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cis-Dichlorobis(*N*,*N*-diethyldithiocarbamato-*S*,*S'*)tin(IV)

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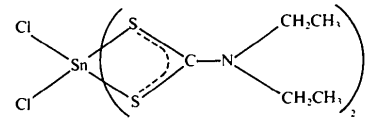
Abstract

The structural features of the title complex, $[SnCl_2(C_5H_{10}NS_2)_2]$, are significantly different to those of the complexes $Me_2Sn(S_2CNR_2)_2$ that have been structurally characterized so far. In the title complex the geometry around the Sn atom is *cis*-octahedral with a Cl—Sn—Cl angle of 91.85 (3)° and an average Sn—Cl bond length of 2.404 (7) Å. Both dithiocarbamato groups behave as bidentate chelating ligands with an average Sn—S bond length of 2.539 (6) Å and an average S—Sn—S bond angle of 71.01 (2)°.

Comment

Crystallographic studies of dithiocarbamato complexes of diorganotin(IV) species $R_2Sn(S_2CNR_2)_2$ have revealed a variety of coordination geometries about the Sn atom, ranging from tetrahedral to distorted octahedral, as well as dithiocarbamato ligands that are either bidentate or monodentate (Fuzue, Kimura, Yasuoka, Kasai & Kakudo, 1970; Kimura, Yasuoka, Kasai & Kakudo, 1972; Sheldrick & Sheldrick, 1970). In the crystal structure of $[(Et_2NCS_2)_2\overline{Sn\{O—C(CH_3)=C(S)}—C(O)—CH_3\}]$, a novel mixed-ligand complex of tin(IV) (Sharma, Bohra & Mehrotra, 1993), both dithiocarbamato ligands are essentially bidentate [average Sn—S bond length 2.547 (4) Å].

The metal environment in the title compound $[Cl_2Sn(S_2CNEt_2)_2]$, (I), differs from that in $Me_2Sn(S_2CNEt_2)_2$ (Lockhart, Manders, Schlemper & Zuckerman, 1986) in having methyl groups replaced by more electronegative chloro groups. This results in a significant change in coordination geometry from distorted *trans*-octahedral in $Me_2Sn(S_2CNEt_2)_2$ to *cis*-octahedral in $Cl_2Sn(S_2CNEt_2)_2$. The structural features of $Cl_2Sn(S_2CNEt_2)_2$ are also significantly different from those of the dimethyltin bis(dithiocarbamates) $Me_2Sn(S_2CNEt_2)_2$ (Lockhart *et al.*, 1986), $Me_2Sn\{S_2CN(CH_2)_4\}_2$ (Lockhart, Manders & Schlemper, 1985) and $Me_2Sn(S_2CNMe_2)_2$ (Kimura *et al.*, 1972) that have been structurally characterized so far. The dithiocarbamato ligands in $Me_2Sn(S_2CNEt_2)_2$ are bidentate, chelating to Sn with one long and one short Sn—S bond [average lengths 2.996 (3) and 2.502 (13) Å, respectively]. However, in the case of $Cl_2Sn(S_2CNEt_2)_2$, the dithiocarbamato moieties behave as symmetrical chelating ligands, with one Sn—S bond only slightly longer than the other [average lengths 2.572 (1) and 2.507 (5) Å]. The slightly longer Sn—S bond in the title compound is considerably shorter than the long Sn—S bonds [average length 2.996 (3) Å] reported for $Me_2Sn(S_2CNEt_2)_2$, indicating the electronic influence of the Cl atoms on the Sn—S bond lengths. The dithiocarbamato S and C atoms are coplanar with Sn but the geometry of the chelation is highly distorted from the square-planar geometry (the S—Sn—S angles range from 70.9 to 160.4°) reported earlier for a number of dimethyltin(IV) dithiocarbamates.


