Structure of Tin(IV) Complexes of 2-(2-Selenidophenyl)iminomethylphenols formed by Electrochemical Cleavage of a Diselenide Bond†

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The anodic oxidation of tin in an acetonitrile solution of the Schiff bases derived from bis(2-aminophenyl) diselenide and an appropriate salicylaldehyde yields tin(IV) compounds. The crystal structure of one, bis[2-(2-selenidophenyl)iminomethylphenoxo]tin(IV), was determined. The tin atom has octahedral co-ordination geometry with facial ligand occupancy. The Sn–N, Sn–O and Sn–Se bond lengths are 2.23(1), 2.04(1) and 2.558(2) Å respectively.

The electrochemical reductive cleavage of a disulfide bond as in compounds I–III has been shown to be an efficient route to metal complexes of copper(II), zinc(II) and cadmium(II) containing anionic sulfur.[1,2] More recently we have described the synthesis and crystal structure of bis[2-(2-sulfidophenyl)-iminomethyl-4,6-dimethoxyphenoxo]tin(IV),[3] which was prepared from Sn as the anode of an electrochemical cell and the Schiff base I [R = H, 3-OEt, 4,6-$(OMe)_2$ or 5-Br].

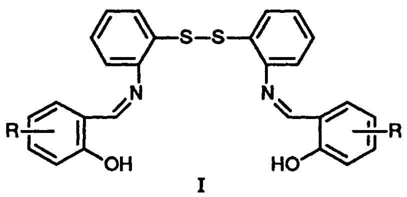
We have now extended this method to the synthesis of neutral complexes containing anionic selenium atoms by electrochemical cleavage of a diselenide bond. Here we report the synthesis of neutral complexes of tin(IV) derived from Schiff bases IV [R = H or 4,6-$(OMe)_2$] and the crystal structure of bis[2-(2-selenidophenyl)iminomethylphenoxo]tin(IV), $[SnL^1{}_2]$.

Experimental

Microanalysis was carried out on a Perkin Elmer 240B microanalyser. Infrared spectra were recorded on a Perkin Elmer 180 spectrophotometer, ^1H and ^{119}Sn spectra on a Bruker WM 250 MHz spectrometer. The Mössbauer spectroscopic data were obtained at 80 K on a constant-acceleration apparatus with a $Ca^{119}SnO_3$ source.

Syntheses.—Acetonitrile and salicylaldehydes were used as supplied. Tin metal (Ega Chemie) was used as rods. Bis(2-aminophenyl) diselenide was prepared by hydrazine hydrate reduction[4] of bis(2-nitrophenyl) diselenide obtained by nucleophilic displacement from 1-chloro-2-nitrobenzene.[5]

Schiff-base Formation.—The Schiff bases were prepared by refluxing bis(2-aminophenyl) diselenide with the corresponding salicylaldehydes in a 1:2 mole ratio using $CHCl_3$ as solvent, until the theoretical amount of water was collected in a Dean–Stark trap. The final brown solutions were concentrated in a rotary evaporator and stirred with hexane to give yellow solids. The purity of the Schiff bases obtained was checked by recording their IR and ^1H NMR spectra.



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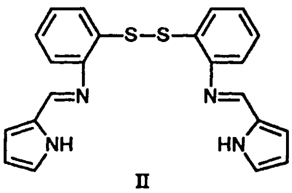

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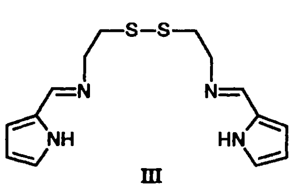

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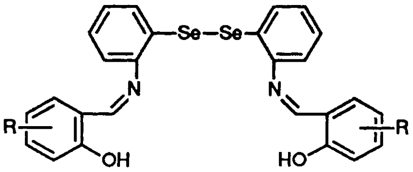

IV

Electrochemical Syntheses.—The electrochemical method used for the synthesis of the complexes was similar to that described by Oldham and Tuck.[6] The cell was a tall-form beaker (100 cm^3), the anode a tin rod and the cathode a platinum wire. All syntheses were carried out in acetonitrile under dry nitrogen, which was gently bubbled through the solution. As the ligands used are poorly soluble it was necessary to use hot acetonitrile. Tetramethylammonium perchlorate was added to the solution as supporting electrolyte. The cell can be summarized as Pt(−)|MeCN + Schiff base|Sn(+). As the electrolysis proceeded hydrogen gas was evolved at the cathode.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Experimental conditions for the electrochemical synthesis and analytical data for the complexes[a]

