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A seven-coordinated tin(IV) complex: dichloro[2,6-diacetylpyridine bis(*S*-benzyl-dithiocarbazato-κ^5S,N,N',N'',S']tin(IV)

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.058
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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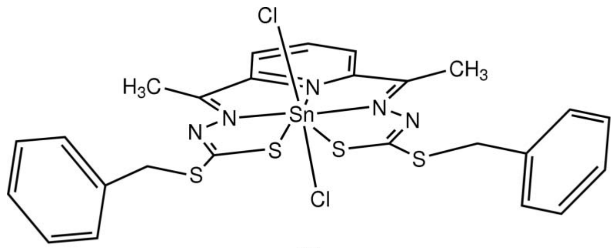
The pentadentate ligand 2,6-diacetypyridine bis(*S*-benzyl-dithiocarbazate) reacts with $SnCl_2 \cdot 2H_2O$ and atmospheric O_2 to form a seven-coordinated Sn^{IV} complex. The asymmetric unit of the title compound, $[Sn(C_{25}H_{23}N_5S_4)Cl_2]$, consists of one half-molecule. One Cl, Sn, N of the pyridine ring and the *para*-C,H atoms lie on a twofold axis. The Sn^{IV} ion is seven-coordinated with a distorted pentadentate bipyramidal geometry. The dithiocarbazate ligand coordinates as a dianionic pentagonal ligand through the pyridine N atom, the two imine N atoms and the two thiocarbazate S atoms, forming the pentagonal plane; the two chloride ions are in axial positions. The complex was also characterized by ^{119}Sn Mössbauer and IR spectroscopies.

Comment

The title complex, (I), was synthesized as part of a research program devoted to the study of the coordination modes of *X*,*N*,*N*,*N*,*X*-pentadentate (*X* = O and S) Schiff bases derived from bis(semicarbazones) and bis(thiosemicarbazones), that we are now extending to bis(dithiocarbazates), with organotin(IV) derivatives of the type $SnCl_2Me_2$, $SnCl_3Me$, $SnCl_2nBu_2$ and $SnCl_2Ph_2$ (Sousa *et al.*, 1994, 1999, 2000, 2002, 2003).



(I)

In an attempt to obtain Sn^{II} compounds analogous to those of Sn^{IV}, we performed the reaction between $SnCl_2 \cdot 2H_2O$ and

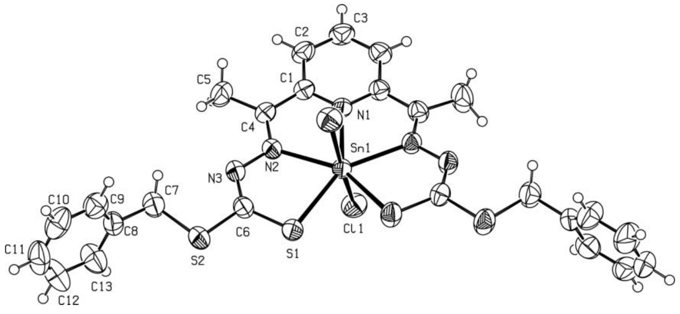


Figure 1
View of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary radius. Unlabelled atoms are related to the labelled atoms by the symmetry code $(-x + 2, y, -z + \frac{1}{2})$.

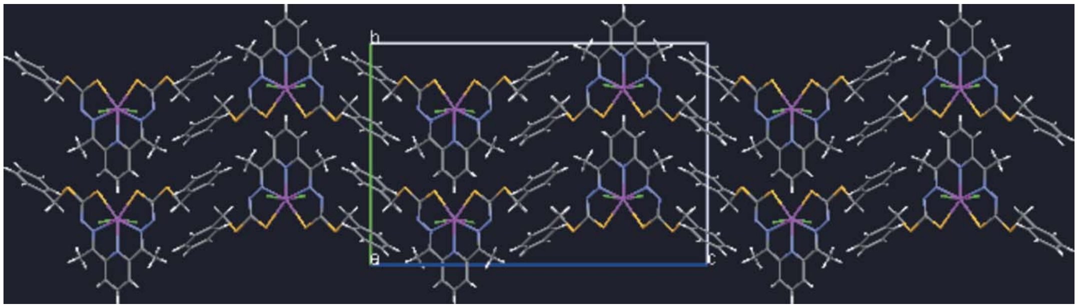


Figure 2
A molecular packing diagram of (I).

