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Direct electrochemical synthesis of tin(IV) complexes of 2-(2-mercaptoethyl)iminomethyl-phenols; the molecular structure of bis{2-(2-mercaptoethyl)iminomethyl-5-bromo-phenoxy}tin(IV)

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Abstract

Anodic oxidation of tin in acetonitrile solutions of Schiff bases (H_2L_2) derived from the required salicylaldehyde and bis(2-aminoethyl)disulfide yielded compounds with general formula SnL_2. The crystal structure of bis{2-(2-mercaptoethyl)iminomethyl-5-bromo-phenoxy}tin(IV) has been determined: orthorhombic, space group *Pbcn* with $a=11.023(1)$, $b=8.376(1)$, $c=22.184(2)$ Å and $Z=4$. The structure was determined by direct methods and refined to $R=0.063$ and $R_w=0.070$. The ion atom is coordinated to the sulfur, nitrogen and oxygen atoms of two dianionic tridentate ligands and the coordination polyhedron around the metallic atom can be described as slightly distorted octahedral. Vibrational, ^{1}H, ^{13}C, ^{119}Sn NMR and Mössbauer spectroscopic data are presented for the synthesized compounds.

Keywords: Electrochemistry; Crystal structures; Tin complexes; Schiff base complexes

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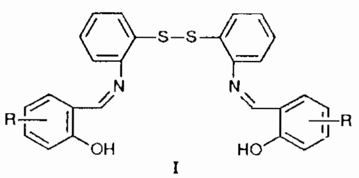
1. Introduction

We have published several papers describing the synthesis, by electrochemical cleavage of disulfide bonds in ligands such as **I** and **II**, of metallic complexes with Schiff bases containing thiolate sulfur atoms, and we have recently reported the crystal structures of bis-{2-[(pyrrol-2-yl)methyleneamino]thiophenolato-*S*,*N*}-zinc(II) [1], bis{2-(2-mercaptophenyl)iminomethyl-4,6-dimethoxyphenoxy}tin(IV) [2] and {(2,2′-bipyridine)-[2-(2-mercaptophenyl)iminomethylphenoxy]}zinc(II) [3].

In this work we report the synthesis of tin(IV) complexes containing ligands (L^n) derived from **III** (R=H ($H_2L_2{}^1$), 4,6-$(OCH_3)_2$ ($H_2L_2{}^2$), 3-OCH_2CH_3 ($H_2L_2{}^3$) or 5-Br ($H_2L_2{}^4$)); the crystal structure of bis{2-(2-mercaptoethyl)iminomethyl-5-bromo-phenoxy}tin(IV) [$SnL_2{}^4$], IR, NMR and Mössbauer spectra of the complexes are also reported.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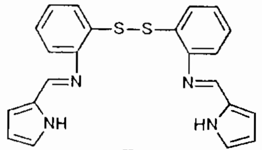
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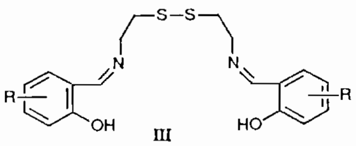
III

2. Experimental

Acetonitrile, cystamine dihydrochloride and the salicylaldehydes were all used as supplied. Tin metal (Ega Chemie) was used as rods.

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Table 1
Experimental conditions of the electrochemical synthesis and analytical data (%)[a] for the complexes

R	Compound	Amount of ligand[b] (g)	Initial voltage[c] (V)	Time (h)	Metal used (mg)	E_f (mol F^{-1})	C (%)	N (%)	H (%)
H	$SnL_2^1 \cdot H_2O$	0.135	15	1	43.9	0.49	45.5 (45.3)	5.9 (6.2)	3.9 (4.1)
4,6-$(OCH_3)_2$	SnL_2^2	0.178	18	1	48.3	0.54	44.9 (45.2)	5.8 (5.9)	3.5 (3.7)
3-OCH_2CH_3	SnL_2^3	0.178	15	1	47.6	0.53	47.0 (46.8)	4.9 (4.9)	4.6 (4.6)
5-Br	SnL_2^4	0.166	17	1.3	57.1	0.49	35.5 (35.0)	4.6 (4.4)	3.5 (3.5)

[a] Calculated values in parentheses.
[b] Plus NEt_4ClO_4 (~10 mg).
[c] Voltage to produce a current of 20 mA.