R	Compound	Amount of ligand (g)[b]	Initial voltage (V)[c]	t/h	Metal used (mg)	E_f/mol F^{-1}	Analysis (%) C	N	H
H	$[SnL^1{}_2]\cdot H_2O$	0.2	15	2	68	0.51	46.0 (45.6)	4.3 (4.1)	2.8(2.9)
4,6-(OMe)$_2$	$[SnL^2{}_2]\cdot 2CNMe$	0.2	20	1	33	0.50	47.3 (46.9)	6.1 (6.4)	3.4(3.7)

[a] Calculated values in parentheses. [b] Plus NMe_4ClO_4 (*ca.* 10 mg). [c] Voltage to produce a current of 15 mA.

Table 2 Final atomic coordinates for $[SnL^1{}_2]$

Atom	x	y	z
Sn	0	0	0.1649(1)
Se(1)	−0.0012(5)	0.2522(3)	0.3002(1)
O(1)	0.036(1)	0.169(2)	0.040(1)
O(2)	0	0.5000	−0.028(2)
N(1)	0.176(1)	0.041(5)	0.163(1)
C(1)	0.233(1)	0.026(7)	0.074(2)
C(2)	0.217(2)	0.109(3)	0.265(2)
C(3)	0.148(2)	0.197(3)	0.340(2)
C(4)	0.195(2)	0.270(4)	0.435(2)
C(5)	0.300(3)	0.266(4)	0.473(3)
C(6)	0.363(2)	0.167(4)	0.396(2)
C(7)	0.328(2)	0.087(3)	0.287(2)
C(8)	0.197(1)	−0.012(9)	−0.028(1)
C(9)	0.098(2)	0.116(3)	−0.042(2)
C(10)	0.076(2)	0.177(3)	−0.159(2)
C(11)	0.138(3)	0.169(4)	−0.250(3)
C(12)	0.236(3)	0.082(3)	−0.231(2)
C(13)	0.269(2)	−0.031(4)	−0.128(1)

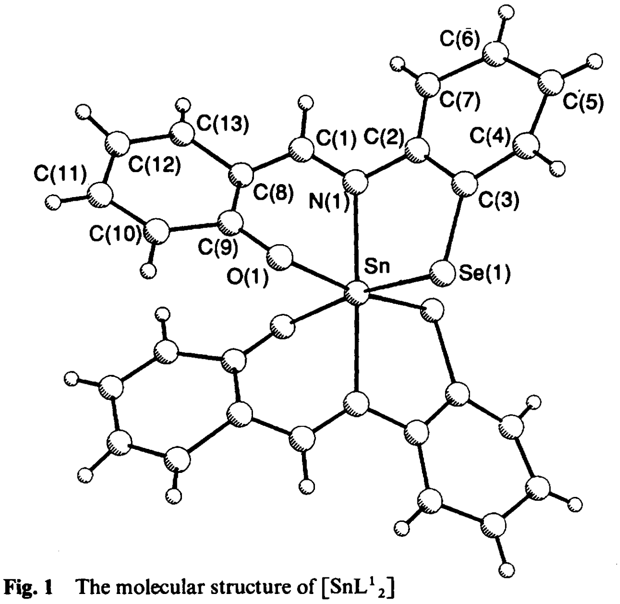

Fig. 1 The molecular structure of $[SnL^1{}_2]$

At the end of the reactions a very small amount of yellow solid was filtered off, but we were unable to recover any characterizable product from it. Concentration of the solution phase by slow evaporation at room temperature yielded crystalline solids which were collected, washed with acetonitrile and diethyl ether and dried *in vacuo*.

Details of the experimental conditions for the reactions and the analytical data for the compounds are in Table 1.

Crystal Structure Determination.—A yellow triangular prism of $[SnL^1{}_2]$ of approximate dimensions 0.25 × 0.25 × 0.10 mm was mounted on a glass fibre in a CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). The cell constants were determined from setting angles for 20 reflections in the range $19.30 < 2\theta < 28.70°$. The systematic absences observed suggested the space group to be $P2_12_12$(18).

