Registry No. *anti-p-(R,S)*-[Co(Me(tren))(NH_3)Cl]($ZnCl_4$), 81521-71-3; $(+)_{505}$-*anti-p-(S)*-[Co(Me(tren))(NH_3)Cl]($ZnCl_4$), 81521-73-5; *s-(RS)*-[Co(Me(tren))(NH_3)Cl]($ZnCl_4$)·H_2O, 81505-45-5; *t*-[Co(Me(tren))(NH_3)Cl]Cl_2, 81497-06-5; $(-)_{505}$-*t*-[Co(Me-(tren))(NH_3)Cl]((+)-$AsC_4H_2O_6$)$_2$, 81521-75-7; $(-)_{505}$-*t*-[Co-(tren))(NH_3)Cl]Cl_2, 81521-76-8; *anti-p-(RS)*-[Co(Me(tren))-(NH_3)Cl](ClO_4)$_2$, 81521-77-9; $(+)_{505}$-*anti-p-(S)*-[Co(Me(tren))-(NH_3)Cl]((+)-$AsC_4H_2O_6$)$_2$, 81521-78-0; $(-)_{505}$-*anti-p-(R)*-[Co-(Me(tren))(NH_3)Cl]($ZnCl_4$), 81521-80-4; *syn-p*-[Co(Me(tren))-(NH_3)Cl](ClO_4)$_2$, 81521-81-5; *syn-p*-[Co(Me(tren))(NH_3)Cl]-($ZnCl_4$), 81521-82-6; *syn-p*-[Co(Me(tren))(NH_3)Cl]Cl_2, 81521-64-4; *s*-[Co(Me(tren))(NH_3)Cl](ClO_4)$_2$, 81497-03-2; *anti-p*-[Co(Me-(tren))(NH_3)Br](ClO_4)$_2$, 81570-13-0; *syn-p*-[Co(Me(tren))(NH_3)-Br](ClO_4)$_2$, 81521-65-5; *s*-[Co(Me(tren))(NH_3)Br](ClO_4)$_2$, 81497-04-3; *anti-p*-[Co(Me(tren))(NH_3)N_3](ClO_4)$_2$, 81521-66-6; *s*-[Co-(Me(tren))(NH_3)N_3](ClO_4)$_2$, 81497-05-4; *syn-p*-[Co(Me(tren))-(NH_3)N_3][CoO_4]$_2$, 81521-67-7; *syn-p-(S)*-[Co(Me(tren))(NH_3)Cl]$^{2+}$, 81521-68-8; *syn-p-(R)*-[Co(Me(tren))(NH_3)Cl]$^{2+}$, 81521-69-9; *s-(S)*-[Co(Me(tren))(NH_3)Cl]$^{2+}$, 81521-70-2; *s-(R)*-[Co(Me-(tren))(NH_3)Cl]$^{2+}$, 81521-59-7; *anti-p*-[Co(Me(tren))(NH_3)$_2$]$^{3+}$, 69208-25-9; *s*-[Co(Me(tren))(NH_3)$_2$]$^{3+}$, 69307-77-3; *t*-[Co(Me-(tren))(NH_3)(OH_2)]$^{3+}$, 81497-00-9; *s*-[Co(Me(tren))(NH_3)(OH_2)]$^{3+}$, 81521-60-0; *anti-p*-[Co(Me(tren))(NH_3)(OH_2)]$^{3+}$, 81521-61-1; *syn-p*-[Co(Me(tren))(NH_3)(OH_2)]$^{3+}$, 81521-62-2; *anti-p*-[Co(Me-(tren))(NH_3)(OH)]$^{2+}$, 81497-01-0; *s*-[Co(Me(tren))(NH_3)(OH)]$^{2+}$, 81521-63-3; Me(tren), 81497-21-4; Me(tren)·3HCl, 81497-22-5; [Co(Me(tren))(NO_2)$_2$]Cl, 81497-02-1; [Co(Me(tren))Cl_2](ClO_4), 69991-09-9; tren, 4097-89-6; CH_3I, 74-88-4; (phenylsulfonyl)aziridine, 10302-15-5; 2,2′-diphthalimidodiethylamine, 63563-83-7; 2,2′-diphthalimido-2″-(benzenesulfamido)triethylamine, 81497-23-6; 2,2′-diphthalimido-2″-(*N*-methylbenzenesulfonamido)triethylamine, 81497-24-7; ethylenimine, 151-56-4; phthalic anhydride, 85-44-9; diethylenetriamine, 111-40-0.

Supplementary Material Available: Listings of crystal positional coordinates and thermal parameters (Table XIII), F_o and F_c (Table XIV), and hydrogen-bonding distances (Table XV) (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Windsor, Windsor, Ontario, Canada N9B 3P4

Direct Electrochemical Synthesis of Benzenethiolato Complexes of Tin(II), Tin(IV), and Lead(II). Molecular Structure of the 2,2′-Bipyridine Adduct of $Sn(SC_6H_5)_4$

J. LAWRENCE HENCHER, MASOOD KHAN, FAROUQ F. SAID, ROBERT SIELER, and DENNIS G. TUCK*

Received August 25, 1981

The electrochemical oxidation of tin into solutions of RSH (R = C_6H_5 $C_6H_4CH_3$) gives $Sn(SR)_2$. When 2,2′-bipyridine (bpy) or 1,10-phenanthroline is added to the solution phase, the product is the tin(IV) species $Sn(SR)_4L$. The electrochemical oxidation is shown to involve Sn(II) as the first product in each case. The crystal structure of $Sn(SC_6H_5)_4$bpy is monoclinic, with a = 13.150 (5) Å, b = 17.438 (6) Å, c = 14.215 (6) Å, β = 93.49 (3)°, V = 3254 (2) Å^3, Z = 4, and space group $P2_1/n$ (C_{2h}^5, No. 14). The molecule has a distorted octahedral SnS_4N_2 kernel, with bond distances of 2.449 (Sn–S) and 2.331 Å (Sn–N). With a lead anode, the product is $Pb(SC_6H_5)_2$; no lead(IV) species could be isolated.

