

The tetrachlorodiphenylstannate(IV) salt of protonated di-2-pyridyl ketone *N*⁴-ethylthiosemicarbazoneRamaier Venkatraman,^a
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Key indicators

Single-crystal X-ray study

T = 102 KMean $\sigma(C-C)$ = 0.002 Å*R* factor = 0.029*wR* factor = 0.066

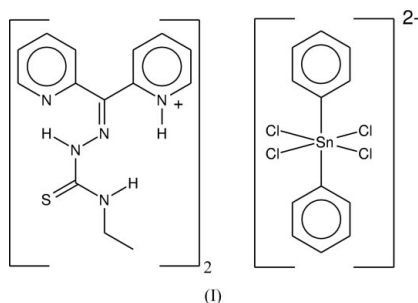
Data-to-parameter ratio = 31.2

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

Reaction of di-2-pyridyl ketone *N*⁴-ethylthiosemicarbazone with SnPh₂Cl₂ resulted in the formation of the title complex salt, namely 2-[(ethylaminothioylhydrazono)(2-pyridyl)methyl]pyridinium tetrachlorodiphenylstannate(IV), (C₁₄H₁₆N₅S)₂[SnCl₄(C₆H₅)₂]. The Sn atom is not coordinated directly by the nitrogen base, but one of the pyridines of dipyridylketone is protonated, forming the cation. The Sn atom of the anion lies on an inversion center; thus, the two phenyl groups are *trans* to each other, with an Sn—C distance of 2.1424 (14) Å. The Sn—Cl distances are 2.5541 (4) and 2.6066 (4) Å. The N—H groups form hydrogen bonds to Cl atoms of the anion and the cation contains an intramolecular N—H···N hydrogen bond.

Comment

Metal complexes of thiosemicarbazones have been found to exhibit, in certain instances, enhanced biological activity (Ali & Livingstone, 1974; Campbell, 1975; Padhye & Kauffman, 1985) compared with the uncomplexed ligands. The thiosemicarbazone moiety acts as a chelating agent for metal ions by binding through the S atom and the hydrazine N atom. The thiosemicarbazone molecule can exist, in solution, as the thione or thiol tautomer. The thione form can act as a neutral bidentate ligand, while the thiol form can be a singly charged bidentate ligand due to the loss of its proton. In metal complexes thiosemicarbazones act as a tridentate ligand with a donor atom other than the thione/thiol S atom and azomethine N atom. The possible ligation in metal complexes can be either as a neutral molecule or a monobasic anion due to loss of a proton from the azomethine N atom. A survey of the literature revealed that only a few organotin(IV) compounds of thiosemicarbazones have been studied (Barbieri *et al.*, 1993; Bamgboye & Bamgboye, 1988; Casas *et al.*, 1994; De Sousa *et al.*, 2001). In contrast to the thiosemicarbazones which coordinate metals through various coordination sites as mentioned above, Ph₂SnCl₂ reacts with di-2-pyridylketone *N*⁴-ethylthiosemicarbazone to give an outer-sphere tin complex.



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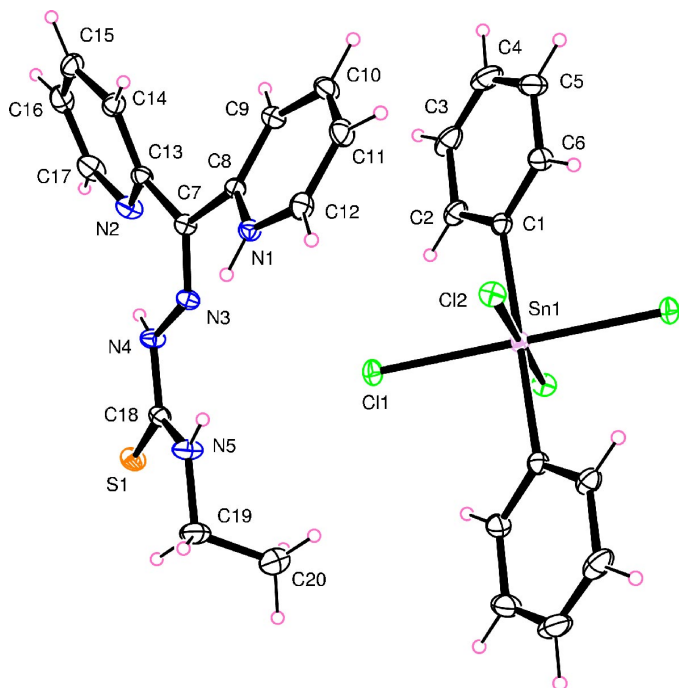


Figure 1
View of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. The unlabeled atoms of the anion and the second cation (not shown) are related by the symmetry code $(-x, 1 - y, -z)$.

