One-electron Transfer Processes in the Reaction of Tin(II) Halides with Substituted *o*-Quinones; Crystal Structure of Bis(3,5-di-t-butylcatecholato)tin–1,10-Phenanthroline–Dimethylformamide (1/1/2)†

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The reaction of SnX_2 (X = Cl, Br, or I) with 3,5-di-t-butyl-1,2-benzoquinone or phenanthrene-9,10-quinone in the presence of 2,2′-bipyridine (bipy) or 1,10-phenanthroline gives the adducts of the appropriate SnX_2(diolate) formed by oxidative addition. Various spectroscopic results (i.r., ^1H, ^{13}C n.m.r.) confirm the conversion of *o*-quinone into the corresponding catecholate. E.s.r. studies show that semiquinone derivatives are intermediates in these processes, and a mechanism is proposed to satisfy both preparative and e.s.r. results in terms of two successive one-electron-transfer processes. The crystal structure of bis(3,5-t-butylcatecholato)tin(IV)–1,10-phenanthroline–dimethylformamide (1/1/2) has been determined by *X*-ray crystallography using the heavy-atom method. Crystal parameters are triclinic, space group $P\bar{1}$, a = 10.761(2), b = 14.357(3), c = 15.361(4) Å, α = 93.5(3), β = 95.8(2), γ = 94.8(3)°, and Z = 2. The structure analysis, based on 3 005 observed reflections [$I > 2\sigma(I)$] gave R = 0.0699. The average Sn–O distance [2.008(8) Å] is typical of tin(IV) compounds and the average C–O distance [1.36(1) Å] again confirms that the ligand is an aromatic 1,2-diolate.

The redox chemistry of Main Group elements is dominated by reactions which formally involve the transfer of pairs of electrons, in contrast to the one-electron processes so often identified in the analogous chemistry of transition-metal ions. The reactions of tin(II) halides with tetrahalogeno-*o*-benzoquinones $Y_4C_6O_2$ (Y = Cl or Br) fall into this category, since it has been shown by both preparative and spectroscopic studies[1] that the overall process is $Sn^{II}X_2$ + *o*-benzoquinone $\longrightarrow$ $Sn^{IV}X_2$(catecholate). Parallel studies of the oxidation of indium(I) halides by a series of substituted *o*-quinones have provided clear evidence of one-electron-transfer processes, demonstrated by e.s.r. spectroscopy, and in such cases the products may be either catecholato or *o*-semiquinonato derivatives of indium(III).[2] The present paper is concerned with preparative and spectroscopic investigations of the reaction of tin(II) halides with the sterically hindered 3,5-di-t-butyl-1,2-benzoquinone and phenanthrene-9,10-quinone; e.s.r. spectroscopy proved to be of great importance in the former case.

In the course of this work, we obtained crystals of the 1,10-phenanthroline adduct of bis(3,5-di-t-butylcatecholato)tin(IV), and the crystal structure of this compound has been established by *X*-ray crystallography.

Experimental

Tin(II) halides (Alfa), 3,5-di-t-butyl-1,2-benzoquinone (dbbq), phenanthrene-9,10-quinone (pq) (Gold Label quality), 1,10-phenanthroline (phen), and 2,2′-bipyridine (bipy) were used as supplied (Aldrich). Solvents were dried and distilled before use, and stored over conventional drying agents. All preparative work was carried out in an atmosphere of dry nitrogen.

Tin analysis of products was by atomic absorption spectrophotometry, and halogen analysis by the Volhard volumetric method. Proton and ^{13}C n.m.r. spectra were run on a Varian EM 360 or Bruker AC-300 L instrument and i.r. spectra on a Nicolet 5DX instrument, using KBr discs.

Preparation of Adducts of Tin(IV) *Catecholato Compounds.*— In experiments involving $SnCl_2$, 0.57 g (3 mmol) of solid was dissolved in acetonitrile (25 cm^3), and a solution of dbbq in the same solvent (3 mmol in 25 cm^3) added slowly over 1 h. This mixture was heated to 50 °C for 3 h, at which point phen or bipy (3 mmol) was added, either in acetonitrile solution or as the solid. The pale yellow solution became brick-red, and a red precipitate formed. This was filtered off, washed with light petroleum (b.p. range 35—60 °C, 2 × 10 cm^3), and dried *in vacuo* at room temperature. The yield of *e.g. dichloro*(3,5-*di-t-butylcatecholato*)*tin*(IV)–1,10-*phenanthroline* was quantitative. Analytical results are given in Table 1. In that Table, as in the text, we use the nomenclature dbbq $\xrightarrow{e}$ dbbsq$^{\bullet}$ $\xrightarrow{e}$ dbc and pq $\xrightarrow{e}$ psq$^{\bullet}$ $\longrightarrow$ pd for the *o*-quinone, *o*-semiquinone anion, and *o*-diolato dianion respectively.