Introduction

Compounds in which tin is bonded to a mercaptide ligand have been known for many years, and the preparative routes to $Sn(SR)_4$ compounds and the corresponding $R_nS(SR')_{4-n}$ species are well established.[1,2] Derivatives of tin(II) with such ligands are not so well-known, although some preparative and spectroscopic work has been reported.[3] Similarly, the chemistry of lead–thiolato compounds is well established.[4]

Applications of direct electrochemical synthesis in inorganic and organometallic chemistry have formed the subject of a number of recent papers from this laboratory. We have recently found that the electrochemical oxidation of a metal in the presence of thiols or disulfides is a convenient direct synthesis of neutral and anionic thiolato complexes of elements such as zinc, cadmium, mercury, gallium, indium, and thallium.[5,6] The present paper reports the extension of this work to tin and lead. Complexes with alkanethiolates were not obtained, but both tin(II), and lead(II) arenethiolates were easily prepared. Appropriate changes in the solution conditions gave rise to adducts of the tin(IV) thiolates with ligands such as 2,2′-bipyridine (bpy), although no such product could be obtained with lead. In the course of characterizing these materials, we carried out an X-ray structural analysis of Sn-$(SC_6H_5)_4$·bpy, and the results of this study lead to a comparison with data for related compounds.

Experimental Section

General Data. Solvents were distilled and dried over molecular sieves. Tin metal was washed with concentrated aqueous hydrochloric acid and distilled water and dried immediately before use. Thiols were used as supplied as were 2,2′-bipyridine and 1,10-phenanthroline.

Metal analysis was by atomic absorption spectrophotometry. Microanalysis was performed by Guelph Chemical Laboratories Ltd.

Electrochemical Procedures. The electrochemical synthesis followed the methods described in earlier papers (e.g., ref 7), with a 100-mL tall-form beaker containing solutions of the composition shown in Table I. The cells were of the general form

$$\mathrm{Pt}_{(-)}/\underset{\text{(acetone)}}{\mathrm{CH_3CN}} + \mathrm{RSH}\ \underset{\text{(phen)}}{\text{(+bpy)}}\ /\mathrm{M}_{(+)} \qquad (\mathrm{M} = \mathrm{Sn, Pb})$$

with the anode (~5 g) suspended into the solution phase on a platinum wire. The experiments were run in an atmosphere of dry nitrogen, with the solution magnetically stirred. Details of the isolation pro-

---

(1) Abel, E. W.; Armitage, D. A. *Adv. Organomet. Chem.* **1967**, *5*, 1.

(2) Schumann, H.; Schumann-Rudisch, I.; Schmidt, M. "Organotin Compounds"; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; Vol. 2, p 297.

(3) Harrison, P. G.; Stobart, S. R. *Inorg. Chim. Acta* **1973**, *7*, 306 and references therein.

(4) Abel, E. W. "Comprehensive Inorganic Chemistry"; Trotman-Dickenson, A. F., Ed.; Pergamon Press: Oxford, 1973; Vol. 2, p 134.

(5) Hencher, J. L.; Khan, M.; Said, F. F.; Tuck, D. G. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 287.

(6) Said, F. F.; Tuck, D. G. *Inorg. Chim. Acta* **1982**, *59*, 1, and unpublished results.

(7) Habeeb, J. J.; Tuck, D. G. *Inorg. Synth.* **1979**, *19*, 257.

0020-1669/82/1321-2787$01.25/0

Table I. Experimental Conditions for the Electrochemical Synthesis of $Sn(SR)_2$ and $Sn(SR)_4L$ Compounds

soln compn[a]								
thiol	*V*, mL	solvent[b]	amt of L, g	voltage,[c] V	time of electrolysis, h	amt of tin dissolved, mg	product	% yield[d]
C_6H_5SH	3	CH_3CN		20	6	155	$Sn(SC_6H_5)_2$	71
m-$CH_3C_6H_4SH$	2	CH_3CN		20	5	91	$Sn(SC_6H_4CH_3)_2$	63
C_6H_5SH	3	acetone	bpy, 0.45	25	3	68	$Sn(SC_6H_5)_4$bpy	82
o-$CH_3C_6H_4SH$	0.5	acetone	bpy, 0.2	20	5	25	$Sn(SC_6H_4CH_3)_4$bpy	78
m-$CH_3C_6H_4SH$	0.5	acetone	bpy, 0.2	25	3	28	$Sn(SC_6H_4CH_3)_4$bpy	76
C_6H_5SH	3	acetone	phen, 0.4	25	3	35	$Sn(SC_6H_5)_4$phen	84
o-$CH_3C_6H_4SH$	0.5	acetone	phen, 0.2	20	5	69	$Sn(SC_6H_4CH_3)_4$phen	75
m-$CH_3C_6H_4SH$	0.5	acetone	phen, 0.2	20	5	81	$Sn(SC_6H_4CH_3)_4$phen	83

[a] Plus 10 mg of tetraethylammonium perchlorate. [b] 50 mL. [c] Voltage required to give an initial current of 10 mA. [d] Based on metal dissolved.

