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(2-Acetylpyridine-κN 4-phenylthiosemicarbazonato-κ^2N^1,S)halogeno-*trans*-dimethyltin(IV) (halogeno = chloro and bromo)

Regina H. P. Francisco,[a]* M. Teresa do P. Gambardella,[a] Gerimário F. de Sousa[b] and Anuar Abras[c]

[a]Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 870, 13560.970 São Carlos, SP, Brazil, [b]Instituto de Química, ICC, Universidade de Brasília, 70910.900 Brasília, DF, Brazil, and [c]Departamento de Física, ICEx, Universidade Federal de Minas Gerais, 30161.970 Belo Horizonte, MG, Brazil
Correspondence e-mail: reginap@iqsc.sc.usp.br

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A thiosemicarbazone derivative, 2-acetylpyridine 4-phenylthiosemicarbazone, was prepared and complexed to Lewis acids, $Sn(CH_3)_2X_2$, X = Cl and Br. The products, $[SnX(C_{14}H_{13}N_4S)(CH_3)_2]$, were characterized by single-crystal X-ray diffraction, and IR, NMR and Mössbauer spectroscopies. They are isomorphous and crystallize in the monoclinic space group $P2_1/n$. The structure determination revealed discrete neutral complexes with the Sn^{IV} atom in a distorted octahedral coordination geometry, with the halogeno ligand and the thiosemicarbazone derivative in the equatorial plane and the methyl groups in axial positions.

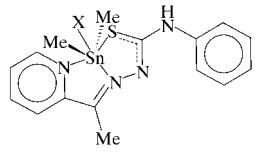
Comment

N,*N*,*S*-Tridentate-*N*(4)-heterocyclic thiosemicarbazones derived from 2-formyl- and 2-acetylpyridine include important classes of compounds with biological activity (West *et al.*, 1991, 1998; Labib *et al.*, 1996).

The chelating behaviour of *N*,*N*,*S*-tridentate thiosemicarbazones revealed three coordination modes. They can act as a neutral *N*(azomethine),*S*-bidentate ligand (Barbieri *et al.*, 1993) and as an anionic (1−) ligand, bonded through *N*,*N*,*S* or through *N*(azomethine),*S* (Bamgboye & Bamgboye, 1988; Labib *et al.*, 1996).

The structure determination of the compounds $[Sn(AP4P)(CH_3)_2Cl]$, (I), and $[Sn(AP4P)(CH_3)_2Br]$, (II), where HAP4P = 2-acetylpyridine 4-phenylthiosemicarbazone, confirmed that they are isomorphous. The chloro derivative is shown in Fig. 1. The crystal structure is built up by discrete molecules. The Sn^{IV} atom has a strongly distorted octahedral coordination geometry, with the equatorial plane occupied by the halogen ligand and the thiosemicarbazone derivative. The methyl groups are in apical positions. Selected bond parameters are given in Tables 1 and 2.

IR spectroscopy of the free ligand and the complexes revealed: (i) the disappearance of the ν(N—H) absorption at 3167 cm^{-1} as a consequence of the deprotonation of HAP4P



(I) X = Cl
(II) X = Br

for complexation through N2, (ii) the ν(C=N) absorption bands at 1597 and 1528 cm^{-1} found in the free ligand are shifted to 1594 and 1549 cm^{-1} in the chloro complex, and to 1595 and 1531 cm^{-1} in the bromo complex, confirming coordination *via* N2 (Labib *et al.*, 1996), (iii) the ν(C=S) vibrations in the free ligand at 1287 and 1218 cm^{-1} are shifted to lower frequencies by 35–69 cm^{-1}. The same trend is exhibited by the absorption at 896 cm^{-1} attributed to ν(C=S), found in the spectra of both complexes at 852 cm^{-1}. These observations and the appearance of bands with ν(C—S) character at 762 cm^{-1} in the spectra of the complexes suggest coordination through thiocarbonyl sulfur (Ferrari *et al.*, 1991). The far IR spectral bands observed at 355 and 410 cm^{-1} for $[Sn(AP4P)(CH_3)_2Cl]$ and at 353 and 410 cm^{-1} for $[Sn(AP4P)(CH_3)_2Br]$ were tentatively assigned to ν(Sn—N) and ν(Sn—S) modes, respectively (Barbieri *et al.*, 1993; Casas *et al.*, 1994).

The ^{1}H NMR (200 MHz) spectrum in $CDCl_3$ of the chloro derivative showed two singlets in the methyl region, at 1.60 and 1.18 p.p.m. [$^2J(^{119}Sn—CH_3)$ = 96.4 Hz] due to two magnetically non-equivalent methyl groups bonded in N=C—CH_3 and Sn—CH_3, respectively. The spectrum in CCl_4 of $[Sn(AP4P)(CH_3)_2Br]$ showed similar singlets at 1.56 and 2.48 p.p.m. [$^2J(^{119}Sn—CH_3)$ = 73.0 Hz].

