3209 reflections
284 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 0.903P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—N14	1.992 (4)	Ni—C3	1.865 (4)
Cu—N21	2.003 (4)	Ni—C1	1.865 (4)
Cu—N17	2.039 (3)	Ni—C2	1.866 (4)
Cu—N11	2.053 (4)	C1—N1	1.144 (5)
Cu—N1	2.474 (4)	C2—N2	1.151 (6)
Cu—O24	2.527 (3)	C3—N3	1.145 (6)
Ni—C4	1.861 (4)	C4—N4	1.150 (5)
N1—C1—Ni	178.1 (4)	C1—N1—Cu	143.7 (3)

All H atoms, except those belonging to the water molecules and the aminoethanol OH group, were located. Their coordinates and isotropic displacement parameters were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1476). Services for accessing these data are described at the back of the journal.

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trans-[2,6-Diacetylpyridine bis(thiosemicarbazone)(1–)]diphenyltin(IV) Chloride

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Abstract

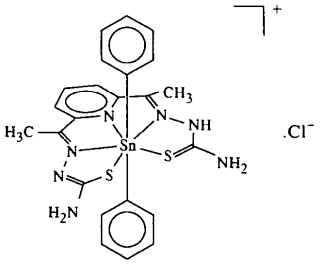
The chelating properties of the pentadentate ligand 2,6-diacetylpyridine bis(thiosemicarbazone) hydrochloride, H_2daptsc.HCl, have been investigated in a new organotin complex, [PhSnPh(Hdaptsc)]Cl {or $[Sn(C_6H_5)_2(C_{11}H_{14}N_7S_2)]Cl$}. The structure determination revealed a monocationic complex consisting of a heptacoordinated Sn^{IV} in a distorted pentagonal-bipyramidal geometry, with the thiosemicarbazone derivative acting as a pentadentate species at the equatorial plane and two phenyl groups at *trans* positions. The chloride acts as a counterion. ^{119}Sn Mössbauer measurements showed that the isomer shift and the quadrupole splitting are consistent with structural interpretation.

Comment

The chelating properties of 2,6-diacetylpyridine bis(thiosemicarbazones) have been investigated. Three different coordination modes have been found. In the most common one, the ligand acts as a dianionic η^5 ligand and coordinates to the central metal through two thiol S, two azomethine N and the pyridine N atom. This coordination mode was observed in diphenyl[2,6-diacetylpyridine bis(thiosemicarbazonate)]tin(IV) bis(dimethylformamide) solvate (Casas *et al.*, 1994). Spectroscopic and X-ray studies showed that 2,6-diacetylpyridine bis(thiosemicarbazones) can also behave as tetradentate dianionic ligands that form square-planar complexes with Ni^{II}, Cu^{II} and Pd^{II} (El-Toukhy, 1991). In this case, the metal ion is coordinated through the pyridine N, the thiolate S, the azomethine N and the thioimide N atom. The other S atom remains in the thione form and does not coordinate. A third coordination mode was reported for the complex *trans*-chloromethyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) chloride methanol solvate in which the Sn^{IV} atom is heptacoordinated and has

a pentagonal-bipyramidal geometry. One of the arms of the η^5 organic ligand, which is in the equatorial plane of the coordination polyhedron, has undergone deprotonation (de Sousa, Filgueiras, Abras, Al-Juaid, Hitchcock & Nixon, 1994). These observations have increased our interest in the structural properties of this ligand and have motivated us to study the product of its reaction with Ph_2SnCl_2.

The structure determination of *trans*-diphenyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) chloride, [PhSnPh(Hdaptsc)]Cl, (I), revealed the occurrence of a



monocationic complex of Sn^{IV} with a chloride counterion (Fig. 1). The complex follows the third coordination mode discussed above. Table 1 contains selected bond distances and angles. The dihedral angle between the phenyl groups at the axial positions is 44.4 (3)°.

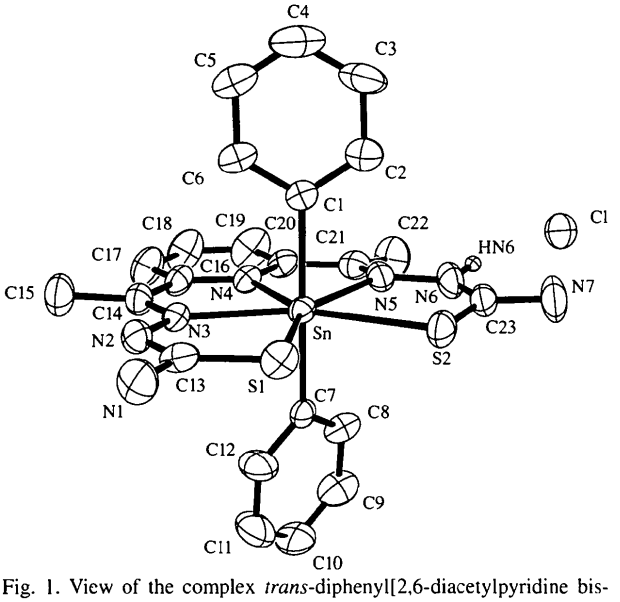


Fig. 1. View of the complex *trans*-diphenyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) chloride, with 50% probability ellipsoids, except for the H atom.