Table II. Analytical and Related Results for $Sn(SR)_2$ and $Sn(SR)_4L$ Compounds

			% Sn		
compd	color	mp, °C	found	calcd	NMR spectra (in $CDCl_3$, rel to Me_4Si, with rel intens)
$Sn(SC_6H_5)_2$	golden yellow	146 dec	35.4	35.1[a]	7.05–7.5 br (Me_2SO-d_6)
$Sn(SC_6H_4CH_3$-*m*$)_2$	white	124 dec	32.3	32.4	2.2 (s, 6), 6.8–7.3 (br, 8)
$Sn(SC_6H_5)_4$bpy	yellow-green	129 (lit. 135–136)[b]	16.9	16.9[c]	7.3–9.2 (br)
$Sn(SC_6H_4CH_3$-*o*)bpy	orange	86	16.2	15.4	2.3 (s, 12), 7.0–8.85 (br, 24)
$Sn(SC_6H_4CH_3$-*m*)bpy	yellow	106	15.6	15.4	2.3 (s, 12), 7.1–8.7 (br, 24)
$Sn(SC_6H_5)_4$phen	yellow	210 dec	15.9	16.1	6.85–8.5 (br, 22), 9.65–9.85 (m, 2)
$Sn(SC_6H_4CH_3$-*o*)phen	orange	166 dec	15.0	14.9	2.25 (s, 12), 6.7–8.4 (br, 22), 9.4–9.65 (m, 2)
$Sn(SC_6H_4CH_3$-*m*)phen	yellow	139 dec	14.0	14.9	2.15 (s, 12), 6.6–8.4 (br, 22), 9.65–9.85 (m, 2)

[a] Anal. Calcd: C, 42.6; H, 3.0. Found: C, 42.2; H, 2.9. [b] Poller, R. C.; Spillman, J. A. *J. Organomet. Chem.* **1966**, *6*, 668. [c] Anal. Calcd: C, 57.4; H, 4.0. Found: C, 56.9; H, 3.8.

cedures, etc., are given below, and analytical results are set out in Table II.

$Sn(SR)_2$ (R = C_6H_5, *m*-$CH_3C_6H_4$). The solution was kept at −10 °C throughout the electrolysis. The product which precipitated as the reaction proceeded was collected, washed with petroleum ether (bp 30–65 °C), and dried. Both compounds are soluble in pyridine and dimethyl sulfoxide, slightly soluble in chloroform, and insoluble in acetone, acetonitrile, and hydrocarbon solvents. The infrared and NMR spectra confirm the presence of the benzenethiolate ligand. The appearance of the *m*-tolyl compound changed on prolonged exposure to air, going from a white solid via a dark brown solid to an oil whose NMR spectrum was identical with that of the starting material. The products of this reaction were not investigated further.

When the cell was run with acetonitrile solutions of *o*-$CH_3C_6H_4SH$, small (milligram) quantities of a very hygroscopic solid were obtained. The NMR spectrum of this material (2.3 (br, s), 7.25 (br, m)) showed the presence of the tolyl group, but no further identification was attempted.

$Sn(SR)_4L$ (R = C_6H_5, *o*- and *m*-$CH_3C_6H_4$; L = bpy, phen). In the case of the SC_6H_5/2,2′-bipyridine complex, the color of the solution changed from yellow to green as the electrolysis proceeded. The small amount of deposited material was removed by filtration, and the volume of the filtrate was reduced to ca. 25 mL; addition of diethyl ether (25 mL) followed by cooling produced crystals which were collected, washed with diethyl ether, and dried. With bpy and *o*- or *m*-$CH_3C_6H_4SH$, the solution was concentrated to 10 mL before adding 10 mL of diethyl ether and 1 mL of petroleum ether; crystals formed when this solution was cooled overnight at 0 °C.

With SC_6H_5/phen, the solvent was evaporated off, producing an oily residue, to which was added 5 mL of acetone and then 30 mL of diethyl ether; crystals were produced after ca. 12 h at 0 °C. The *o*-tolyl product was isolated in a similar fashion. For *m*-tolyl, the oily residue was treated with 10 mL of CH_3CN, 30 mL of diethyl ether, and 5 mL of petroleum ether to produce orange crystals.

$Pb(SC_6H_5)_2$. The solution phase consisted of 40 mL of acetonitrile, 1 mL of C_6H_5SH, and 20 mg of tetraethylammonium perchlorate; in a typical experiment, a voltage of 25 V produced a current of 20 mA, and 0.24 g of lead dissolved from the anode over a 5-h period. As the electrolysis proceeded, gas was evolved at the cathode and a yellow solid deposited in the bottom of the cell; this was eventually collected, washed with petroleum ether, and dried. Anal. Calcd for $PbC_{12}H_{10}S_2$: Pb, 48.7; C, 33.9; H, 2.4. Found: Pb, 47.9; C, 33.6; H, 2.4. The yield was >90%, based on metal dissolved. The same material was obtained from a cell containing 2,2′-bipyridine + C_6H_5SH + CH_3CN.

Reactions Involving *n*-C_4H_9SH and (*t*-$C_4H_9)_2S_2$. Electrolysis at room temperature in either acetone or acetonitrile resulted in dissolution of the tin anode in the usual way, and with current efficiencies (see below) which indicate the formation of a tin(II) species. A fine rust red powder deposited in the cell, and as the reaction proceeded tin metal deposited on the cathode. Despite repeated attempts, we were not able to recovery any identifiable tin compounds from the solution phase of such experiments.