2.1. Schiff base formation

A suspension of cystamine dihydrochloride (1 mmol) in 20 cm^3 absolute ethanol was stirred for 4 h with 1 mol dm^{-3} methanolic NaOH (2 mmol). The solvent was evaporated in vacuo and the white solid residue extracted with five 5 cm^3 portions of $CHCl_3$, which was evaporated to yield the free base. This was dissolved in 25 cm^3 of dry benzene, mixed with the salicylaldehyde derivative (2 mmol in 15 cm^3 of the same solvent) and refluxed in a Dean–Stark apparatus until the theoretical amount of water had collected in the trap. The reaction mixture was concentrated in vacuo to give oils which solidified upon stirring in diethyl ether. The purity of the Schiff bases was verified by IR and ^{1}H NMR spectroscopies prior to use in the electrochemical synthesis.

2.2. Electrochemical synthesis

The electrochemical method used for the synthesis of the complexes was similar to that described by Tuck and co-workers [4]. The cells were of the general type $Pt(-)/CH_3CN+H_2L_2/Sn(+)$ comprising a 100 ml beaker containing a solution of the ligand (H_2L_2) and a supporting electrolyte (~10 mg of tetraethylammonium perchlorate) in ~50 cm^3 of acetonitrile, a platinum wire cathode, and a tin anode suspended from a platinum wire. All experiments were carried out under dry nitrogen, which was bubbled through the solution.

During the electrolysis hydrogen gas was evolved at the cathode. At the end of the electrolysis a small amount of a uncharacterizable yellow solid was isolated by filtration. Concentration of the electrolyte solutions by evaporation at room temperature gave crystalline solids which were isolated and washed with cold acetonitrile and diethyl ether. The complex containing the bromine-substituted ligand (L^4) gave crystals suitable for X-ray study. Details of the solution composition, the electrochemical conditions and analytical data for the complexes are given in Table 1.

2.3. Physical measurements

Microanalysis was performed by a Carlo-Erba EA1108 microanalyser. IR spectra were recorded in KBr mulls on a Perkin-Elmer 180 spectrophotometer; ^{1}H, ^{13}C and ^{119}Sn NMR spectra were obtained with a Bruker WM 250 MHz instrument using $CDCl_3$ as solvent. The Mössbauer spectroscopic measurements were carried out at 80 K on a constant-acceleration apparatus with a $Ca^{119}SnO_3$ source.

2.4. Crystal structure determination

A yellow prismatic crystal of approximate dimensions $0.20 \times 0.15 \times 0.30$ mm was mounted on a glass fiber and used for data collection on a CAD4 Enraf-Nonius four-circle automatic diffractometer. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range 18.03–24.79°. The orthorhombic space group *Pbcn* was assumed due to extinctions observed. Data were collected at 293 K using Cu Kα radiation ($\lambda = 1.54056$ Å) and the $\omega/2\theta$ scan technique. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was made [5]. A summary of crystal data, experimental detail and refinement results are listed in Table 2. See also Section 4.

2.5. Structure solution and refinement

The structure was solved by direct methods [6] and refined on F by the full-matrix least-squares method [7], with unit weight and anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were located from geometrical considerations (C–H = 0.95 Å), and added to the structure factor calculations as fixed contributions ($B_{iso} = 4.0$ Å^2); their positional parameters were not refined. A secondary extinction correction was applied [8]. The final coefficient, refined in the last least-square cycle, was $2.30(1) \times 10^{-7}$. The final R value was 0.063, with

Table 2
Summary of crystal data for SnL_2^4

Chemical formula	$C_{18}H_{16}Br_2N_2O_2S_2Sn$
Formula weight	634.98
Crystal system	orthorhombic
Space group	*Pbcn*
a (Å)	11.023(1)
b (Å)	8.376(1)
c (Å)	22.184(2)
Volume of unit cell (Å^3)	2048.2(7)
Z	4
D_c (g cm^{-3})	2.059
μ (cm^{-1})	168.32
F(000)	1224
Absorption correction: min./max./av.	0.776/1.476/1.008
Max. (sin θ)/λ	0.605
Total no. reflections measured; θ range (°)	3900; 5–69
No. unique reflections (R_{int})	2646 (0.032)
No. unique reflections (criterion)	1379 ($I > 3\sigma(I)$)
R	0.063
R_w	0.070

$R_w = 0.070$ (124 parameters; $S = 4.54$; maximum Δ/σ in the final cycle 0.001; maximum $\Delta q = 1.564$ e Å^{-3}). Atomic scattering factors were from International Tables for X-ray Crystallography [9]. Computations were performed on a DECMicro VAX 3500 computer, and molecular graphics from SCHAKAL [10].