A least-squares plane calculated through the 21 atoms of the equatorial plane indicated maximum deviations from planarity of −0.140 (6) to 0.193 (6) Å. There are some differences between the bond distances and angles in the two arms of the ligand since the S1 atom, which is in the thiolate form, is more basic than S2, which is in the thione form (see Table 1). Corresponding differences were seen in the structure of *trans*-chloromethyl[2,6-diacetylpyridine bis(thiosemicarbazone)]tin(IV) chloride methanol solvate (de Sousa, Filgueiras, Abras, Al-Juaid, Hitchcock & Nixon, 1994).

In the complex dichloro[2,6-diacetylpyrydine bis(semicarbazone)]tin(IV) dichloride dihydrate (Sommerer & Palenik, 1991), both ligand arms are protonated and the bond lengths in the two arms are similar [Sn—O 2.127 (5) and 2.123 (6) Å; Sn—N 2.272 (7) and 2.259 (6) Å].

In the case of diphenyl[2,6-diacetylpyridine bis(thiosemicarbazonate)]tin(IV) bis(dimethylformamide) solvate (Casas *et al.*, 1994), the ligand loses both the protons (from azomethine N atoms) and only small differences in bond distances and angles around Sn^{IV} are observed [2.593 (1) and 2.603 (1) Å for Sn—S, and 2.427 (4) and 2.421 (4) Å for Sn—N].

The chloride interacts with the complex through hydrogen bonds. The protons HN6 and HN7*B* interact with the counterion at distances of N6—Cl 3.071 (5), HN6···Cl 2.24 (7), N7···Cl 3.216 (7) and HN7*B*···Cl 2.44 (7) Å, and angles of N6—HN6···Cl 157 (6) and N7—HN7*B*···Cl 150 (6)°. The complex related by $(\frac{1}{2}-x,\ y-\frac{1}{2},\ \frac{1}{2}-z)$ interacts with the chloride through the proton HN1*B* and the distances and angle are N1′···Cl 3.236 (5), HN1*B*′···Cl 2.49 (7) Å and N1′—HN1*B*′···Cl 153 (6)°. The complex related by $(1-x,\ -y,\ -z)$ interacts with the counterion through the protons HN7*A* and HN7*B*. The distances are N7″···Cl 3.166 (5), HN7*A*″···Cl 2.90 (8) and HN7*B*″···Cl 2.83 (7) Å, and the angles are N7″—HN7*A*″···Cl 105 (7) and N7″—HN7*B*″···Cl 105 (5)°. The interactions are shown in Fig. 2.

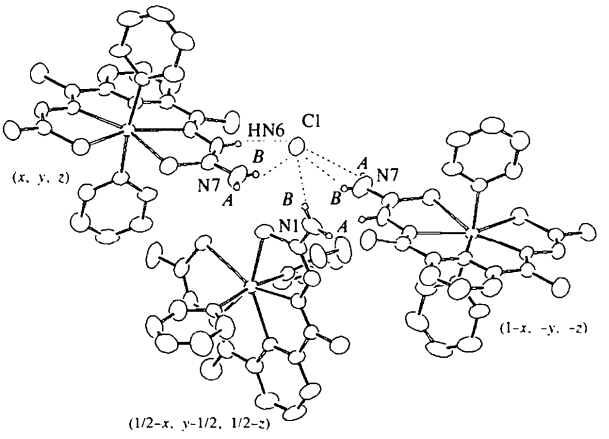


Fig. 2. *ORTEP* (Johnson, 1965) view of the interactions around the chloride, with 50% probability ellipsoids, except for the H atom.

A semiquantitative relationship of the Mössbauer quadrupole splitting (Δ) and the *R*—Sn—*R* angle has been reported for a series of distorted heptacoordinated diorganotin(IV) derivatives (Carini *et al.*, 1989; Abras,

de Sousa & Filgueiras, 1994). The equation is $|\Delta| = 4[R](1 - 3/4\sin^2\theta)^{1/2}$, where θ is the angle R—Sn—R and $[R]$ is the partial quadrupole splitting of the group R. Inserting the values $\Delta = 3.13(1)$ mm s^{-1} and $\theta = 167.9(2)°$ of our complex in the above equation, we obtain [Ph] = -0.80 mm s^{-1}, which agrees very well with the value previously calculated ([Ph] = -0.78 mm s^{-1}) using [PhSnPh(dapa)] data [Δ = 3.12 (2), θ = 176.4 (4)°; Carini *et al.*, 1989].