For the Pb/*n*-C_4H_9SH system, approximately 100 mg of lead dissolved in 2 h (20 V, 10 mA), and a yellow solid formed as in the thiophenol experiments. This compound contained 44.2% Pb (cf. Calcd for $PbC_8H_{18}S_2$: Pb, 53.8). When either *t*-C_4H_9SH or (*t*-$C_4H_9)_2S_2$ was used in place of thiophenol, a current of ~20 mA was recorded for a 20-V applied voltage, but no lead thiolate compounds could be isolated. The quantity of lead which dissolved was small (approximately 50 mg in 3 h), and the analytical results on the products did not correspond to any reasonable formula.

Crystallographic Analysis. A pale yellow rectangular-shaped crystal of $Sn(SC_6H_5)_4$bpy mounted directly on a thin-glass fiber with its axis parallel to the long dimension was used to obtain both the cell dimensions and the intensities. All data were obtained at room temperature on a four-cycle Syntex $P2_1$ diffractometer under computer control, following the procedure described elsewhere.[8] The space group $P2_1/n$ (C_{2h}^5, No. 14) was determined from systematic absences ($h0l$ if $h + l = 2n + 1$; $0k0$ if $k = 2n + 1$). The data was corrected for Lorentz and polarization effects, but no absorption corrections were applied. Scattering factors, including anomalous dispersion and correction terms ($\Delta f'$) and $\Delta f''$) for Sn and S atoms were taken from ref 9. The cell constants and other related crystal data are given in Table III.

The structure was solved by sharpened Patterson and Fourier methods by using the computer programs SHELX 77 and other methods described previously.[8,10] In the least-squares analysis, all atoms except hydrogen were refined anisotropically in blocks as follows: Sn, S-

---

(8) Khan, M.; Steevensz, R. C.; Tuck, D. G.; Noltes, J. G.; Corfield, P. W. R. *Inorg. Chem.* **1980**, *19*, 3407.

(9) "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(10) Khan, M.; Tuck, D. G. *Acta Crystallogr., Sect. B* **1982**, *38*, 803.

Table III. Summary of Crystal Data, Intensity Collection, and Structural Refinement for $C_{34}H_{30}N_2S_4Sn_4$, $Sn(SC_6H_5)_4bpy$

cell constants	$a = 13.150$ (5) Å, $b = 17.438$ (6) Å, $c = 14.215$ (6) Å, $\beta = 93.49$ (3)°
cell volume	$V = 3254$ (2) Å^3
space group	$P2_1/n$ (C_{2h}^5, No. 14)
Z	4
M_r	711.16
ρ(calcd)	1.452 g cm^{-3}
abs coeff	$\mu = 9.72$ cm^{-1}
cryst dimens	0.5 × 0.2 × 0.2 mm
radiation	Mo Kα ($\lambda = 0.71069$ Å)
2θ angle	4–50°
scan type	coupled θ(crystal)/2θ(counter)
scan width	Kα_1 − 1° to Kα_2 + 1°
scan speed	variable, 2.02–4.88° min^{-1}
bkgd time/scan time	0.5
total reflctns measd (including stds)	6172 ($h,k,\pm l$)
unique av data	4264 [$F_o^2 > 3\sigma(F_o)^2$]; $R(I) = 1.9\%$
no. of parameters (NP)	398, blocked, see text
$R = (\Sigma\Delta/\Sigma\lvert F_o\rvert)$	0.0301
$R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$	0.0344

Table IV. Atomic Coordinates for $Sn(SC_6H_5)_4bpy$

	x/a	y/b	z/c
Sn	0.18797 (2)	0.17240 (1)	−0.08501 (1)
S(1)	0.22295 (9)	0.08589 (5)	−0.21972 (7)
S(2)	0.36591 (8)	0.20542 (6)	−0.02727 (6)
S(3)	0.15875 (8)	0.04671 (5)	−0.00689 (6)
S(4)	0.12716 (9)	0.24933 (5)	0.04885 (6)
N(1)	0.0220 (2)	0.1829 (1)	−0.1509 (2)
N(2)	0.1754 (2)	0.2753 (1)	−0.1900 (2)
C(1)	0.2535 (3)	0.3215 (2)	−0.2051 (3)
C(2)	0.2508 (4)	0.3759 (2)	−0.2752 (3)
C(3)	0.1640 (4)	0.3813 (3)	−0.3339 (3)
C(4)	0.0825 (4)	0.3350 (2)	−0.3199 (3)
C(5)	0.0890 (3)	0.2823 (2)	−0.2452 (2)
C(6)	0.0033 (3)	0.2339 (2)	−0.2218 (2)
C(7)	−0.0935 (3)	0.2388 (3)	−0.2659 (3)
C(8)	−0.1702 (4)	0.1936 (3)	−0.2353 (4)
C(9)	−0.1505 (3)	0.1431 (3)	−0.1631 (3)
C(10)	−0.0531 (3)	0.1395 (2)	−0.1230 (3)
C(11)	0.1969 (3)	0.1343 (2)	−0.3258 (3)
C(12)	0.2775 (4)	0.1782 (2)	−0.3627 (3)
C(13)	0.2616 (6)	0.2166 (4)	−0.4488 (4)
C(14)	0.1683 (7)	0.2110 (4)	−0.4977 (4)
C(15)	0.0904 (5)	0.1661 (4)	−0.4640 (3)
C(16)	0.1074 (4)	0.1295 (3)	−0.3775 (3)
C(21)	0.4475 (3)	0.1595 (2)	−0.1042 (3)
C(22)	0.4902 (3)	0.1976 (4)	−0.1745 (3)
C(23)	0.5532 (5)	0.1594 (6)	−0.2342 (4)
C(24)	0.5764 (6)	0.0856 (6)	−0.2194 (6)
C(25)	0.5374 (5)	0.0456 (5)	−0.1481 (7)
C(26)	0.4712 (4)	0.0836 (3)	−0.0894 (5)
C(31)	0.1541 (3)	0.0659 (2)	0.1152 (3)
C(32)	0.2398 (4)	0.0830 (3)	0.1696 (3)
C(33)	0.2347 (6)	0.0924 (4)	0.2675 (4)
C(34)	0.1448 (7)	0.0815 (4)	0.3062 (4)
C(35)	0.0577 (7)	0.0646 (4)	0.2537 (4)
C(36)	0.0628 (4)	0.0584 (3)	0.1562 (3)
C(41)	0.1261 (4)	0.3440 (2)	0.0018 (3)
C(42)	0.0377 (5)	0.3723 (3)	−0.0444 (3)
C(43)	0.0368 (7)	0.4444 (3)	−0.0852 (4)
C(44)	0.1222 (7)	0.4877 (4)	−0.0776 (5)
C(45)	0.2097 (7)	0.4646 (4)	−0.0307 (5)
C(46)	0.2111 (5)	0.3889 (3)	0.0107 (4)