Similar results were reported for trigonal bipyramidal complexes with analogous coordination geometry, $[Me_2SnCl_2ImSOMe]$ [ImSOMe = 1-methyl-2-(methylsulfinyl)-imidazole] and $[Me_2SnClFPT]$ (FPT = 2-formylpyridine thiosemicarbazone) (Sousa *et al.*, 1996; Labib *et al.*, 1996). In these cases, the tin–proton coupling constants, $^2J(^{119}Sn—CH_3)$, are 91.45 (acetone-d_6) and 96.0 Hz (DMSO-d_6), respectively. These data suggest that in solution, these complexes, which are pentacoordinated and have ambidentate

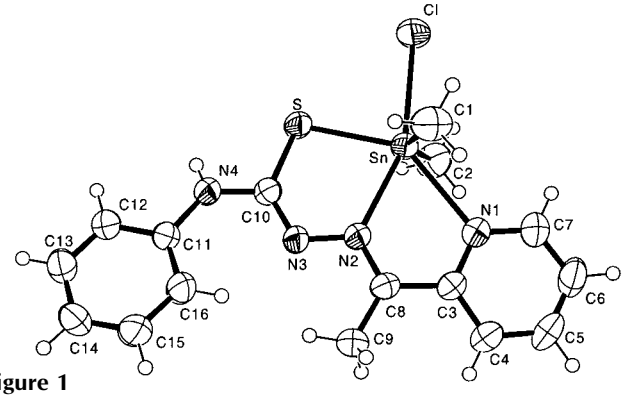


Figure 1
View of (I) with displacement ellipsoids plotted at the 50% probability level.

ligands, probably have a strong intramolecular Sn—N(py) interaction.

The isomer shifts (δ) of the complexes {[Sn(AP4P)-$(CH_3)_2$Cl] 1.38 mm s^{-1} and [Sn(AP4P)$(CH_3)_2$Br] 1.42 mm s^{-1}} are lower than the values observed for the parent acids [$(CH_3)_2SnCl_2$ 1.49 mm s^{-1} and $(CH_3)_2SnBr_2$ 1.59 mm s^{-1}] as a result of rehybridization to a higher coordination for Sn^{IV} in the complexes, leading to a participation smaller than 25% for the *s* orbital (Sousa *et al.*, 1996; Stocker & Sano, 1968). The lower isomer shift value for the chloro complex compared with the bromo complex is consistent with the electronegativity of the present ligands.

The quadrupole splittings (Δ) {3.35 mm s^{-1} for [Sn(AP4P)-$(CH_3)_2$Cl] and 3.40 mm s^{-1} for [Sn(AP4P)$(CH_3)_2$Br]} are very close, indicating the charge distributions around the tin nucleus are similar and highly asymmetric, with highly distorted geometries.

Experimental

The compound 2-acetylpyridine 4-phenylthiosemicarbazonoato, HAP4P, was prepared by refluxing equimolar ethanolic solutions of 4-phenylthiosemicarbazide and 2-acetylpyridine for 30 min. A light yellow crystalline solid was obtained with m.p. = 444–447 K.

To obtain the title complexes, the ligand (0.20 mmol) dissolved in CH_3OH (10 ml) was refluxed for 5 min. Then $Sn(CH_3)_2X_2$ (0.21 mmol), X = Cl or Br, dissolved in CH_3OH was added and refluxed for 1 h. After cooling the solution and slow evaporation of the solvent, crystalline compounds were obtained, with yields of about 70%. The complex with Cl has m.p. = 443–445 K and that with Br has m.p. = 440–452 K.

Elemental analysis using a HERAEUS CHN indicated for $C_{14}H_{14}N_4S$: calculated C 62.20, H 5.22, N 20.72%; observed C 60.86, H 5.09, N 20.32%; for $C_{16}H_{19}ClN_4SSn$: calculated C 42.37, H 4.22, N 12.35%; observed C 42.31, H 4.19, N 12.25%; for $C_{16}H_{19}BrN_4SSn$: calculated C 38.59, H 3.85, N 11.25%; observed C 37.07, H 3.55, N 11.12%.

The complexes were studied at room temperature by IR, ^{1}H NMR and ^{119}Sn Mössbauer (using a constant acceleration moving $CaSnO_3$ source) spectroscopies.