Experimental

The yellow ligand, H_2daptsc.HCl, was prepared in quantitative yield from 2,6-diacetylpyridine and thiosemicarbazide (de Sousa *et al.*, 1994). To obtain the title compound, 0.21 mmol of the H_2daptsc.HCl was partially dissolved by refluxing for 20 min in dry CH_3OH and added to 0.24 mmol of Ph_2SnCl_2 dissolved in the same solvent. The resulting mixture was refluxed for 1 h. After cooling and filtering, a clear solution was obtained. Slow evaporation of the solvent led to a bright yellow crystalline solid. The ligand and the complex were analyzed (C, H, N) using a HERAEUS CHN rapid elemental analyzer; for the ligand, observed: C 39.80, H 5.06, N 29.21%; calculated for $C_{11}H_{16}ClN_7S_2$: C 38.20, H 4.86, N 28.36%; for the complex, observed: C 44.59, H 3.94, N 16.18%; calculated for $C_{23}H_{24}ClN_7S_2Sn$: C 44.79, H 3.89, N 15.90%. Both the ligand and the complex did not melt up to 523 K. The coordination compound was studied at room temperature by ^{119}Sn Mössbauer spectroscopy using a constant acceleration spectrometer moving a $CaSnO_3$ source. The samples were analyzed at 85 K. All spectra were computer-fitted assuming Lorentzian line shapes.

Crystal data

$[Sn(C_6H_5)_2(C_{11}H_{14}N_7S_2)]Cl$
M_r = 616.77
Monoclinic
$P2_1/n$
a = 8.537 (1) Å
b = 15.946 (5) Å
c = 18.756 (4) Å
β = 92.53 (2)°
V = 2551 (2) Å^3
Z = 4
D_x = 1.606 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–18°
μ = 1.297 mm^{-1}
T = 293 (2) K
Prismatic
0.15 × 0.15 × 0.03 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.862, T_{max} = 0.999
5730 measured reflections
5165 independent reflections

3805 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 26.29°
$h = -10 \rightarrow 0$
$k = -19 \rightarrow 0$
$l = -23 \rightarrow 23$
3 standard reflections frequency: 120 min intensity decay: 2.9%

Refinement

Refinement on F^2
$R(F)$ = 0.036
$wR(F^2)$ = 0.078
S = 1.039
5165 reflections
322 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 5.2803P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = -0.53 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sn—C1	2.163 (4)	C16—N4	1.347 (6)
Sn—C7	2.170 (4)	C16—C17	1.381 (7)
Sn—N4	2.348 (4)	C17—C18	1.362 (8)
Sn—N3	2.353 (4)	C18—C19	1.376 (9)
Sn—N5	2.491 (4)	C19—C20	1.396 (7)
Sn—S1	2.592 (1)	C20—N4	1.346 (6)
Sn—S2	2.703 (1)	C20—C21	1.472 (7)
S1—C13	1.731 (5)	C21—N5	1.290 (6)
C13—N2	1.322 (6)	C21—C22	1.498 (7)
C13—N1	1.351 (6)	N5—N6	1.377 (6)
N1—HN1*A*	0.94 (7)	N6—C23	1.347 (7)
N1—HN1*B*	0.81 (7)	N6—HN6	0.88 (7)
N2—N3	1.371 (5)	C23—N7	1.327 (7)
N3—C14	1.290 (6)	C23—S2	1.694 (6)
C14—C16	1.475 (7)	N7—HN7*A*	0.71 (7)
C14—C15	1.498 (7)	N7—HN7*B*	0.86 (7)
C1—Sn—C7	167.9 (2)	C16—C14—C15	119.8 (4)
C1—Sn—S1	97.4 (1)	N4—C16—C17	121.0 (5)
C1—Sn—N3	91.7 (1)	N4—C16—C14	116.9 (4)
C1—Sn—N4	85.5 (1)	C14—C16—C17	122.0 (5)
C1—Sn—N5	84.0 (1)	C16—C17—C18	118.4 (5)
C1—Sn—S2	93.5 (1)	C17—C18—C19	121.0 (5)
C7—Sn—S1	94.5 (1)	C18—C19—C20	118.9 (5)
C7—Sn—N3	89.9 (1)	N4—C20—C19	119.6 (5)
C7—Sn—N4	83.9 (1)	N4—C20—C21	117.5 (4)
C7—Sn—N5	86.3 (2)	C19—C20—C21	122.9 (5)
C7—Sn—S2	90.1 (1)	C20—N4—C16	121.0 (4)
S1—Sn—N3	74.4 (1)	C20—N4—Sn	121.5 (3)
N3—Sn—N4	69.1 (1)	C16—N4—Sn	117.5 (3)
N4—Sn—N5	65.9 (1)	N5—C21—C20	114.9 (4)
N5—Sn—S2	70.9 (1)	N5—C21—C22	125.2 (5)
C13—S1—Sn	97.9 (2)	C20—C21—C22	119.9 (5)
N2—C13—N1	114.1 (5)	C21—N5—N6	118.5 (4)
N2—C13—S1	129.4 (4)	C21—N5—Sn	119.8 (3)
N1—C13—S1	116.4 (4)	N6—N5—Sn	121.2 (3)
C13—N2—N3	114.8 (4)	C23—N6—N5	120.6 (4)
C14—N3—N2	117.1 (4)	N7—C23—N6	114.8 (5)
C14—N3—Sn	119.5 (3)	N7—C23—S2	120.6 (5)
N2—N3—Sn	123.3 (3)	N6—C23—S2	124.6 (4)
N3—C14—C16	116.8 (4)	C23—S2—Sn	102.6 (2)
N3—C14—C15	123.3 (5)		