3. Results and discussion

The anodic oxidation of tin metal in an electrochemical cell containing a solution of the ligand H_2L_2 in acetonitrile gave solutions which after air concentration at room temperature yielded compounds with the general formula SnL_2.

The electrochemical efficiency, E_f, defined as moles of metal dissolved per Faraday of charge, was found to be about 0.5 mol F^{-1}. This value shows that the anodic oxidation leads initially to Sn(II) species, which are further oxidized in solution to Sn(IV). The reactions at each electrode were as follows.

Cathode: $\frac{1}{2} H_2L_2 + 2e^- \longrightarrow L^{2-} + \frac{1}{2} H_2$

Anode: $L^{2-} + Sn \longrightarrow SnL + 2e^-$

$SnL + \frac{1}{2} H_2L_2 \longrightarrow SnL_2 + \frac{1}{2} H_2$

The nature of the latter reaction is far from clear at this stage, but such behavior has been observed in the syntheses of other Sn(IV) complexes by electrochemical procedures [2,11]. A possible alternative reaction scheme would involve the formation, at the cathode, of L_2^{2-} anions which subsequently migrate to the anode to form the product $Sn^{II}(L_2)$ in accordance with to the reaction sequence.

Cathode: $H_2L_2 + 2e^- \longrightarrow L_2^{2-} + H_2$

Anode: $L_2^{2-} + Sn \longrightarrow Sn^{II}(L_2) + 2e^-$

This would be followed by intramolecular oxidative insertion of Sn(II) into the S–S bond.

3.1. Description of the structure of SnL_2^4

Fig. 1 shows the molecular structure of SnL_2^4 and the numbering system used. Final atomic coordinates are listed in Table 3 and bond lengths and angles, with e.s.d.s, are given in Table 4.

The tin atom is located on a two-fold axis of a slightly distorted octahedral coordination polyhedron in which the sulfur, nitrogen and oxygen atoms of the two symmetrically related dianionic tridentate ligands form a meridional arrangement. Maximum deviation from the best plane defined by the three donor atoms of each ligand and the nitrogen of the other is 0.01 Å, and the tin atom lies 0.1 Å out of this plane. The dihedral angle between the two O–N–S–N planes is

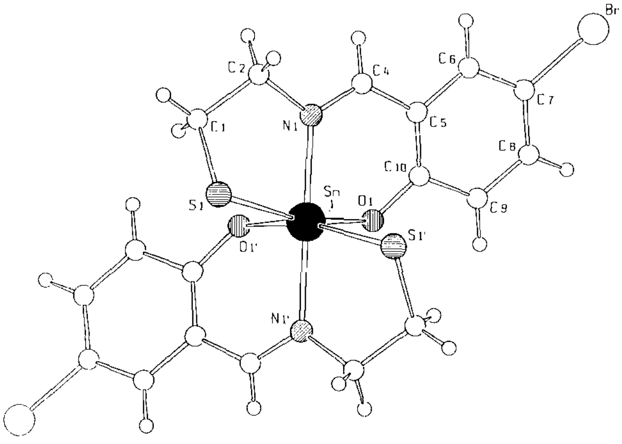

Fig. 1. Perspective view of SnL_2^4 molecule showing the numbering scheme. Symmetry code: $-x, y, 0.5-z$.