2,6-diacetypyridine bis(*S*-benzyldithiocarbazate) in MeOH under aerobic conditions. The title complex was synthesized *via* oxidation of the Sn^{II} to Sn^{IV}, due to the presence of atmospheric O_2 in the solution. The formation of Sn^{IV} complexes from Sn^{II} halides is not uncommon; thus, the reaction of Sn^{II} with a range of ligands in the presence of air had been reported to produce Sn^{IV} derivatives (Selvaraju & Panchanatheswaran, 1997).

IR spectroscopy of the free ligand and the complex revealed (*a*) the disappearance of the ν(N—H) absorption at 3170 cm^{-1} as a consequence of the double deprotonation of the N2 atoms of 2,6-diacetypyridine bis(*S*-benzyldithiocarbazate); (*b*) the ν(C=N) absorptions bands at 1640, 1598 and 1569 cm^{-1}, found in the free ligand, are shifted to 1600, 1569 and 1533 cm^{-1}, respectively, confirming *N*,*N*′,*N*″-coordination (Sousa et al., 1999); (*c*) the ν(N—N) band of the free ligand at 1103 cm^{-1} is shifted to higher wavenumbers, 1131 cm^{-1}, supporting coordination of the ligand *via* the azomethine N atoms (Akbar *et al.*, 2001; Selvaraju & Panchanatheswaran, 1997); (*d*) the appearance of a band with ν_a(S—C—S) character at 997 cm^{-1} in the spectrum of the complex, suggests S-coordination *via* the thiolate form (Akbar *et al.*, 2001).

In the Mössbauer spectrum of (I), the isomer shift (δ) and the quadrupole splitting (Δ) values are 0.60 and 0.47 mm s^{-1}, respectively; they are lower than the values observed in the parent acid $SnCl_2$.2 H_2O, where δ = 4.06 (2) and Δ = 0.66 (4) mm s^{-1} (Birchall *et al.*, 1971). Similar values were reported in related complexes with analogous coordination geometry, namely [$SnCl_2$(Hdaptsc)]Cl [where Hdaptsc is 2,6-diacetylpyridine bis(thiosemicarbazone)], δ = 0.61 and Δ = 0.66 mm s^{-1} (Sousa *et al.*, 1994).

The asymmetric unit of (I) consists of one half-molecule, with atoms Cl1, Sn1, N1, C3 and H3 lying on a twofold rotation axis. The geometry around Sn^{IV} can be described as distorted pentagonal bipyramidal (Table 1). The dithiocarbazate ligand coordinates as an S,*N*,*N*′,*N*″,*S*′-pentadentate ligand, occupying equatorial positions, while two chloride ions occupy axial positions (Fig. 1). The phenyl rings deviate by 77.9 (1)° from the mean plane of the rest of the heavy atoms of the ligand.

The Sn—S, Sn—N1 and Sn—N2 bond distances in (I) are very similar to those found in the Sn^{II} compound [$Sn(C_{13}H_{17}N_7S_2)(CH_3OH)_2$]·$CH_3OH$ (Bermejo *et al.*, 2004) [$C_{13}H_{19}N_7S_2$ = 2,6-diacetypyridine bis(4-*N*-methilthiosemicarbazone); where Sn—S = 2.554 (5) and 2.567 (6) Å, Sn—*N*(pyridine) = 2.24 (2) Å, and Sn—N = 2.31 (2) and 2.35 (2) Å]. The two Sn—Cl distances are longer than those found in [$SnCl_2(C_{11}H_{15}N_7O_2)$]$Cl_2$·$2H_2O$ (Sommerer & Palenik, 1991) [$C_{11}H_{15}N_7O_2$ = 2,6-diacetylpyridine bis(semicarbazone); 2.354 (2) and 2.368 (2) Å]. However, the Cl—Sn—Cl bond angle in (I) is smaller than that found in [$SnCl_2(C_{11}H_{15}N_7O_2)$]$Cl_2$·$2H_2O$ [176.94 (8)°], indicating that (I) is more distorted.

