle geometric parameters for comparison with extended Hückel theory (Hoffmann, 1963) and molecular-mechanics calculations previously carried out on this compound (Baudrion, 1992).

For compound (I), the helicoidal 2_1 axis is determined by four non-observed reflections; $0k0$, $k = 1, 3, 5$ and 7. Refinement in the non-centrosymmetric space group Pc gives rise to a molecular inversion center; therefore, the structure has been solved in space group $P2_1/c$.

2,4′-Bithiazole, which does have an inversion center, is located on the crystallographic symmetry center $\frac{1}{2}$,0,0, and because of this it is not possible to distinguish between positions 1 and 5 of the heterocycle. The structure has been solved by considering S/C $[\frac{1}{2}(S + C)]$ as a hybrid atom on these positions. In other words, the crystal structure can be considered to be the result of the packing of two molecules *A*