(1)–S(4) every cycle; N(1), N(2), C(1)–C(10), H(1)–H(10), C(11)–C(16), and H(11)–H(16) in alternate cycles with C(21)–C(26), H(21)–H(26), C(31)–C(36), H(31)–H(36), C(41)–C(46), and H(41)–H(46). The hydrogen atoms were fixed in an ideal geometry, r(C–H) = 0.95 Å, and treated isotropically.

The atomic coordinates are given in Table IV, and the interatomic distances in Table V. Tables of thermal parameters, least-squares planes, and observed and calculated structure factor amplitudes are available as supplementary data.

Table V. Interatomic Distances (Å) and Angles (Deg) for $Sn(SC_6H_5)_4bpy$[a, b]

Sn–S(1)	2.502 (1)	Sn–S(4)	2.499 (1)
Sn–S(2)	2.499 (1)	Sn–N(1)	2.329 (3)
Sn–S(3)	2.497 (1)	Sn–N(2)	2.333 (3)
S(1)–C(11)	1.743 (4)	S(3)–C(31)	1.772 (4)
S(2)–C(21)	1.769 (4)	S(4)–C(41)	1.781 (4)
N(1)–C(6)	1.355 (4)	C(7)–C(8)	1.371 (7)
N(1)–C(10)	1.324 (5)	C(3)–C(9)	1.365 (7)
C(6)–C(7)	1.387 (5)	C(5)–C(6)	1.462 (5)
C(9)–C(10)	1.371 (6)		
N(2)–C(5)	1.347 (4)	C(1)–C(2)	1.375 (6)
N(2)–C(1)	1.333 (5)	C(3)–C(4)	1.366 (7)
C(4)–C(5)	1.404 (5)	C(2)–C(3)	1.376 (7)
S(1)–Sn–S(2)	100.3 (1)	S(1)–Sn–N(2)	89.0 (1)
S(1)–Sn–S(3)	81.5 (1)	N(1)–Sn–N(2)	69.8 (1)
S(1)–Sn–S(4)	171.3 (1)	S(2)–Sn–N(1)	161.7 (1)
S(1)–Sn–N(1)	87.2 (1)	S(2)–Sn–N(2)	93.5 (1)
S(4)–Sn–S(2)	87.9 (1)	S(4)–Sn–S(3)	93.9 (1)
S(4)–Sn–N(1)	85.9 (1)	S(3)–Sn–N(2)	162.3 (1)
S(4)–Sn–N(2)	93.5 (1)	S(3)–Sn–N(1)	94.7 (1)
S(2)–Sn–S(3)	102.9 (1)		
Sn–S(1)–C(11)	109.6 (1)	Sn–S(3)–C(31)	106.6 (1)
Sn–S(2)–C(21)	106.5 (1)	Sn–S(4)–C(41)	102.0 (1)
Sn–N(1)–C(6)	118.3 (2)	Sn–N(2)–C(5)	117.8 (2)
Sn–N(1)–C(10)	122.2 (2)	Sn–N(2)–C(1)	122.9 (2)
C(6)–N(1)–C(10)	119.5 (3)	C(5)–N(2)–C(1)	118.9 (3)
N(1)–C(6)–C(5)	116.1 (3)	N(2)–C(5)–C(6)	116.8 (3)
N(1)–C(6)–C(7)	119.7 (3)	N(2)–C(5)–C(4)	120.7 (3)
C(5)–C(6)–C(7)	124.1 (3)	C(6)–C(5)–C(4)	122.6 (3)
C(6)–C(7)–C(8)	119.6 (4)	C(5)–C(4)–C(3)	119.0 (4)
C(7)–C(8)–C(9)	120.0 (4)	C(4)–C(3)–C(2)	120.1 (4)
C(8)–C(9)–C(10)	118.1 (4)	C(3)–C(2)–C(1)	118.1 (4)
C(9)–C(10)–N(1)	123.0 (4)	C(2)–C(1)–N(2)	123.2 (4)
C–C–C in Ph	117.5 (7)–123.2 (7)		

[a] Estimated standard deviations in parentheses. [b] Librational corrections: Sn–S, 0.007; Sn–N, 0.006; C–S, 0.005; C–N, 0.003; C–C, 0.004.