When $SnBr_2$ was used under the above conditons, no precipitation occurred on addition of bipy or phen. After being cooled to room temperature, the brown solution was filtered to remove any suspended material; addition of diethyl ether (50 cm^3) to this filtrate gave a brown solid which was collected, washed, and dried. This solid is $SnBr_2$(dbc)•L (L = bipy or phen).

Tin(II) iodide was dissolved in acetonitrile–dimethylformamide (dmf) (2:1, v/v), since it is only slightly soluble in acetonitrile. The solution resulting from reaction with dbbq and phen was concentrated by reducing the volume by *ca.* 60%. No solid appeared at this point, but after several days at room temperature under nitrogen, red crystals of *bis*(3,5-*t-butylcatecholato*)*tin*(IV)–1,10-*phenanthroline–dimethylformamide* (2/2/3) appeared (Found: C, 62.3; H, 6.55; N, 5.65, Sn, 14.1. $C_{40}H_{48}N_2O_4Sn{\cdot}1.5C_3H_7NO$ requires C, 62.9; H, 6.95; N, 5.75; Sn, 14.0%). This compound loses dimethylformamide (dmf) on standing, as is easily shown by following the intensity of the ν(C=O) band of dmf at 1 677 cm^{-1}. The crystal used in the

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Analytical and ^{1}H n.m.r. results

Compound[a]	Analysis[b]/%		Chemical shift[c]	Assignment
	Sn	Halogen		
$SnCl_2$(dbc)•bipy	20.9 (21.0)	12.5 (12.5)	8.83 (m) (2)	bipy $H^{3,3'}$
			8.59 (m) (2)	bipy $H^{4,4'}$
			8.21 (m) (2)	bipy $H^{5,5'}$
			7.70 (m) (2)	bipy $H^{6,6'}$
			6.58 (m) (2)	dbc, H^3,H^5
			1.39 (s) (9)	dbc, C_4H_9
			1.18 (s) (9)	dbc, C_4H_9
$SnCl_2$(dbc)•phen[d]	20.2 (20.1)	12.2 (12.0)	9.22 (m) (2)	phen H^2,H^9
			8.83 (m) (2)	phen H^4,H^7
			8.60 (m) (2)	phen H^5,H^6
			8.22 (m) (2)	phen H^3,H^8
			6.57 (m) (2)	dbc, H^3,H^5
			1.38 (s) (9)	dbc, C_4H_9
			1.20 (s) (9)	dbc, C_4H_9
$SnCl_2$(pd)•bipy	21.3 (21.4)	12.6 (12.8)	9.08—7.05	[e]
$SnBr_2$(dbc)•bipy	18.2 (18.1)	24.9 (24.4)	[f]	
$SnBr_2$(dbc)•phen	17.6 (17.5)	23.0 (23.5)	[f]	
$SnBr_2$(pd)•bipy	18.6 (18.5)	21.9 (22.3)	[f]	
SnI_2(pd)•phen[g]	15.5 (15.6)	33.5 (33.4)		

[a] dbc = 3,5-Di-t-butylcatecholato anion; pd = phenanthrene-9,10-diolato anion. [b] Calculated values are given in parentheses. [c] Solutions in $(CD_3)_2SO$. Values in p.p.m. relative to $SiMe_4$; s = singlet, m = multiplet. Numbers in parentheses show relative integrated intensities. [d] Found: C, 53.2; H, 5.50; N, 4.95. $C_{26}H_{28}Cl_2N_2O_2Sn$ requires C, 52.9; H, 4.80; N, 4.75%. [e] Individual integration not possible. [f] Spectrum essentially identical to that of corresponding chloro compound. [g] Found: C, 40.6; H, 2.40; N, 3.70. $C_{22}H_{16}I_2N_2O_2Sn$ requires C, 41.0; H, 2.10; N, 3.70%.