Crystal data. $C_{26}H_{20}N_2O_3Se_2Sn$, M 685.07, orthorhombic, $a = 12.516(6)$, $b = 7.888(4)$, $c = 11.886(5)$ Å, $U = 1173(2)$ Å^3, $Z = 2$, $D_c = 1.939$ g cm^{-3}, $F(000) = 664$, $\mu = 41.95$ cm^{-1}.

With ω–2θ scanning, a total of 2355 reflections were collected in the range $\theta = 0$–25°. From 2150 unique reflections ($R_{int} = 0.044$), 1355 with $I_o > 2\sigma(I_o)$ were considered as observed and used for refinement. An empirical absorption correction was applied using the program DIFABS.[7] The data were corrected for Lorentz and polarization effects.

The structure was resolved by the Patterson method to find the Se atom. The remaining non-hydrogen atoms were found by subsequent Fourier synthesis, prior to anisotropic refinement. Hydrogen atoms were placed in chemically reasonable positions, except for those bound to the water molecule which were ignored. Correlation problems, caused by the Se and Sn atoms conforming to pseudo-mirror planes perpendicular to c, hindered refinement. The final cycle of full-matrix least-squares refinement based on 150 variable parameters converged to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.070$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}} = 0.068$, with $w = 1/[\sigma^2(F_o) + 0.03F_o{}^2]$. Refinement of the alternative enantiomers did not produce a significantly different R. Neutral atom scattering factors were taken from ref. 8. All calculations were performed using the TEXSAN[9] crystallographic software package.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

Results and Discussion

The electrochemical oxidation of metallic tin in acetonitrile in the presence of the preformed diselenide Schiff base gave solutions which, after evaporation in air at room temperature, yielded compounds $[SnL_2]$. The electrochemical efficiency E_f, defined as moles of metal dissolved per Faraday of charge, was about 0.5 mol F^{-1}. This value and the evolution of hydrogen at the cathode, are compatible with the formation of Sn^{II} followed by oxidation to Sn^{IV} in the solution (Scheme 1). This behaviour has been observed in the electrochemical synthesis of other tin(IV) complexes.[3,10]

$$\begin{array}{ll} \text{cathode:} & \tfrac{1}{2}\text{IV} + 2e^- \longrightarrow L^{2-} + \tfrac{1}{2}H_2 \\ \text{anode:} & L^{2-} + Sn \longrightarrow [SnL] + 2e^- \\ & [SnL] + \tfrac{1}{2}\text{IV} \longrightarrow [SnL_2] + \tfrac{1}{2}H_2 \end{array}$$

Scheme 1

Structure of $[SnL^1{}_2]\cdot H_2O$.—The molecular structure of $[SnL^1{}_2]$, with the atom labelling, is illustrated in Fig. 1. Final atomic coordinates are given in Table 2 and bond lengths and angles, with estimated standard deviations, in Table 3. The tin atom is co-ordinated to the selenium, imino nitrogen and phenolate oxygen atoms of two bianionic tridentate ligands. A crystallographic two-fold axis, which passes through the tin atom, relates the two ligands. The co-ordination polyhedron of the Sn atom is a slightly distorted octahedron: the metal atom is only 0.024 Å below the best equatorial plane defined by the two oxygen atoms and the two selenium atoms, and the angle defined by the two *trans* axial nitrogens and the tin atom is 179.0(8)° very close to the expected 180°. In addition, the angles determined by the tin atom and pairs of *cis* donor atoms are close to 90°.

In the complex the ligands adopt a position such that the complex can be described as a facial isomer, with a dihedral angle of only 10° between the planes defined by the three donor atoms of each ligand. This contrasts with the structure of the analogous sulfido derivative, in which the two ligands are arranged meridionally around the tin atom.[3] In each ligand the phenyl rings are planar, and the four-atom C–C–N–C chain linking the rings is also nearly planar. However, the two phenyl rings are twisted in the same direction with respect to the C–C–N–C chain with torsion angles of C(1)N(1)C(2)C(3) 150(4)° and N(1)C(1)C(8)C(9) 48(7)°, so allowing facial arrangement of the three donor atoms.

