Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1386). Services for accessing these data are described at the back of the journal.

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Bis{[2,6-diacetylpyridine bis(2-furoylhydrazone)(1−)]dimethyltin(IV)} *trans*-Tetrachlorodimethylstannate(IV)

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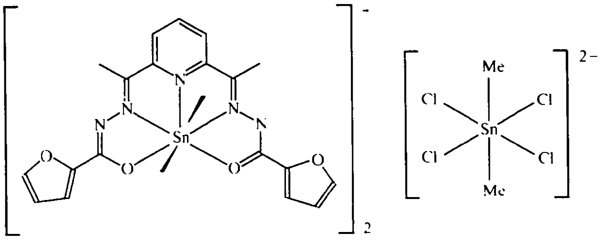
Abstract

The structure of the title compound, $[Sn(CH_3)_2(C_{19}H_{16}N_5O_4)]_2[SnCl_4(CH_3)_2]$, revealed the presence of two complexes. One is monocationic and consists of a heptacoordinated Sn^{IV} atom in a distorted pentagonal-bipyramidal geometry, with an aroylhydrazone ligand acting as a pentadentate species in the equatorial plane and two methyl groups in axial positions. The other complex is dianionic and has a hexacoordinated Sn^{IV} atom at the origin.

Comment

The chelating properties of 2,6-diacetylpyridine bis(aroylhydrazone)s (aroyl is benzoyl, picolinoyl, salicyloyl, thenoyl or aminobenzoyl) have been investigated and only one complexation mode has been found, *i.e.* with the aroylhydrazone ligands acting as pentadentate molecules and coordinating through the two enolate O, the two azomethine N and the pyridyl N atoms (Pelizzi *et al.*, 1984; Carini *et al.*, 1989).

The structure determination of bis{[2,6-diacetylpyridine bis(2-furoylhydrazone)(1−)]dimethyltin(IV)} *trans*-tetrachlorodimethylstannate(IV), (I), revealed the occurrence of two monocationic complexes surrounding a dianionic one, as shown in Fig. 1.



(I)

In the cation, $[Me_2Sn(Hdapf)]^+$, where Hdapf is 2,6-diacetylpyridine bis(2-furoylhydrazone), the ligand in the equatorial plane of the coordination polyhedron is planar, except for the furan groups, which have a dihedral angle of 24.7 (3)° between them. One furan ring (C15–C18, O3) makes a dihedral angle of 21.7 (3)° with the equatorial plane and an angle of 5.5 (3)° with the other furan ring (C19–C22, O4). Both furan rings have atoms with high displacement parameters, especially the C21, C22 and O4 atoms. The presence of a disorder effect in these atoms was investigated, but the calculations did not show any significant improvement of the model.

A selection of bond distances and angles are given in Table 1. Differences can be observed between the bond parameters in both arms of the ligand. The discrepancies in the distances were found in the pairs Sn2—O1/Sn2—O2 and Sn2—N2/Sn2—N4. The pairs of discrepant angles are O1—Sn2—N2/O2—Sn2—N4 and N2—Sn2—N3/N4—Sn2—N3. These differences occur because during the complexation process, the azomethine N1 atom loses its proton and the azomethine N5

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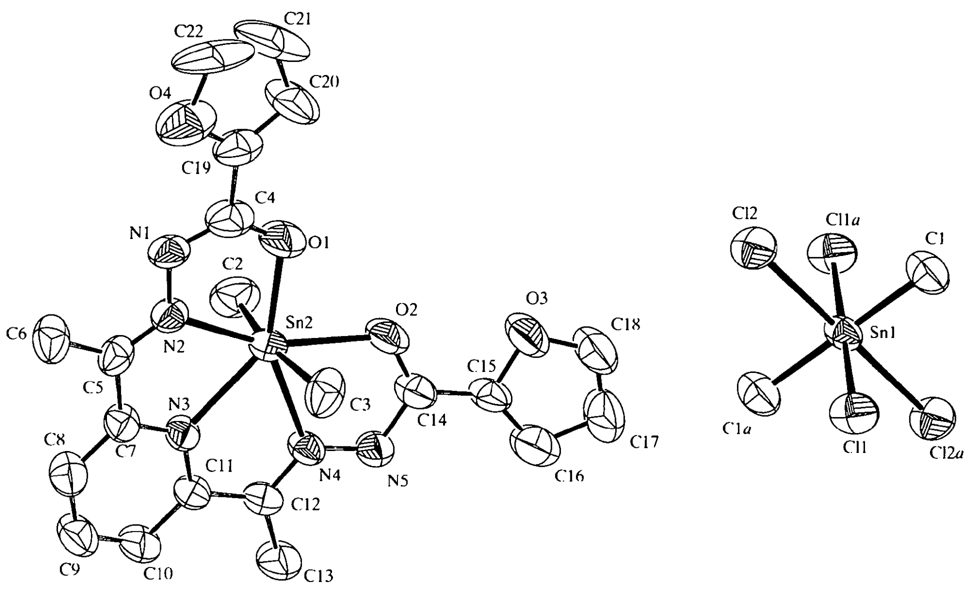