We report here the structure of a complex salt, namely 2-[(ethylaminothiopylhydrazono)(2-pyridyl)methyl]pyridinium tetrachlorodiphenylstannate(IV), (I). Similar tin complexes with other ligands have been recently reported (Teo *et al.*, 2000; Ouyang *et al.*, 1998; Hazell *et al.*, 1998, Casas *et al.*, 1996; Teoh *et al.*, 1992).

The salt consists of a thiosemicarbazone cation in a general position and a tetrachlorodiphenylstannate anion on an inversion center. These ions and the atom-labeling scheme are shown in Fig. 1. The Sn atom is bound to four Cl atoms and two phenyl groups to give an octahedral geometry with *trans* phenyl groups. The SnCl₄ unit is planar by symmetry, and all C—Sn—Cl angles are within one degree of orthogonal. The C₁₄H₁₆N₅S⁺ cation has one protonated pyridine N atom (N1); all nitrogen-bound H atoms were located in a difference map (Teo *et al.*, 2000) and refined. Such protonation is unusual for complex salts involving thiosemicarbazones, which are normally protonated at the imine N atom (N4). The protonated pyridine N atom (N1) of the dipyridyl unit and the N atom (N5) that carries the ethyl group both form hydrogen bonds with a Cl atom of the anion. The imino N atom (N4) forms an intramolecular hydrogen bond with the unprotonated pyridine. Details of these interactions are given in Table 2.

Experimental

The tin complex of di-2-pyridyl ketone *N*⁴-thiosemicarbazone was prepared by the following procedure: 0.21 mmol of the ligand was dissolved in 15 ml of methanol under reflux; to this was added a 5 ml solution of 0.24 mmol dichlorodiphenyltin in methanol. The resulting

mixture was refluxed for 1 h. Cooling followed by slow evaporation produced yellow crystals (*ca* 65% yield), with a melting point above 523 K. IR spectra were obtained in the 4000–400 cm⁻¹ range in KBr pellets on a Nicolet 670 FT-IR spectrometer ($\nu_{\text{N-H}}$ 3320–3345 cm⁻¹ (br), $\nu_{\text{C=N}}$ 1530–1550 cm⁻¹, $\nu_{\text{C=S}}$ 850 cm⁻¹).

Crystal data

(C₁₄H₁₆N₅S)₂[SnCl₄(C₆H₅)₂]
M_r = 987.45
 Triclinic, *P* $\bar{1}$
a = 7.4878 (10) Å
b = 12.009 (2) Å
c = 13.585 (2) Å
 α = 110.872 (9)°
 β = 102.803 (7)°
 γ = 100.404 (7)°
V = 1066.9 (3) Å³

Z = 1
D_x = 1.537 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7524 reflections
 θ = 2.5–33.7°
 μ = 0.99 mm⁻¹
T = 102 K
 Fragment, yellow
 0.35 × 0.30 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
 with an Oxford Cryosystems
 Cryostream cooler
 ω scans with κ offsets
 Absorption correction: multi-scan
 (HKL SCALEPACK;
 Otwinowski & Minor, 1997)
T_{min} = 0.696, *T_{max}* = 0.820

34148 measured reflections
 8420 independent reflections
 7364 reflections with *I* > 2σ(*I*)
R_{int} = 0.022
 θ_{max} = 33.7°
h = -11 → 11
k = -18 → 18
l = -21 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.029
wR (*F*²) = 0.066
S = 1.05
 8420 reflections
 270 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.6943P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.87 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.82 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0072 (7)

Table 1

Selected geometric parameters (Å, °).

Sn1—C1	2.1424 (14)	N2—C13	1.3518 (19)
Sn1—Cl1	2.5541 (4)	N3—C7	1.2996 (18)
Sn1—Cl2	2.6066 (4)	N3—N4	1.3476 (16)
S1—C18	1.6794 (15)	N4—C18	1.3786 (18)
N1—C12	1.3356 (18)	N5—C18	1.3243 (19)
N1—C8	1.3541 (17)	N5—C19	1.457 (2)
N2—C17	1.3356 (19)		
Cl1—Sn1—Cl1	90.82 (4)	C7—N3—N4	120.13 (12)
Cl1—Sn1—Cl2	90.56 (4)	N3—N4—C18	118.33 (12)
Cl1—Sn1—Cl2	90.516 (15)	C18—N5—C19	125.27 (13)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...Cl2 ⁱ	0.840 (19)	2.421 (19)	3.2279 (13)	161.4 (17)
N4—H4N...N2	0.86 (2)	2.01 (2)	2.6723 (18)	133.0 (17)
N5—H5N...Cl2 ⁱ	0.88 (2)	2.60 (2)	3.3103 (15)	138.7 (17)

Symmetry code: (i) 1 - *x*, 1 - *y*, -*z*.

H atoms on carbon were treated as riding in idealized positions, with C—H = 0.95–0.99 Å, depending on atom type. A torsional parameter was refined for the methyl group. Displacement parameters for H atoms were assigned as $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the attached atom (1.5 U_{eq} for methyl). The coordinates of H atoms bonded to nitrogen were refined freely.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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