Table 3
Positional parameters and their e.s.d.s for SnL_2^4

Atom	*x*	*y*	*z*	B_{iso} (Å^2)
Sn(1)	0.000	0.2195(1)	0.250	2.83(2)
Br(1)	0.3343(2)	−0.0977(3)	0.51903(7)	6.27(4)
S(1)	0.0546(3)	0.4082(5)	0.1712(2)	4.95(8)
O(1)	−0.0006(8)	0.037(1)	0.3110(4)	4.0(2)
N(1)	0.1971(9)	0.200(1)	0.2587(4)	2.8(2)
C(1)	0.197(1)	0.305(2)	0.1548(6)	5.1(3)
C(2)	0.274(1)	0.281(2)	0.2123(6)	4.3(3)
C(4)	0.252(1)	0.146(1)	0.3062(5)	3.2(2)
C(5)	0.196(1)	0.061(1)	0.3554(5)	3.2(2)
C(6)	0.274(1)	0.028(2)	0.4043(5)	3.5(3)
C(7)	0.229(1)	−0.057(2)	0.4535(5)	3.8(3)
C(8)	0.112(1)	−0.104(2)	0.4552(6)	4.4(3)
C(9)	0.034(1)	−0.071(2)	0.4067(6)	4.1(3)
C(10)	0.079(1)	0.014(1)	0.3554(5)	2.9(2)

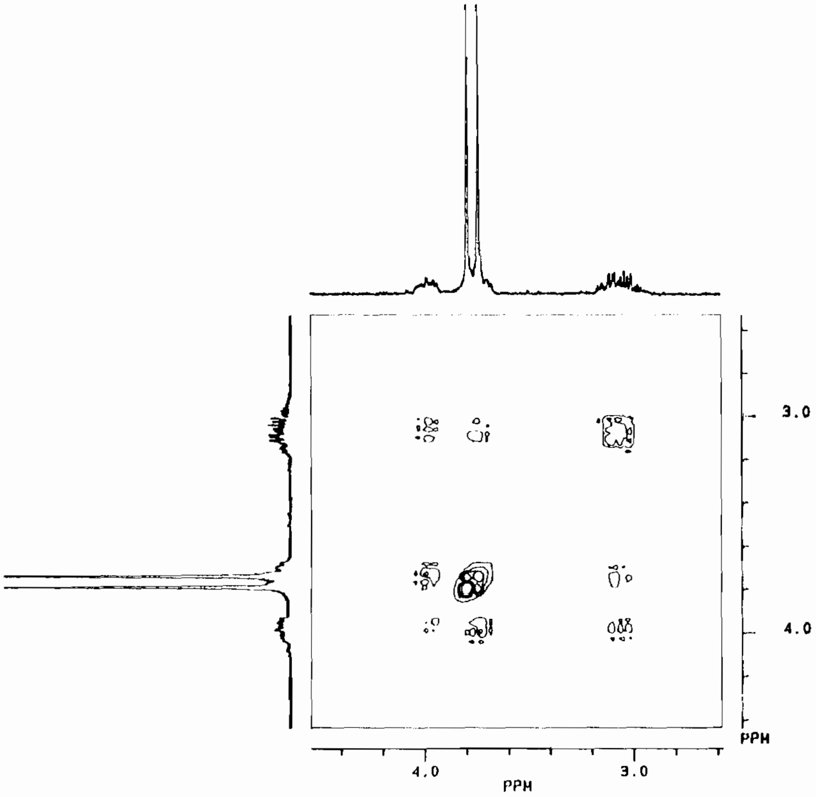

Fig. 2. H,H COSY spectrum of SnL_2^2.