Fig. 1. View of the title complex, $[Me_2Sn(Hdapf)]_2[Me_2SnCl_4]$. Displacement ellipsoids are drawn at the 50% probability level.

atom remains protonated. So, the O1 atom coordinates in the enolate form, while O2 is in the keto form. The former has its basicity enhanced compared with the O2 atom, and the Sn—O1 distance is shortened.

This complex seems to be the first case in a series of 2,6-diacetylpyridine bis(aroylhydrazone)s to suffer a partial deprotonation of the ligand. The other complexes, for example, $[Et_2Sn(dapt)]$ (Carini *et al.*, 1989), $[Cl_2Sn(dappc)].H_2O$ (Delledonne *et al.*, 1987), $[Ph_2Sn(dapa)]$ (Pelizzi *et al.*, 1984) and $[^nPr_2Sn(daps)]$ (Pelizzi & Pelizzi, 1980), suffered deprotonation in both arms of the ligand and consequently there are no important differences between the O atoms [dapt is 2,6-diacetylpyridine bis(2-thenoylhydrazone), dappc is 2,6-diacetylpyridine bis(2-picolinoylhydrazone), dapa is 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) and daps is 2,6-diacetylpyridine bis(2-salicyloylhydrazone)].

A similar partial deprotonation was observed for *trans*-diphenyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) chloride (Moreno *et al.*, 1997).

The dianionic complex, $[Me_2SnCl_4]^{2-}$, has the Sn^{IV} atom at the origin, *i.e.* at the inversion center. Its observed bond lengths and angles are in agreement with other published data (Smart & Webster, 1976; Valle *et al.*, 1988).

There are N5—HN5···Cl1($-x$, $1-y$, $-z$) hydrogen-bonding interactions among the cations and anions [N5—HN5 0.82 (6), N5···Cl1 3.500 (5), HN5···Cl1 2.69 (6) Å and N5—HN5···Cl1 170 (6)°]. These interactions define the packing mode.

The IR spectrum indicated $\nu(CO) = 1640\,cm^{-1}$, practically constant after complexation, compared with $\nu(CO) = 1630\,cm^{-1}$ for the free ligand. It was observed also that the broad and strong ligand band became thin upon complexation.

The ^1H NMR (250 MHz) spectrum in $CDCl_3$ showed three singlets in the methyl region occurring at δ = 6.98, 0.99 [$^2J(^{119}Sn-^1H)$ = 80.00 Hz] and 0.37 p.p.m. [$^2J(^{119}Sn-^1H)$ = 107.7 Hz], due to three magnetically non-equivalent methyl groups bonded in $N{=}CO{-}CH_3$, $Sn1{-}CH_3$ and $Sn2{-}CH_3$, respectively. According to the literature, the use of the Lockart–Manders equation (Lockhart & Manders, 1986) for $[Me_2SnCl_2]^{2-}$ indicates a C—Sn—C angle of 131° (in solution), which is consistent with octahedral Sn^{IV} units, with two methyl groups in *trans* positions.

The complexes bis(2-aminocarbonyl)anilinium dimethyltetrachlorostannate(IV) (Nasser *et al.*, 1984) and bis(2-aminopyridinium) dimethyltetrachlorostannate(IV) (Valle *et al.*, 1988) have identical coordination geometry for Sn^{IV}. In these cases, the tin-proton coupling constants, $^2J(^{119}Sn-^1H)$, are 92.8 (CD_3OD) and 72.2 Hz ($CDCl_3$), respectively.