The Sn–N and Sn–O bond lengths, 2.23(1) and 2.04(1) Å respectively, are close to the average values found in the octahedral compound bis-[2-(2-sulfidophenyl)iminomethyl-4,6-dimethoxyphenoxo]tin(IV), 2.17 and 2.07 Å,[3] and are also very similar to the 2.217(3) and 2.093(2) Å found in the organotin compound [$SnPh_2L$] [L = the tridentate dianion of the Schiff base 2-(*o*-hydroxyphenyl)benzothiazoline], which exhibits trigonal-bipyramidal co-ordination.[11] However, the Sn–O bond length is shorter than the 2.21(2) Å found in the six-co-ordinate complex [*N*,*N*′-ethylenebis(salicylideneiminato)]-dimethyltin(IV).[12] The Sn–N distance is just under the range 2.24–2.37 Å reported for other octahedral complexes.[12] No data for Sn–Se distances in octahedral tin(IV) compounds could be found in the literature, but the value 2.558(2) Å is as expected, longer than the average value found in tetrahedral $Sn(SePh)_4$, 2.512 Å.[13]

The crystal structure is completed by a water molecule, which is located on a crystallographic two-fold axis at a distance of 2.77(1) Å from the co-ordinated phenolate oxygen atoms. Infinite hydrogen-bonded chains of complex and water molecules are thus formed parallel to the *b* axis (Fig. 2).

The IR spectra of both complexes are consistent with the X-ray data presented above. There are no bands attributable to ν(O–H), indicating that the phenolic hydrogen is lost in the electrochemical procedure, and the band attributable to ν(C=N) is shifted to lower wavenumbers by 10–20 cm^{-1}. These features show that co-ordination takes place through the phenolic oxygen and azomethine nitrogen atoms.[14]

The ^1H NMR spectra of the complexes (Table 4) do not show the OH signal which for the free ligand appears as a singlet around δ 12.6, confirming deprotonation of the ligand. The HC=N signals, between δ 8.5 and 8.9, are slightly shifted as compared with the free ligand. The aromatic protons are found around δ 6.5–7.5, and two singlets at δ 5.8 and 5.5 in the spectrum of the 4,6-dimethoxy derivative are attributed to the two protons of the tetrasubstituted ring. In the spectrum of this complex the signal of the two OCH_3 groups appears as two separated singlets at δ 3.8 and 3.6. The coupling constants $J(^{119}Sn\text{–}N\text{=}CH)$ 39.1 for [$SnL^1{}_2$] and 39.9 Hz for [$SnL^2{}_2$] are similar to that found for the sulfido derivative,[3] and indicative of a strong N–Sn co-ordination bond. The ^{119}Sn NMR spectrum of [$SnL^1{}_2$], recorded in $CDCl_3$ with $SnMe_4$ as standard, shows a signal at δ −608.8.

Table 3 Bond distances (Å) and angles (°) for [$SnL^1{}_2$]

Sn–Se(1)	2.558(2)	C(4)–C(5)	1.39(4)
Sn–O(1)	2.04(1)	C(5)–C(6)	1.45(4)
Sn–N(1)	2.23(1)	C(6)–C(7)	1.51(3)
Se(1)–C(3)	1.97(2)	C(8)–C(9)	1.60(5)
O(1)–C(9)	1.32(2)	C(8)–C(13)	1.49(2)
N(1)–C(1)	1.28(2)	C(9)–C(10)	1.50(3)
N(1)–C(2)	1.43(2)	C(10)–C(11)	1.33(3)
C(1)–C(8)	1.33(3)	C(11)–C(12)	1.43(4)
C(2)–C(3)	1.42(3)	C(12)–C(13)	1.57(3)
C(2)–C(7)	1.42(3)	O(1) · · · O(2)	2.77(1)
C(3)–C(4)	1.40(3)		
Se(1)–Sn–Se(1′)	102.1(1)	Se(1)–C(3)–C(2)	122(1)
Se(1)–Sn–O(1)	87.1(4)	Se(1)–C(3)–C(4)	120(2)
Se(1)–Sn–O(1′)	164.2(4)	C(2)–C(3)–C(4)	117(2)
Se(1)–Sn–N(1)	84.2(8)	C(3)–C(4)–C(5)	131(3)
Se(1)–Sn–N(1′)	96.4(8)	C(4)–C(5)–C(6)	109(3)
O(1)–Sn–O(1′)	86.9(7)	C(5)–C(6)–C(7)	128(2)
O(1)–Sn–N(1)	71.6(7)	C(2)–C(7)–C(6)	113(2)
O(1)–Sn–N(1′)	107.6(7)	C(1)–C(8)–C(9)	102(3)
N(1)–Sn–N(1′)	179.0(8)	C(1)–C(8)–C(13)	123(2)
Sn–Se(1)–C(3)	88.5(7)	C(9)–C(8)–C(13)	116(2)
Sn–O(1)–C(9)	117(1)	O(1)–C(9)–C(8)	125(2)
Sn–N(1)–C(1)	123(1)	O(1)–C(9)–C(10)	119(2)
Sn–N(1)–C(2)	114(1)	C(8)–C(9)–C(10)	116(2)
C(1)–N(1)–C(2)	123(2)	C(9)–C(10)–C(11)	129(3)
N(1)–C(1)–C(8)	126(2)	C(10)–C(11)–C(12)	113(3)
N(1)–C(2)–C(3)	120(2)	C(11)–C(12)–C(13)	129(2)
N(1)–C(2)–C(7)	117(2)	C(8)–C(13)–C(12)	114(3)
C(3)–C(2)–C(7)	123(2)		