The fractional coordinates for the four H atoms were determined in a difference Fourier map calculated after convergence of the refinement with all the other atoms. They were refined (N—H distances 0.71–0.94 Å).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976) and *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: DOS 6.0, VAX editor.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1300). Services for accessing these data are described at the back of the journal.

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trans-Dichlorobis(ferrocenyldiphenylphosphine-*P*)platinum(II)–Benzene (1/2)

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(*Received 25 March 1997; accepted 28 May 1997*)

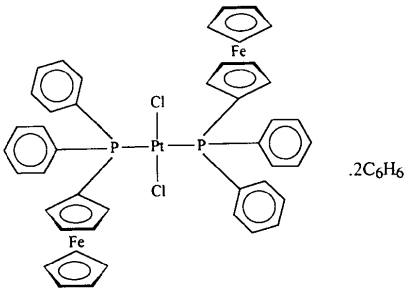
Abstract

The structure determination of the title compound, $[PtCl_2(C_{22}H_{19}FeP)_2].2C_6H_6$, shows the Pt^{II} moiety to have a square-planar geometry with the bulky phosphine ligands in a *trans* orientation; each molecule crystallizes with two benzene solvent molecules. The compound crystallizes in the triclinic space group $P\bar{1}$ with one mole per unit cell. Bond distances and angles of the coordination polyhedron are Pt—P = 2.318 (2), Pt—Cl = 2.301 (2) Å and P—Pt—Cl = 87.56 (7)°. The structure is compared to analogous platinum(II)–dichloro complexes containing two *trans* tertiary phosphine ligands.

Comment

Some of the work performed by our research group involves the tuning of chemical behaviour of complexes by introduction of certain functionalized ligand systems. The evaluation of the complex by means of as many techniques as possible, *e.g.*, X-ray structural, multinuclear NMR, IR spectroscopy and reaction kinetics is of prime importance to quantify the effect of the specific ligand on the complex under investigation. Complexes containing P atoms and ferrocene moieties can be ideally investigated by ^{31}P NMR and cyclic voltametry.

One such system includes the systematic study of complexes of the general type $[Pt(R)(Cl)(L)_2]$, where L can be tertiary phosphine, arsine or stibene ligands (Otto, Roodt & Leipoldt, 1995; Roodt, Otto & Leipoldt, 1995; Otto & Roodt, 1996). Ferrocenyldiphenylphosphine was one of the ligands used, where R = Me and Ph, and since there is so little known about this specific phosphine, we determined the X-ray structure of the title complex, (I), to obtain some additional information on the coordination mode of this unsymmetrical phosphine ligand.



(I)

The molecular geometry is shown in Fig. 1 and the title compound is compared with structural data for analogous compounds in the literature (Table 2). It is clear from Table 2 that a relatively short Pt—P bond length is obtained for the title compound, indicative of strong Lewis basicity. One would expect a rather large steric demand for this phosphine ligand which will tend to lengthen the bond. The Pt—Cl bond distances and P—Pt—Cl angles are within normal limits. The P—C bond distances to the phenyl rings are within normal limits for this type of bond, while the P—C bond with the ferrocenyl moiety is appreciably shorter, *i.e.* 0.032 (8) Å. The same tendency was also observed previously in a structural study of the uncoordinated PPh_2Fc ligand (Adeleke & Lui, 1993) (where Fc = ferrocenyl). All C—C bonds and angles in the benzene

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