(I)

It has been reported that the coordination geometry in dimethyltin(IV) dithiocarbamates is badly distorted from octahedral. The Me—Sn—Me angle in $Me_2Sn\{S_2CN(CH_2)_4\}_2$ (137.3°) is intermediate between *cis* and *trans* (Lockhart *et al.*, 1985) and is quite similar to that in $Me_2Sn(S_2CNMe_2)_2$ (136°) (Kimura *et al.*, 1972). Unlike the above, the Cl—Sn—Cl angle of 91.85 (3)° in $Cl_2Sn(S_2CNEt_2)_2$ indicates an only slightly distorted *cis*-octahedral

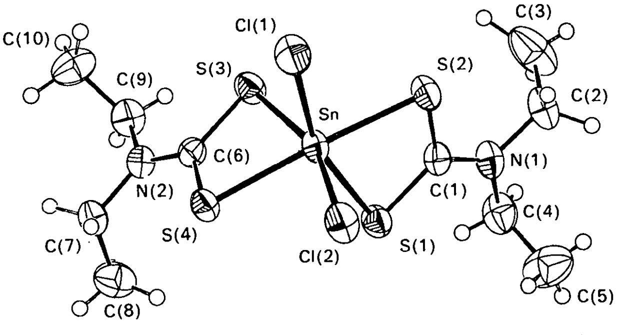


Fig. 1. A *PLATON* (Spek, 1990) plot of the title complex. Displacement ellipsoids are shown at the 50% probability level.

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coordination around Sn. It appears that both electronic and steric factors are responsible for this distortion away from the regular octahedral geometry. The crystal packing appears to be governed by normal van der Waals interactions and weak hydrogen bonding between the Cl atoms and the C atoms of the terminal methyl groups.

Experimental

Dichlorobis(*N*,*N*-diethyldithiocarbamato-*S*,*S*′)tin(IV) was prepared by the method described by Srivastava & Bhargava (1978). Single crystals suitable for X-ray crystallographic work were obtained by recrystallization from a mixture of dichloromethane and *n*-hexane.

Crystal data

$[SnCl_2(C_5H_{10}NS_2)_2]$
$M_r = 486.14$
Triclinic
$P\bar{1}$
$a = 7.169$ (4) Å
$b = 9.244$ (2) Å
$c = 15.308$ (2) Å
$\alpha = 93.79$ (1)°
$\beta = 99.10$ (3)°
$\gamma = 109.53$ (3)°
$V = 936.3$ (6) Å^3
$Z = 2$
$D_x = 1.724$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6$–12°
$\mu = 2.076$ mm^{-1}
$T = 295$ K
Plate
0.35 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.86$, $T_{max} = 0.99$
3282 measured reflections
3282 independent reflections
3018 observed reflections $[|F^2| > 3\sigma(F^2)]$

$\theta_{max} = 25°$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$
2 standard reflections
frequency: 30 min
intensity variation: none

Refinement

Refinement on F
$R = 0.018$
$wR = 0.031$
$S = 0.94$
3018 reflections
252 parameters
All H-atom parameters refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.33$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SDP* (Enraf–Nonius, 1983)

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

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

	x	y	z	B_{eq}
Sn	0.25558 (2)	0.23800 (2)	0.24942 (1)	2.780 (3)
Cl(1)	0.55747 (9)	0.26432 (9)	0.19282 (4)	4.57 (1)
Cl(2)	0.2720 (1)	0.49411 (7)	0.21986 (5)	4.41 (1)
S(1)	0.01906 (8)	0.22995 (7)	0.36049 (4)	3.48 (1)
S(2)	0.45409 (8)	0.28222 (7)	0.40553 (4)	3.52 (1)
S(3)	0.14705 (8)	−0.05869 (6)	0.23329 (4)	3.38 (1)
S(4)	−0.02515 (8)	0.12578 (6)	0.11723 (4)	3.13 (1)
N(1)	0.2176 (3)	0.2491 (2)	0.5266 (1)	3.47 (4)
N(2)	−0.1880 (3)	−0.1811 (2)	0.1087 (1)	2.88 (4)
C(1)	0.2277 (3)	0.2532 (2)	0.4414 (1)	2.91 (4)
C(2)	0.3983 (4)	0.2771 (3)	0.5961 (2)	4.19 (6)
C(3)	0.4305 (5)	0.1315 (4)	0.6183 (3)	7.28 (9)
C(4)	0.0273 (4)	0.2189 (3)	0.5597 (2)	4.42 (6)
C(5)	0.0045 (5)	0.3648 (4)	0.5967 (2)	6.82 (8)
C(6)	−0.0398 (3)	−0.0545 (2)	0.1481 (1)	2.72 (4)
C(7)	−0.3505 (3)	−0.1770 (3)	0.0387 (2)	3.51 (5)
C(8)	−0.5240 (4)	−0.1611 (3)	0.0764 (2)	4.88 (7)
C(9)	−0.2045 (4)	−0.3359 (3)	0.1324 (2)	3.69 (5)
C(10)	−0.1333 (4)	−0.4241 (3)	0.0671 (2)	5.22 (7)