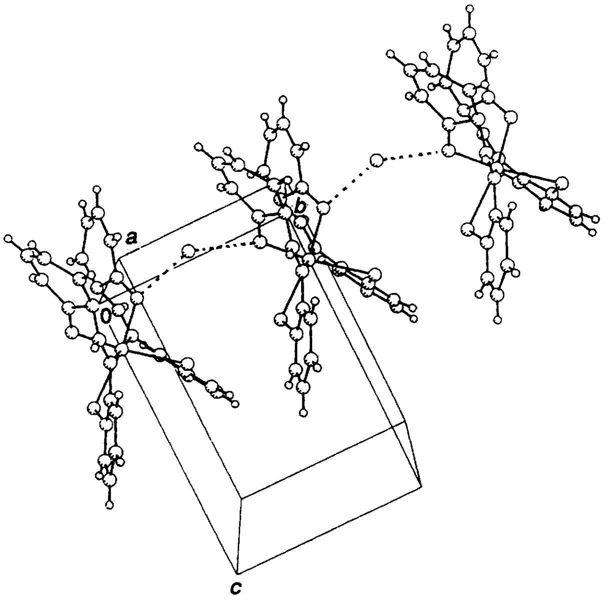

Fig. 2 A view of the unit cell of [$SnL^1{}_2$], showing proposed hydrogen bonds

Table 4 Proton and ^{119}Sn NMR data

	δ(Schiff base)			δ(SnL_2)			
R	OH	N=CH	R	N=CH	R	$J(^{119}Sn\text{–}N\text{=}CH)$/Hz	$\delta(^{119}Sn)$
H	12.7 (s, 1 H)	8.6 (s, 1 H)	—	8.5 (s, 1 H)	—	39.1	
4,6-$(OMe)_2$	12.5 (s, 1 H)	9.0 (s, 1 H)	3.8 (s, 6 H)	8.9 (s, 1 H)	3.8 (s, 3 H) 3.6 (s, 3 H)	39.9	−608.8

Table 5 Mössbauer parameters (mm s^{-1})[a]

R	δ[b]	ΔE_Q	Γ
H	0.83	0.69	0.87
4,6-$(OMe)_2$	0.76	0.51	0.75

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

The ^{119}Sn Mössbauer spectra (Table 5) show parameters characteristic of inorganic tin(IV) derivatives with slightly distorted octahedral geometry. As expected, the presence of the two methoxy groups does not affect the isomer shift because they do not influence the electron density of the aromatic ring; on the contrary, some influence is evident on the quadrupole splitting, as the symmetry around the tin atom is apparently increased. A comparison with the homologous sulfur derivatives[3] shows that the quadrupole splitting remains virtually the same. This seems to indicate that the small differences in the bond angles and distances around the tin atom between the two pairs of homologous complexes are compensated by a redistribution of electrons in the s and p tin orbitals. Further, this redistribution may explain the decrease in isomer shift (about 0.2 mm s^{-1}) as it cannot be due to differences between the electronegativities of sulfur and selenium.

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