Results and Discussion

Preparation. The direct electrochemical oxidation of tin provides a route to the tin(II)–thiolate complexes $Sn(SC_6H_6)_2$ and $Sn(SC_6H_4CH_3\text{-}m)_2$. Measurements of the electrochemical efficiency, E_F, defined as moles of metal dissolved per faraday of electricity, for the Sn/C_6H_5SH system gave $E_F = 0.49$ mol faraday^{-1}, compatible with the following reaction scheme:

$$\text{cathode:}\quad 2C_6H_5SH + 2e^- \rightarrow 2C_6H_5S^- + H_2(g) \qquad (1)$$

$$\text{anode:}\quad 2C_6H_5S^- + Sn \rightarrow Sn(SC_6H_5)_2 + 2e^- \qquad (2)$$

Similar sets of reactions have been proposed earlier for other metal/thiolate systems,[5,6] and here as elsewhere one of the peculiar advantages of the electrochemical method is the formation of low oxidation state species as the oxidation takes place from the zero oxidation state metal.

In the presence of the neutral bidentate donors bpy and phen, the product of the electrochemical oxidation is the appropriate tin(IV) adduct $Sn(SR)_4L$. Interestingly, the E_F value does not change significantly from that reported above (e.g., for Sn/C_6H_5SH/bpy, $E_F = 0.45$ mol faraday^{-1}), from which we conclude that reactions occurring away from the anode are responsible for the oxidation $Sn^{II} \rightarrow Sn^{IV}$. The nature of this reaction is far from clear. There is no visible formation of hydrogen in the bulk solution phase, as would be expected if $Sn(SR)_2$ reacted with RSH. Similarly we could not detect any reaction when $Sn(SC_6H_5)_2$ was added to a solution of C_6H_5SH. Further work on this problem is planned.

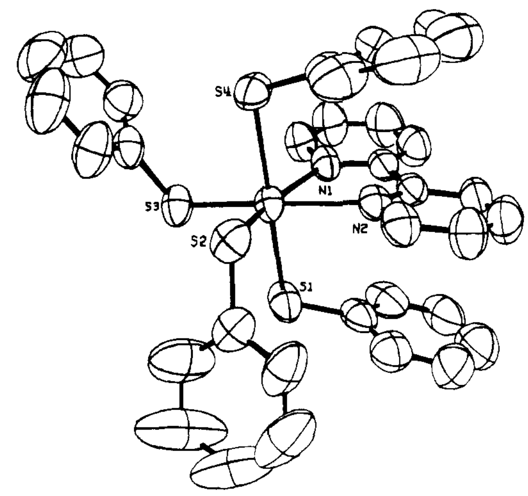

Figure 1. Stereochemistry of $Sn(SC_6H_5)_4bpy$: ORTEP diagram, 50% probability for all atoms other than hydrogen.

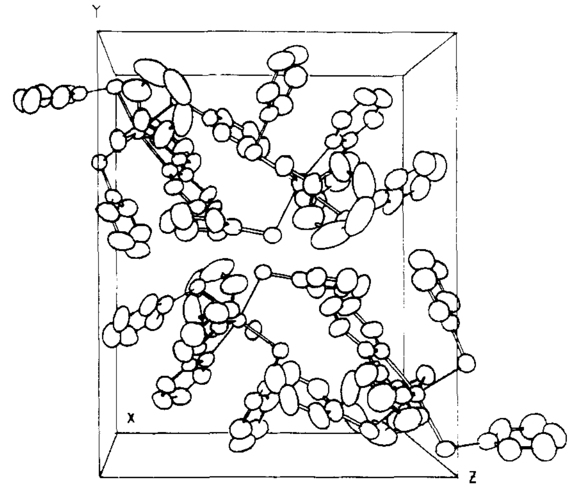

Figure 2. Packing of $Sn(SC_6H_5)_4bpy$ in the unit cell; hydrogen atoms are omitted.

With electrolysis involving n-C_4H_9SH or $(t\text{-}C_4H_9S)_2$ (cf. ref 6), the E_F values again indicate oxidation of the metal to tin(II) species (E_F = 0.45 and 0.53 mol F^{-1}, respectively), but we were not able to isolate solid products from these reactions, despite the wide variety of experimental conditions investigated. The products obtained had variable but high tin content, and both microanalysis and NMR spectra demonstrated the almost complete absence of organic groups. The addition of neutral bidentate donors to the electrolytic cell did not affect the situation substantially. It appears that the presumed $Sn(SR)_2$ products, whose formation is evidenced by the current efficiency of ~0.5 mol faraday^{-1}, decompose under the experimental conditions to tin (poly?) sulfide, which is insoluble, leaving soluble organic products in solution. Similar results were found with lead and alkanethiols, and the explanation may be the same in both cases, namely, the instability of the C–S bond in the anion, or in the RS radical formed on discharge of RS^- at the anode, leading to the formation of SnS_x and unidentified organosulfur compounds. A further complication is the deposition of tin on the cathode as the electrolysis proceeds, and its seems clear that these systems do not lend themselves to the direct syntheses established with arenethiols.

The products of the electrochemical oxidation of lead in the presence of thiophenol is $Pb(SC_6H_5)_2$, but the failure to obtain lead derivatives of alkanethiols by this method is disappointing and surprising, given the known properties of these compounds. In addition to decomposition suggested above, some reaction occurred at the cathode, and it may be that the presumed $Pb(SR)_2$ compound is soluble in acetonitrile and undergoes decomposition at the cathode (cf. ref 4).