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

Sn—Cl(1)	2.4005 (7)	N(1)—C(1)	1.320 (4)
Sn—Cl(2)	2.4075 (7)	N(1)—C(2)	1.476 (3)
Sn—S(1)	2.5720 (7)	N(1)—C(4)	1.476 (4)
Sn—S(2)	2.5118 (6)	N(2)—C(6)	1.317 (2)
Sn—S(3)	2.5714 (6)	N(2)—C(7)	1.465 (3)
Sn—S(4)	2.5021 (5)	N(2)—C(9)	1.470 (3)
S(1)—C(1)	1.726 (2)	C(2)—C(3)	1.492 (6)
S(2)—C(1)	1.737 (2)	C(4)—C(5)	1.499 (6)
S(3)—C(6)	1.728 (2)	C(7)—C(8)	1.498 (4)
S(4)—C(6)	1.736 (2)	C(9)—C(10)	1.502 (4)
Cl(1)—Sn—Cl(2)	91.85 (3)	Sn—S(4)—C(6)	86.75 (6)
Cl(1)—Sn—S(1)	160.35 (2)	C(1)—N(1)—C(2)	122.0 (2)
Cl(1)—Sn—S(2)	89.43 (2)	C(1)—N(1)—C(4)	122.9 (2)
Cl(1)—Sn—S(3)	92.47 (2)	C(2)—N(1)—C(4)	115.1 (2)
Cl(1)—Sn—S(4)	104.96 (2)	C(6)—N(2)—C(7)	122.0 (2)
Cl(2)—Sn—S(1)	92.05 (2)	C(6)—N(2)—C(9)	122.9 (2)
Cl(2)—Sn—S(2)	103.31 (2)	C(7)—N(2)—C(9)	115.2 (2)
Cl(2)—Sn—S(3)	160.74 (3)	S(1)—C(1)—S(2)	116.8 (1)
Cl(2)—Sn—S(4)	89.67 (3)	S(1)—C(1)—N(1)	122.1 (2)
S(1)—Sn—S(2)	70.93 (2)	S(2)—C(1)—N(1)	121.0 (2)
S(1)—Sn—S(3)	90.18 (3)	N(1)—C(2)—C(3)	112.9 (3)
S(1)—Sn—S(4)	94.31 (2)	N(1)—C(4)—C(5)	112.2 (2)
S(2)—Sn—S(3)	95.50 (3)	S(3)—C(6)—S(4)	116.8 (1)
S(2)—Sn—S(4)	160.41 (2)	S(3)—C(6)—N(2)	122.1 (2)
S(3)—Sn—S(4)	71.09 (2)	S(4)—C(6)—N(2)	121.2 (2)
Sn—S(1)—C(1)	85.13 (8)	N(2)—C(7)—C(8)	111.8 (2)
Sn—S(2)—C(1)	86.82 (7)	N(2)—C(9)—C(10)	112.1 (2)
Sn—S(3)—C(6)	84.72 (7)		