Table 2. Summary of crystal data, intensity collection, and structure refinement for $Sn(dbc)_2$•phen•2dmf, $C_{34}H_{42}N_4O_4Sn$

Cell constants	$a = 10.761(2)$, $b = 14.357(3)$, $c = 15.361(4)$ Å, $\alpha = 93.5(3)$, $\beta = 95.8(2)$, $\gamma = 94.8(3)°$
Cell volume, U/Å^3	2 330(1)
Crystal system	Triclinic
Space group	$P\bar{1}$
M	884.7
Z, F(000)	2, 928
D_c, D_m/g cm^{-3}	1.26, 1.20
Crystal dimensions/mm	0.10 × 0.20 × 0.50
μ/cm^{-1}	5.25
Radiation	Mo-K_α, $\lambda = 0.710\ 69$ Å
Monochromator	Highly oriented graphite
Temperature/°C	20
2θ range/°	4—45
Scan type	Coupled θ (crystal)—2θ (counter)
Scan width	$K_{\alpha_1} - 1°$ to $K_{\alpha_2} + 1°$
Scan speed/° min^{-1}	Variable, 2.02—4.88
Background time/scan time	0.5
Total reflections	4 596 ($+h$, $\pm k$, $\pm l$)
Unique data [$I > 2\sigma(I)$]	3 005
No. of parameters	347 (two blocks of 172 and 175)
$R = (\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|^2)^{\frac{1}{2}}$	0.0699
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.0719
$\Delta\rho_{max.}$/e Å^{-3}	0.72
Shift: error (max.)	0.05

X-ray crystallographic study proved to be the bis(dimethylformamide) solvate (see below).

In an attempt to establish the mode of formation of $Sn(dbc)_2$•phen, we repeated the reaction under different conditions. Tin(II) iodide (1.2 g, 3.2 mmol) was suspended in toluene (25 cm^3) and a solution of dbbq (0.71 g, 3.2 mmol) in the same solvent (25 cm^3) added dropwise. The quinone solution changed colour from red to light brown on contact with the suspension. After all the dbbq had been added, the mixture was refluxed for 4 h, after which a wine-red solution was obtained; 2,2′-bipyridine (0.50 g, 3.2 mmol) was then added to produce a red-orange precipitate. Refluxing was continued for a further hour, after which the mixture was cooled, and the product filtered off, washed with light petroleum (3 × 20 cm^3), and dried *in vacuo*. Yield 0.58 g (0.74 mmol) of SnI_4•bipy (i.r. spectrum establishes presence of bipy) (Found: I, 64.5; Sn, 15.8. $C_{10}H_8I_4N_2Sn$ requires I, 64.9; Sn, 15.2%). We were unable to identify an oily product which was obtained from the filtrate after removing the solvent by evaporation.

The procedures with phenanthrene-9,10-quinone were similar. For example, tin(II) iodide (0.80 g, 2.15 mmol) was suspended in a solution of pq (0.45 g, 2.15 mmol) in toluene (50 cm^3), and the mixture refluxed gently for 6 h. On addition of 1,10-phenanthroline (0.39 g, 2.15 mmol) to the deep red solution, a purple precipitate was obtained. Refluxing was continued for 1 h, after which the mixture was cooled to room temperature and the precipitate collected, washed with light petroleum (3 × 20 cm^3), and dried *in vacuo*. The yield of SnI_2(pd)•phen was quantitative.

Crystallographic Studies.—A suitable crystal of bis(3,5-di-t-butylcatecholato)tin(IV)–1,10-phenanthroline–dimethylformamide (1/1/2) (**1**) was sealed in a capillary (see Table 2 for crystal size and other relevant parameters.) Diffraction results were collected using a Syntex $P2_1$ diffractometer following the procedures described previously.[3] The unit-cell dimensions were determined from 55 strong reflections in the range 15 < 28 < 25°. The intensities of three monitor reflections changed by 34% during the 150 h required for data collection, and the appropriate decay corrections were applied. Corrections were also applied for Lorentz and polarization effects, but no absorption correction was necessary because of the low absorption coefficient.

There were no systematic absences, and the space group $P\bar{1}$ was therefore used and later assumed to be correct in view of the successful refinement of the structure. Computation was carried out on the Amadahl 580/5850 computer at the University of Manitoba Computer Services Departments. The position of the