Table 4
Selected bond distances (Å) and angles (°) for SnL_2^4

Sn(1)–S(1)	2.432(4)	N(1)–C(4)	1.30(1)
Sn(1)–S(1)′	2.432(4)	C(1)–C(2)	1.54(2)
Sn(1)–O(1)	2.039(9)	C(4)–C(5)	1.43(2)
Sn(1)–O(1)′	2.039(9)	C(5)–C(6)	1.41(2)
Sn(1)–N(1)	2.19(1)	C(5)–C(10)	1.36(2)
Sn(1)–N(1)′	2.19(1)	C(6)–C(7)	1.39(2)
Br(1)–C(7)	1.89(1)	C(7)–C(8)	1.35(2)
S(1)–C(1)	1.83(2)	C(8)–C(9)	1.41(2)
O(1)–C(10)	1.33(1)	C(9)–C(10)	1.43(2)
N(1)–C(2)	1.50(2)		
S(1)–Sn(1)–S(1)′	98.9(1)	N(1)–C(2)–C(1)	108(2)
S(1)–Sn(1)–O(1)	164.5(3)	N(1)–C(4)–C(5)	126(1)
S(1)–Sn(1)–O(1)′	90.5(3)	C(4)–C(5)–C(6)	115(2)
S(1)–Sn(1)–N(1)	82.4(2)	C(4)–C(5)–C(10)	123(2)
S(1)–Sn(1)–N(1)′	103.4(2)	C(6)–C(5)–C(10)	121(2)
S(1)–Sn(1)–O(1)	90.5(3)	C(5)–C(6)–C(7)	120(1)
S(1)–Sn(1)–O(1)′	164.5(3)	Br(1)–C(7)–C(6)	119(1)
S(1)–Sn(1)–N(1)	103.4(2)	Br(1)–C(7)–C(8)	121(1)
S(1)–Sn(1)–N(1)′	82.4(2)	C(6)–C(7)–C(8)	120(1)
O(1)–Sn(1)–O(1)′	83.1(3)	C(7)–C(8)–C(9)	120(1)
O(1)–Sn(1)–N(1)	83.6(3)	C(8)–C(9)–C(10)	120(1)
O(1)–Sn(1)–N(1)′	89.9(3)	O(1)–C(10)–C(5)	126(2)
O(1)–Sn(1)–N(1)	83.6(3)	O(1)–C(10)–C(9)	116(2)
N(1)–Sn(1)–N(1)′	171.3(3)	C(5)–C(10)–C(9)	118(2)
C(2)–N(1)–C(4)	117(2)	S(1)–C(1)–C(2)	112(1)

Numbers in parentheses are e.s.d.s in the least significant digits. Symmetry code $-x$, y, $0.5-z$.

90.70°, and the bond angle between the tin and two adjacent donor atoms is almost 90°.

The Sn–N and Sn–O bond distances (2.19(1) and 2.039(9) Å, respectively) are close to those observed in other octahedral Sn complexes containing similar ligands: (cf. average values of 2.17 and 2.07 Å, respectively, in bis{2-(2-mercaptophenyl)iminomethyl-4,6-dimethoxyphenoxy}tin(IV) [2]; and 2.23 and 2.05 Å, respectively, in bis{2-(2-selenidophenyl)iminomethylphenoxy}tin(IV) [12]), and in the trigonal bipyramidal organotin compound $(C_6H_5)_2SnL$, where L is the dianionic tridentate Schiff base 2-[(*o*-hydroxyphenyl)benzothiazoline] (2.22 and 2.09 Å, respectively) [13]. The Sn–S bond length (2.432(4) Å) is in the same range as that observed in bis{2-(2-mercaptophenyl)iminomethyl-4,6-dimethoxyphenoxy}tin(IV) (2.47 Å) [2], $Sn(C_5H_4NS)_4$ (2.469 Å) [14] and the mixed octahedral complex $Sn(C_6H_5S)_4 \cdot$bipy (2.50 Å) [11].

In each ligand the phenyl ring is planar and the phenolic oxygen and imine group lie in the ring plane. Bond lengths and angles within the Schiff base are as expected; in particular, the C–N bond length (1.30 Å) is typical of a C=N bond [15].

3.2. Spectroscopic studies

The IR spectra of the complexes are consistent with the above structural data. In the spectra there are no

Table 5
^1H and ^{119}Sn NMR data

Compound	OH	N=CH	Aromatic	N–CH$_2$	S–CH$_2$	R	$J(^{119}Sn–N=CH)$	δ ^{119}Sn
$H_2L_2^1$	13.2s	8.38s	6.8–7.4	3.92t	3.04t			
SnL_2^1		8.42s	6.7–7.3	4.06m (Hα)	3.15m (Hα)		39.9	
				3.84m (Hβ)	3.10m (Hβ)			
$H_2L_2^2$	11.4s	8.45s	5.94d, 5.69d	3.78t	2.95t	3.78 (OCH_3)		
SnL_2^2		8.63s	5.8d, 5.5d	4.0m (Hα)	2.95m (Hα)	3.7, 3.8	39.9	−457.7
				3.75m (Hβ)	3.05m (Hβ)			
$H_2L_2^3$	9.5s	8.37s	6.8–7.0	3.91t	3.01t	4.13m, 1.5t		
SnL_2^3		8.41s	6.6–6.9	4.1m (Hα)	3.0m (Hα)	3.9m, 1.28t	39.9	−459.0
				3.9m (Hβ)	3.4m (Hβ)			