An empirical absorption correction was applied to the data by measuring the intensities of four reflections with χ close to 90° for different values of ψ ($0<\psi<360°$ in steps of 10°) and using the program *EAC* from *SDP* (Enraf–Nonius, 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: NA1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Salophene–Uranium–Water Complex

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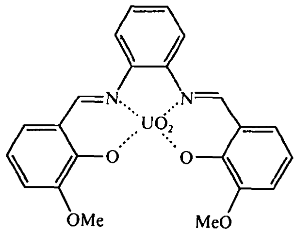
Abstract

In dioxo{2,2′-[1,2-phenylenebis(nitrilomethylidyne)]-bis(6-methoxyphenolato)(2−)-*N*,*N*′,*O*,*O*′}uranium–water (2/3), $2[UO_2(C_{22}H_{18}N_2O_4)].3H_2O$, the two independent uranium cations have pentagonal bipyramidal coordination.

Comment

Normally, metal cations (Cu^{2+}, Ni^{2+}, Pd^{2+}, Zn^{2+}) in a salophene moiety have square-planar coordination (Holm & O'Connor, 1971; van Staveren, van Eerden, van Veggel, Harkema & Reinhoudt, 1988). As a result of the large radius of the uranium cation, the salophene moiety in the title compound (I) is distorted and pentagonal bipyramidal coordination is found. The bowl-like shape of the salophene moiety is also found in related solid-state structures with angles of the adjacent aromatic rings (50.8–53.0° and 50.2–52.6°) comparable to those reported previously (van Staveren, van Eerden, van Veggel, Harkema & Reinhoudt, 1988; van Doorn, Bos, Harkema, van Eerden, Verboom & Reinhoudt, 1991; van Doorn, Schaafstra, Bos, Harkema, van Eerden, Verboom & Reinhoudt, 1991). The water molecule at the fifth coordination site can be exchanged for other neutral molecules, which is of critical importance for molecular recognition by metalloreceptors.



(I)

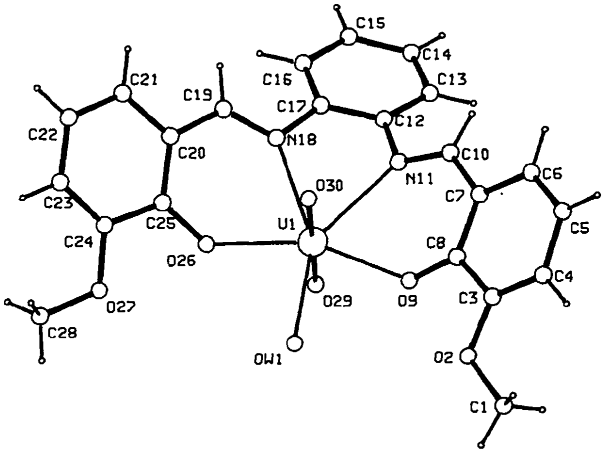


Fig. 1. View of the title complex including the atom numbering. The numbering of the second independent molecule is obtained by adding 30 to the numbers given.

Experimental

The title complex was synthesized according to the procedures of van Doorn, Bos, Harkema, van Eerden, Verboom & Reinhoudt (1991), to investigate its structure and coordination. A crystal suitable for X-ray analysis was obtained by slow evaporation of the solvent from a solution in $CHCl_3$.

Crystal data

$2[UO_2(C_{22}H_{18}N_2O_4)].3H_2O$
$M_r = 1342.9$
Triclinic
$P\bar{1}$
$a = 12.056\ (6)$ Å
$b = 12.293\ (5)$ Å
$c = 15.843\ (6)$ Å
$\alpha = 84.01\ (4)°$
$\beta = 74.91\ (6)°$
$\gamma = 86.29\ (5)°$
$V = 2253\ (2)$ Å^3
$Z = 2$
$D_x = 1.98$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 23 reflections
$\theta = 6$–$12°$
$\mu = 6.88$ mm^{-1}
$T = 293$ K
Parallelepiped
0.7 × 0.4 × 0.1 mm
Orange