The best computer fitting of the ^{119}Sn Mössbauer spectrum showed two quadrupole splitting patterns indicative of the presence of two different Sn^{IV} sites, which are in a 2:1 ratio. This result is in accordance with the structure determined by single-crystal X-ray diffraction. The most abundant site, with isomer shift δ = 1.29 mm s^{-1} and quadrupole splitting Δ = 3.96 mm s^{-1}, was assigned to the heptacoordinated Sn^{IV} atom of the $[Me_2Sn(Hdapf)]^+$ cation. The other site, having δ = 1.56 mm s^{-1} and Δ = 4.11 mm s^{-1}, corresponds to the hexacoordinated Sn^{IV} atom of the anion, $[Me_2SnCl_4]^{2-}$, and this agrees well with early results reported in the literature (Nasser *et al.*, 1984).

Experimental

2,6-Diacetylpyridine bis(2-furoylhydrazone), H_2(dapf), was prepared by refluxing an EtOH solution of 2,6-diacetylpyridine and 2-furoic acid hydrazide (1:2 molar ratio) for about 1 h. After cooling, the pale-yellow compound (m.p. 518–520 K) was filtered and dried under vacuum over $CaCl_2$. The complex was obtained by treating a hot MeOH solution of H_2(dapf) with Me_2SnCl_2, dissolved in the same solvent, in a 1:1 molar ratio. The resulting mixture was refluxed for 1 h and filtered to give a clear solution which, after cooling and slow evaporation of the solvent, provided the product as yellow crystals, which did not melt up to 523 K. Analysis calculated for $C_{44}H_{50}Cl_4N_{10}O_8Sn_3$: C 39.08, H 3.70, N 10.36%; found: C 38.65, H 3.27, N 10.32%. The ^{119}Sn Mössbauer spectrum was taken at 80 K using a $CaSnO_3$ source at room temperature.

Crystal data

$[Sn(CH_3)_2(C_{19}H_{16}N_5O_4)]_2$-$[SnCl_4(CH_3)_2]$
$M_r = 1344.81$
Monoclinic
$P2_1/c$
$a = 19.464\,(2)$ Å
$b = 10.087\,(2)$ Å
$c = 13.993\,(2)$ Å
$\beta = 105.993\,(9)°$
$V = 2641.0\,(7)$ Å^3
$Z = 2$
$D_x = 1.691$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$18°$
$\mu = 1.669$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.18 × 0.13 × 0.08 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.762$, $T_{\max} = 0.875$
5519 measured reflections
5357 independent reflections

3254 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 26.29°$
$h = 0 \rightarrow 24$
$k = -12 \rightarrow 0$
$l = -17 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 5.7%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.068$
$S = 1.032$
5357 reflections
331 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0085P)^2 + 7.1578P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.661$ e Å^{-3}
$\Delta\rho_{\min} = -0.511$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn1—C1	2.108 (6)	Sn2—O1	2.227 (4)
Sn1—Cl1	2.609 (2)	Sn2—N2	2.263 (5)
Sn1—Cl2	2.623 (2)	Sn2—N3	2.314 (4)
Sn2—C3	2.098 (6)	Sn2—N4	2.446 (4)
Sn2—C2	2.104 (6)	Sn2—O2	2.474 (4)
C1—Sn1—Cl1	87.5 (2)	C2—Sn2—N3	92.1 (2)
C1—Sn1—Cl2	88.0 (2)	N2—Sn2—N3	69.6 (2)
Cl1—Sn1—Cl2	90.89 (5)	C3—Sn2—N4	85.3 (2)
C3—Sn2—C2	166.0 (3)	C2—Sn2—N4	87.6 (2)
C3—Sn2—O1	90.2 (2)	N3—Sn2—N4	66.0 (2)
C2—Sn2—O1	90.9 (3)	C3—Sn2—O2	83.0 (2)
C3—Sn2—N2	97.3 (2)	C2—Sn2—O2	83.0 (3)
C2—Sn2—N2	96.2 (2)	O1—Sn2—O2	90.1 (2)
O1—Sn2—N2	70.1 (2)	N4—Sn2—O2	64.19 (14)
C3—Sn2—N3	96.1 (2)		

The fractional atomic coordinates of the HN5 atom were determined in a difference Fourier map, calculated after convergence of the refinement with all the other atoms. The positions of all the others H atoms were calculated and assigned an isotropic displacement parameter of 0.076 Å^2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: DOS 6.0 VAX editor.

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