Table 6
^{13}C NMR data for complexes

Compound	C_1	C_2	$C_{4,6}$	$C_{3,5}$	CH=N	N–CH$_2$	S–CH$_2$	R
$H_2L_2^1$	118.88	161.24	132.71	118.95	166.62	58.24	39.47	
			131.72	117.26				
SnL_2^1	117.41		136.02	123.19	171.21	58.56	27.33	
			134.76	117.41				
$H_2L_2^2$	102.65	172.64	160.94	94.95	166.52		39.37	55.68 (OCH_3)
			160.04	88.74				55.62 (OCH_3)
SnL_2^2	104.18	171.02	167.27	97.77	164.56	58.63	27.60	55.64 (OCH_3)
			161.89	89.58				55.35 (OCH_3)
$H_2L_2^3$	118.87	151.93	123.39	147.87	166.72	57.91	39.46	64.95 (OCH_2)
			118.33	115.89				15.14 (CH_3)
SnL_2^3	116.86	158.76	126.63	151.55	171.45	58.12	27.19	64.65 (OCH_2)
			119.12	118.79				14.92 (CH_3)

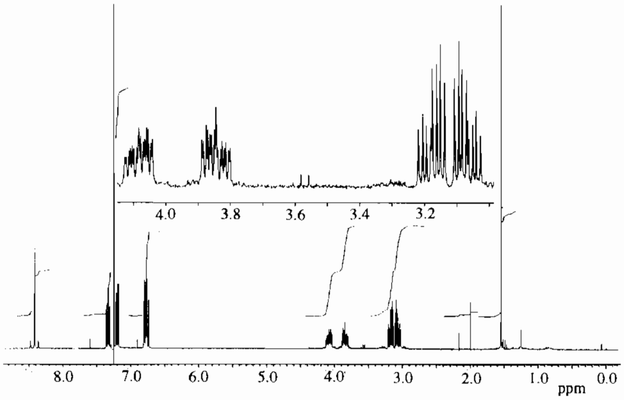

Fig. 3. ^1H NMR spectrum of SnL_2^1 in $CDCl_3$.

bands assignable to ν(O–H), indicating loss of the phenolic hydrogen of the free ligand, and the ν(C=N) band is shifted to lower frequency by between 10 and 20 cm^{-1}. These features indicate coordination through the oxygen and nitrogen atoms.

In the ^1H NMR spectra (Table 5) the lowfield signal corresponding to the phenolic OH in the free ligands is not seen, confirming the deprotonation of this group. The signals for HC=N (between 8.3 and 8.6 ppm) are shifted slightly further downfield than those of the free ligand, while the aromatic signals for the di- or tri-substituted complexes (6.5–7.5 ppm) shift very slightly upfield, as do those of the tetrasubstituted 4,6-dimethoxy derivative SnL_2^2, which appear as two upfield singlets (5.8 and 5.5 ppm). The methoxy group appears as two separate singlets (3.7 and 3.8 ppm) in this compound.

Both N–CH$_2$ and S–CH$_2$ methylene hydrogens appear as pairs of triplets in the ligands, but in the complexes they are chemically non-equivalent. This confirms that the nitrogen and sulfur atoms are coordinated, fixing the –CH_2CH_2– rotamer and thus holding the hydrogens in chemically different environments.

Table 7
Mössbauer parameters (mm s^{-1})[a]

Compound	δ^b	ΔE_Q	Γ
SnL_2^2	0.63	0.37	0.78
SnL_2^3	0.66	0.57	0.80
SnL_2^4	0.67	0.66	0.82

[a] Spectra were recorded at 80 K.
[b] Relative to SnO_2 at room temperature.