The electrochemical efficiency for the C_6H_5SH/Pb system was found to be 0.45 mol faraday^{-1}. Following the arguments used above, this implies that the anode reaction is

$$Pb + 2RS^- \rightarrow Pb(SR)_2 + 2e^-$$

The formation of the lead(II) product parallels the chemistry of tin in this sense, but with lead the addition of 2,2′-bipyridine does not cause any change in the oxidation state of the metal in the final product. The behavior of the lead(II) compound is of course in keeping with the known chemistry of this element.

Structure of $Sn(SC_6H_5)_4bpy$. The molecular structure of the 2,2′-bipyridine adduct of $Sn(SC_6H_5)_4$, the preparation of which was first reported briefly by Poller and Spillman[11] is shown in Figure 1; the unit cell is given in Figure 2. The coordination kernel is a distorted octahedral SnS_4N_2 unit; details of bond distances and angles are given in Table V. Few examples of complexes of this type are known, so that the electrochemical synthesis should have some useful applications in this context, especially since the acceptor properties of $Sn(SR)_4$ species do not appear to have been studied in detail, other than some preparative[12] and Mössbauer[13] investigations of derivatives of $Sn(TDT)_2$ (TDT = 3,4-toluenedithiolate) and related compounds.

It is clear from the results in Table V that the tin–sulfur bonds in the compound are all equal within experimental error, so that there is no detectable trans effect arising from differing S–Sn–S and S–Sn–N interactions. The average bond distance, 2.449 Å, is close to the sum of the covalent radii (1.40 + 1.04 = 2.49 Å).[14] Bond distances for Sn–S bonds have been reported for a number of compounds, and Lindley and Carr[15] have reviewed the results for organotin dithiocarbamates up to 1974. For octahedral complexes, the Sn–S bond lengths lie between 2.497 (4) and 2.613 (5) Å, while for trigonal-bipyramidal species the range is 2.33 (1)–2.449 (5) Å. For tetrakis(dimethyldithiocarbamate)tin(IV), which has a SnS_6 kernel, the Sn–S bonds to the monodentate ligands are 2.500 (6) and 2.536 (6) Å, with values of 2.510 (4), 2.515 (4), 2.596 (4), and 2.707 (5) Å found for the two chelated ligands.[16] Other relevant compounds and bond distances are as follows: for diphenyltin 2-(*o*-hydroxyphenyl)benzothiazoline, (Schiff's base)[17] (SnC_2ONS kernel) 2.496 (1); for triphenyltin 2-methylbenzenethiolate[18] (SnC_3S kernel) 2.420 (8); triphenyltin 2,6-dibromobenzenethiolate[18] (SnC_3S kernel) 2.44 (2) Å. These results show that there is some slight decrease in the bond length with decreasing coordination number, but the small number of compounds and the wide variation in chemical composition prevent one from drawing any conclusion other than that the present results are clearly compatible with existing literature values. The S–C bond distances in $Sn(SC_6H_5)_4bpy$ show much greater variation than do the Sn–S lengths, with S(1)–C(11) significantly shorter than the other three; this may be the result of interaction between this ligand

---

(11) Poller, R. C.; Spillman, J. A. *J. Organomet. Chem.* **1966**, *6*, 668.

(12) Poller, R. C.; Spillman, J. A. *J. Chem. Soc. A* **1966**, 958.

(13) Epstein, L. M.; Straub, D. K. *Inorg. Chem.* **1965**, *4*, 1551.

(14) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London, 1975; p 236.

(15) Lindley, P. F.; Carr, P. *J. Cryst. Mol. Struct.* **1974**, *4*, 173.

(16) Potenza, J.; Johnson, R. J.; Mastropaola, D. *Acta Crystallogr., Sect. B* **1976**, *B32* 941.

(17) Preut, H.; Haupt, H.-J.; Huber, F.; Cefalu, R.; Barbieri, R. *Z. Anorg. Allg. Chem.* **1974**, *407*, 257.

(18) Bokii, N. G., Struchkov, Yu. T.; Krautsov, D. N.; Rokhlina, E. M. *J. Struct. Chem.* **1974**, *15*, 424.

and the 2,2′-bipyridine. Again the values are reasonably close those reported for other thiophenol derivatives.[17,18]

The only other tin(IV)–2,2′-bipyridine complex whose structure has been reported[19] is the adduct of $(C_6H_5)_2SnCl_2$, in which the trans-phenyl groups are almost perpendicular to the SnN_2Cl_2 plane. The Sn–N bond length in $Sn(SC_6H_5)_4$bpy (av 2.331 Å) is close to those in $(C_6H_5)_2SnCl_2$·bpy (2.344 (6) and 2.375 (6) Å) and well within the range of values found in other organotin compounds, as reviewed by Harrison, King, and Richards.[19] The bite of the 2,2′-bipyridine is essentially the same in both compounds, as is the twist of the bipyridine rings.

Finally we note that the C–C bond lengths in the phenyl rings (not shown in Table V) lie in the range 1.35–1.45 (1) Å, and the C–C–C angles are in the range 117.5–123.2 (7)°. These call for no comment, being entirely compatible with accepted values.