Compound (I)

Crystal data

$[Sn(CH_3)_2(C_{14}H_{13}N_4S)Cl]$	D_x = 1.63 Mg m^{-3}
M_r = 453.55	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
a = 10.273 (2) Å	θ = 10–18°
b = 15.238 (2) Å	μ = 1.63 mm^{-1}
c = 11.976 (2) Å	T = 293 (2) K
β = 95.63 (1)°	Prism, yellow
V = 1865.7 (5) $Å^3$	0.55 × 0.40 × 0.35 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.025
$\omega/2\theta$ scans	θ_{max} = 29.97°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -14 \rightarrow 14$
T_{min} = 0.481, T_{max} = 0.566	$k = -21 \rightarrow 0$
5664 measured reflections	$l = -16 \rightarrow 0$
5426 independent reflections	3 standard reflections
4243 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 1.4%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.8405P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.033	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.102	$\Delta\rho_{max}$ = 0.99 e $Å^{-3}$
S = 1.072	$\Delta\rho_{min}$ = −0.56 e $Å^{-3}$
5426 reflections	
211 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °) for (I).

Sn—C1	2.120 (4)	N1—C3	1.337 (4)
Sn—C2	2.124 (4)	C3—C8	1.487 (4)
Sn—N2	2.351 (2)	C8—N2	1.296 (3)
Sn—S	2.4728 (8)	N2—N3	1.377 (3)
Sn—N1	2.560 (3)	N3—C10	1.301 (3)
Sn—Cl	2.6772 (9)	C10—S	1.750 (3)
N1—C7	1.331 (5)		
C1—Sn—C2	145.09 (18)	C1—Sn—Cl	87.73 (11)
C1—Sn—N2	95.09 (13)	C2—Sn—Cl	86.22 (12)
C2—Sn—N2	103.31 (13)	S—Sn—Cl	81.94 (3)
C1—Sn—S	107.35 (13)	N1—Sn—Cl	136.90 (7)
C2—Sn—S	105.77 (12)	C8—N2—N3	114.2 (2)
N2—Sn—S	76.08 (6)	C8—N2—Sn	125.09 (19)
C1—Sn—N1	81.70 (13)	N3—N2—Sn	120.48 (17)
C2—Sn—N1	79.54 (14)	C10—N3—N2	115.5 (2)
N2—Sn—N1	65.30 (9)	N3—C10—S	127.9 (2)

Compound (II)

Crystal data

$[SnBr(CH_3)_2(C_{14}H_{13}N_4S)]$	D_x = 1.764 Mg m^{-3}
M_r = 497.92	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
a = 10.1858 (9) Å	θ = 10–19°
b = 15.3819 (18) Å	μ = 3.61 mm^{-1}
c = 12.0726 (7) Å	T = 293 (2) K
β = 97.560 (6)°	Prism, yellow
V = 1875.1 (3) $Å^3$	0.22 × 0.20 × 0.10 mm
Z = 4	

Table 2
Selected geometric parameters (Å, °) for (II).

Sn—C1	2.111 (5)	N1—C7	1.338 (7)
Sn—C2	2.115 (6)	C3—C8	1.470 (7)
Sn—N2	2.325 (4)	C8—N2	1.310 (6)
Sn—S	2.4743 (12)	N2—N3	1.371 (5)
Sn—N1	2.523 (4)	N3—C10	1.319 (6)
Sn—Br	2.9075 (6)	C10—S	1.739 (5)
N1—C3	1.333 (6)		
C1—Sn—C2	144.2 (3)	C1—Sn—Br	86.49 (16)
C1—Sn—N2	95.3 (2)	C2—Sn—Br	84.76 (18)
C2—Sn—N2	106.3 (2)	S—Sn—Br	80.60 (3)
C1—Sn—S	107.31 (18)	N1—Sn—Br	137.21 (10)
C2—Sn—S	105.40 (18)	C8—N2—N3	114.5 (4)
N2—Sn—S	76.43 (10)	C8—N2—Sn	124.1 (3)
C1—Sn—N1	82.7 (2)	N3—N2—Sn	121.0 (3)
C2—Sn—N1	80.4 (2)	C10—N3—N2	114.9 (4)
N2—Sn—N1	66.12 (14)	N3—C10—S	128.1 (4)
S—Sn—N1	142.07 (10)		

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.548, T_{max} = 0.697
5663 measured reflections
5433 independent reflections
3161 reflections with $I > 2\sigma(I)$

R_{int} = 0.050
θ_{max} = 29.95°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 4.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.106
S = 1.054
5433 reflections
211 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 3.6976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

The fractional atomic coordinates of the HN4 atoms (for both compounds) were found in a difference Fourier map, calculated after convergence of the refinement with all other atoms and refined. The final N4—HN4 distances are short: 0.72 (4) and 0.73 (5) Å, respectively, for the compounds with Cl and Br. The positions of all other H atoms were calculated with C—H distances of 0.96 Å for methyl groups and 0.93 Å for others, and they were assigned an isotropic displacement parameter 20% greater than that of the heavy atom to which they were bonded. In the complex with Cl, the maximum and minimum electronic density residuals are, respectively, 0.89 and 0.73 Å from the Sn. In the complex with Br, the maximum is 0.94 Å from Sn and the minimum is 0.37 Å from H9*A*.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Frenz, 1978); program(s) used to solve structure: *SDP*; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1234). Services for accessing these data are described at the back of the journal.

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