In the case of SnL_2^2, signal intensities suggested, and an H,H COSY experiment (Fig. 2) confirmed, that one of the N–CH_2 methylenic hydrogens overlapped one of the signals of the OCH_3 groups. In the complexes these signals appear as multiplets, due to coupling between the four methylene hydrogens. A double irradiation experiment confirmed that in the complexes, the signals for the N–CH_2 group also show coupling to the imine hydrogen ($J \approx 1.5$ Hz). In the case of SnL_2^1 (Fig. 3) the coupling constants for the methylenes fall in the expected ranges for geminal ($J \approx 13$ Hz), *cis*-vicinal ($J \approx 4$ Hz) and *trans*-vicinal ($J \approx 7$ Hz) couplings. The $J(^{119}Sn–N=CH)$ coupling constants (all ~39 Hz, as in analogous compounds) [2,12] indicate strong N–Sn coordination.

In the ^{13}C NMR spectra of the complexes (Table 6) the signals assigned to the N–CH_2 and HC=N carbon atoms are shifted downfield of the corresponding signals in the free ligand spectrum, except for the HC=N signal of the 4,6-dimethoxy derivative. This tin compound also shows a Mössbauer spectrum slightly different from the other (vide infra); we do not know if this behavior is due to a structural or to an electronic effect. It should be noted that the presence of the bulky methoxy substituent in the 6 position could introduce steric effect which may force the imine group out of the plane of the aromatic ring. In all cases the S–CH_2 carbon is shifted upfield in the complex.

In the ^{119}Sn NMR spectra the Sn signal appeared at −458 ppm relative to Me_4Sn, as observed in bis-{2-(2-mercaptophenyl)iminomethyl-4,6-dimethoxyphenoxy}tin(IV) (which has the same atoms around the tin atom) [2].

The ^{119}Sn Mössbauer spectra (Table 7) did not differ essentially from those of inorganic Sn(IV) complexes with slightly distorted octahedral geometry. The isomer shifts (0.63–0.67 mm^{-1}) were not affected by the ring substituents, suggesting that the electron density distribution is similar in all compounds. However, the low quadrupole splitting (0.37 mm^{-1}) of the dimethoxy derivative (SnL_2^2) indicates a higher symmetry around the metallic atom.

4. Supplementary material

Crystallographic data have been deposited as Supplementary Publication No. CSD 57979. Copies can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, Germany.

References

[1] J. Castro, J. Romero, J.A. García-Vázquez, M.L. Durán, A. Castiñeiras, A. Sousa and D.E. Fenton, *J. Chem. Soc., Dalton Trans.*, (1990) 3225.

[2] E. Labisbal, A. de Blas, J.A. García-Vázquez, J. Romero, M.L. Durán, A. Sousa, N.A. Bailey, D. Fenton, P.B. Leeson and R.V. Parish, *Polyhedron, 11* (1992) 227.

[3] E. Labisbal, J.A. García-Vázquez, C. Gómez, A. Macías, J. Romero, A. Sousa, U. Englert and D.E. Fenton, *Inorg. Chim. Acta, 203* (1993) 67.

[4] J.J. Habeeb, D.G. Tuck and F.H. Walters, *J. Coord. Chem., 8* (1978) 27.

[5] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

[6] C.M. Sheldrick, *SHELXS86*, program for solution of crystal structures from X-ray diffraction data, University of Göttingen, Germany, 1986.

[7] B.A. Frenz & Associates Inc., *Structure Determination Package; SDP/VAX V.2.2*, College Station, Texas, USA, and Enraf-Nonius, Netherlands, 1985.

[8] W.H. Zachariasen, *Acta Crystallogr., 16* (1963) 1139.

[9] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974.

[10] E. Keller, *SCHAKAL*, program for plotting molecular and crystal structures, University of Freiburg, Germany, 1988.

[11] J.L. Hencher, M. Khan, F.F. Said, R. Sieler and D.G. Tuck, *Inorg. Chem., 21* (1982) 2787.

[12] E. Labisbal, J. Romero, M.L. Durán, J.A. García-Vázquez, A. Sousa, U. Russo, R. Pritchard and M. Renson, *J. Chem. Soc., Dalton Trans.*, (1993) 755.

[13] H. Preut, H.J. Haupt, F. Huber, R. Cefalu and R. Barbieri, *Z. Anorg. Allg. Chem., 407* (1974) 257.

[14] L.C. Damude, P.A.W. Dean, V. Manivannan, R.S. Srivastava and J.J. Vittal, *Can. J. Chem., 68* (1990) 1323.

[15] J.N. Brown, R.L. Towns and L.M. Trefonas, *J. Am. Chem. Soc., 92* (1972) 7436.