The molecules pack as shown in Fig. 2, involving π–π interactions between the phenyl rings of adjacent molecules (symmetry code: $1 - x, \frac{1}{2} - y, 1 - z$), (distance between centroids = 4.10 Å and perpendicular distance = 3.53 Å).

Experimental

The ligand 2,6-diacetylpyridine bis(*S*-benzyldithiocarbazate) was synthesized according to the literature procedure of Akbar *et al.* (2001). To prepare (I), the ligand (0.20 mmol) was dissolved in MeOH (10 ml) and refluxed for 5 min. $SnCl_2$·$2H_2O$ (0.21 mmol) dissolved in the same solvent was then added and the resulting solution heated under reflux for a further hour. After cooling the solution and slow evaporation of the solvent, yellow crystals were obtained (yield 70%, m.p. > 543 K).

Crystal data

[$Sn(C_{25}H_{23}N_5S_4)Cl_2$]
M_r = 711.31
Monoclinic, $C2/c$
a = 7.6309 (5) Å
b = 15.724 (1) Å
c = 23.972 (2) Å
β = 93.235 (1)°
V = 2871.7 (3) Å^3
Z = 4

D_x = 1.645 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5552 reflections
θ = 2.6–30.9°
μ = 1.39 mm^{-1}
T = 291 (2) K
Prism, orange
0.29 × 0.14 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: analytical (*SHELXTL/PC*; Sheldrick 1997b)
T_{min} = 0.709, T_{max} = 0.947
11652 measured reflections

2541 independent reflections
2120 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.0°
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.059
S = 0.94
2541 reflections
170 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.020
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Sn1—N1	2.274 (3)	S2—C7	1.813 (3)
Sn1—N2	2.327 (2)	N1—C1	1.340 (3)
Sn1—Cl1	2.4070 (8)	N2—C4	1.285 (4)
Sn1—S1	2.5528 (8)	N2—N3	1.378 (3)
S1—C6	1.715 (3)	N3—C6	1.299 (4)
S2—C6	1.745 (3)		
N1—Sn1—N2	68.65 (6)	Cl1^{i}—Sn1—S1^{i}	90.30 (3)
N2^{i}—Sn1—N2	137.31 (12)	S1—Sn1—S1^{i}	76.64 (4)
N2^{i}—Sn1—Cl1^{i}	92.58 (6)	C6—S2—C7	102.85 (15)
N2—Sn1—Cl1^{i}	83.51 (6)	C1—N1—Sn1	119.85 (17)
N1—Sn1—Cl1	84.63 (2)	C4—N2—N3	115.8 (3)
N2—Sn1—Cl1	92.58 (6)	C6—N3—N2	114.0 (2)
Cl1^{i}—Sn1—Cl1	169.26 (4)	N1—C1—C4	115.4 (3)
N1—Sn1—S1	141.68 (2)	N2—C4—C1	115.5 (3)
N2^{i}—Sn1—S1	148.44 (6)	N3—C6—S2	117.3 (2)
N2—Sn1—S1	73.69 (6)	S1—C6—S2	114.01 (18)
Cl1^{i}—Sn1—S1	98.14 (3)	C8—C7—S2	108.6 (2)
Cl1—Sn1—S1	90.30 (3)		

Symmetry code: (i) $-x+2, y, -z+\frac{1}{2}$.

H atoms were located in a difference Fourier map and refined as riding [C—H = 0.93 or 0.96 Å and $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$].

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *MERCURY* (Bruno *et al.*, 2002) and *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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