Structure of $Pb(SC_6H_5)_2$. In the course of characterizing $Pb(SC_6H_5)_2$, we recorded both NMR and infrared spectra. The ^1H NMR spectrum (in dimethyl-d_6 sulfoxide) shows a broad absorption centered at 7.1 ppm from Me_4Si; the parent C_6H_5SH has a much sharper resonance at 6.5 ppm. The infrared spectrum has no unexpected features above 500 cm^{-1}; the far-infrared spectrum has absorptions at 474 s, 416 m, 145 m, br and 120 w cm^{-1}, similar to the far-infrared spectra of $M(SC_6H_5)_2$ (M = Zn, Cd, Hg), reported elsewhere,[6] and especially to that of the cadmium compound. The bands at 474, 416, and 174 cm^{-} are tentatively identified as modes of the ligand, leaving absorptions at 338, 319, 252, and 220 cm^{-1} as modes of the metal–sulfur kernel. It has been suggested elsewhere[6] that the benzenethiolate derivatives of group 2B are polymeric in the solid state, and the far-infrared spectrum implies a similar conclusion for $Pb(SC_6H_5)_2$.

Acknowledgment. This work was supported in part by a grant from Imperial Oil Ltd. and by Operating Grants (to D.G.T.) from the National Sciences and Engineering Research Council of Canada. We thank Mr. N. Seudeal for help in running the far-infrared spectra.

Registry No. $Sn(SC_6H_5)_2$, 22881-46-5; Sn(S-*m*-$CH_3C_6H_4)_2$, 81616-24-2; $Sn(SC_6H_5)_4$bpy, 12119-13-0; $Sn(SC_6H_5)_4$phen, 81616-65-1; Sn(S-*o*-$CH_3C_6H_4)_4$bpy, 81616-66-2; Sn(S-*o*-$CH_3C_6H_4)_4$phen, 81616-67-3; Sn(S-*m*-$CH_3C_6H_4)_4$bpy, 81616-68-4; Sn(S-*m*-$CH_3C_6H_4)_4$phen, 81616-69-5; $Pb(SC_6H_5)_2$, 32812-89-8.

Supplementary Material Available: Tables of thermal parameters, least-squares planes, and observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

---

(19) Harrison, P. G.; King, T. J.; Richards, J. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1723.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

X-ray Photoelectron Spectra of Inorganic Molecules. 31.[1] Satellite Structure Associated with the Core-Electron Binding Energies of Alkyl and Aryl Isocyanide Complexes of the Transition Metals

W. S. MIALKI and R. A. WALTON*

Received December 11, 1981

The observation of shake-up satellite structure associated with the N 1s and C 1s binding energies in the X-ray photoelectron spectra (XPS) of a range of six- and seven-coordinate alkyl and aryl isocyanide complexes of zerovalent and divalent chromium, molybdenum, and tungsten and the complexes $[Re(CNCMe_3)_6]PF_6$ and $[Rh(CNCMe_3)_4]PF_6$ expands considerably the occurrence of this phenomenon within compounds of the second and third transition series. By comparison with literature data for mononuclear and polynuclear metal carbonyls it is concluded that these satellites most probably arise from $M(d) \rightarrow \pi^*(CNR)$ and $M(d) \rightarrow \pi^*(CNAr)$ excitations accompanying the primary photoemission processes.

Introduction

The similarities between the photoelectron spectra of transition-metal carbonyl complexes and the corresponding spectra of metal surfaces containing adsorbed CO[2,3] have led to detailed experimental[2-4] and theoretical[5] studies of the X-ray photoelectron spectra (XPS) of mononuclear and polynuclear cluster metal carbonyls. The focus of much of the recent interest has been the measurement and assignment of the shake-up satellite structure associated with the metal, the C 1s, and the O 1s primary photolines.[2-5] The interpretation of these satellites is particularly important in the modeling of the electronic structure of discrete molecular transition-metal carbonyl species to that of metal surfaces containing adsorbed CO. In addition to this application of XPS to the characterization of catalytically important surfaces, shake-up satellites are of interest from another point of view. While a common feature in the XPS of salts and complexes of many first-row transition metal ions, they are rarely encountered in the spectra of complexes of the second- and third-row transition elements.[6,7] The one major exception to this experimental observation is the shake-up satellites that are observed in the XPS of carbonyls of the second and third transition series.[2,4,8]

Our recent discovery of satellite structure in the XPS of the homoleptic alkyl isocyanide complexes of molybdenum(II) of the type $[Mo(CNR)_7](PF_6)_2$, where R = CH_3, CMe_3, or C_6H_{11},[9] was the first instance where this phenomenon has been reported in complexes containing these ligands. Furthermore, studies on the XPS of metal isocyanide complexes provide the opportunity to gather the necessary experimental XPS data with which to model the binding of isocyanide ligands to metal

---

(1) Part 30: Brisdon, B. J.; Griffin, G. F.; Pierce, J.; Walton, R. A. *J. Organomet. Chem.* **1981**, *219*, 53.

(2) Plummer, E. W.; Salaneck, W. R.; Miller, J. S. *Phys. Rev. B: Condens. Matter* **1978**, *18*, 1673.

(3) Freund, H. J.; Plummer, E. W. *Phys. Rev. B: Condens. Matter* **1981**, *23*, 4859.

(4) Bancroft, G. M.; Boyd, B. D.; Creber, D. K. *Inorg. Chem.* **1978**, *17*, 1008.

(5) Hall, M. B.; Sherwood, D. E., Jr. *Inorg. Chem.* **1979**, *18*, 2324.

(6) Brisk, M. A.; Baker, A. D. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *7*, 197.

(7) Vernon, G. A.; Stucky, G.; Carlson, T. A. *Inorg. Chem.* **1976**, *15*, 278.

(8) Pignataro, S. *Z. Naturforsch., A* **1972**, *27A*, 816.

(9) Brant, P.; Mialki, W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 5453.