Table 3. Final fractional co-ordinates for non-hydrogen atoms of Sn(dbc)$_2$•phen•2dmf, with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	0.130 5(1)	0.261 0(1)	0.316 6(1)	C(27)	0.535 5(13)	−0.112 2(10)	0.321 9(9)
O(1)	0.272 7(7)	0.184 3(5)	0.365 9(5)	C(28)	0.658 8(17)	−0.104 4(14)	0.264 6(13)
O(2)	0.161 2(8)	0.167 2(6)	0.222 6(5)	C(29)	0.493 6(18)	−0.208 2(13)	0.319 0(13)
O(3)	−0.017 6(7)	0.335 4(5)	0.270 7(5)	C(30)	0.583 5(16)	−0.099 6(13)	0.408 2(11)
O(4)	0.221 6(7)	0.373 5(5)	0.271 4(5)	C(31)	0.215 4(14)	0.006 9(10)	0.107 8(9)
O(5)	0.238 1(24)	0.881 4(17)	0.769 7(16)	C(32)	0.244 1(16)	0.086 9(12)	0.040 7(11)
O(6)	0.253 6(18)	0.609 3(14)	0.503 8(13)	C(33)	0.079 9(16)	0.011 2(13)	0.124 2(12)
N(1)	−0.003 2(9)	0.167 1(8)	0.393 6(7)	C(34)	0.255 7(17)	−0.085 2(12)	0.069 0(12)
N(2)	0.092 4(10)	0.319 0(8)	0.450 6(7)	C(41)	0.016 9(11)	0.417 6(8)	0.231 4(7)
N(3)	0.344 2(20)	0.796 3(16)	0.853 0(13)	C(42)	−0.065 3(11)	0.479 9(8)	0.191 4(7)
N(4)	0.392 6(18)	0.654 9(12)	0.575 0(12)	C(43)	−0.027 1(11)	0.562 6(9)	0.148 1(8)
C(1)	−0.053 0(15)	0.094 8(10)	0.363 2(11)	C(44)	0.097 2(11)	0.580 0(9)	0.147 4(7)
C(2)	−0.131 4(14)	0.039 0(11)	0.423 0(16)	C(45)	0.183 6(10)	0.521 9(8)	0.189 5(7)
C(3)	−0.160 9(17)	0.057 1(15)	0.508 2(14)	C(46)	0.144 8(10)	0.439 2(8)	0.231 4(7)
C(4)	−0.108 3(14)	0.131 6(13)	0.537 8(13)	C(47)	−0.119 4(14)	0.631 1(10)	0.103 6(9)
C(5)	−0.031 9(12)	0.187 8(10)	0.478 9(10)	C(48)	−0.086 9(20)	0.632 0(16)	0.007 8(14)
C(6)	0.021 4(13)	0.266 7(9)	0.509 9(10)	C(49)	−0.115 0(18)	0.729 1(14)	0.128 1(14)
C(7)	−0.010 1(17)	0.289 4(14)	0.600 5(10)	C(50)	−0.257 2(24)	0.616 2(20)	0.125 4(18)
C(8)	0.037 8(17)	0.369 1(15)	0.622 9(11)	C(51)	0.323 3(12)	0.545 7(9)	0.188 1(8)
C(9)	0.106 7(15)	0.423 7(13)	0.562 1(13)	C(52)	0.409 0(12)	0.469 0(10)	0.141 9(9)
C(10)	0.134 8(12)	0.396 9(11)	0.473 6(9)	C(53)	0.347 8(15)	0.640 4(10)	0.138 6(10)
C(11)	−0.132 4(17)	0.155 4(18)	0.626 9(14)	C(54)	0.361 9(13)	0.550 4(10)	0.279 5(9)
C(12)	−0.085 3(18)	0.230 2(17)	0.657 7(12)	C(61)	0.259 3(24)	0.732 1(18)	0.881 5(17)
C(21)	0.307 9(10)	0.106 2(8)	0.318 8(7)	C(62)	0.457 1(23)	0.778 3(19)	0.899 3(17)
C(22)	0.399 5(10)	0.040 0(8)	0.342 9(7)	C(63)	0.335 0(47)	0.860 4(34)	0.811 3(28)
C(23)	0.435 1(11)	−0.039 8(8)	0.295 0(7)	C(64)	0.498 5(33)	0.687 1(25)	0.586 5(22)
C(24)	0.373 8(11)	−0.045 1(9)	0.221 7(8)	C(65)	0.322 1(44)	0.638 7(34)	0.645 8(31)
C(25)	0.282 7(11)	0.017 8(9)	0.192 7(8)	C(66A)	0.276 4(53)	0.669 0(38)	0.552 7(37)
C(26)	0.248 6(10)	0.098 4(8)	0.243 0(7)	C(66B)	0.405 0(63)	0.593 3(48)	0.507 2(45)

tin atom was determined by the heavy-atom method, and the remaining non-hydrogen atoms were located from a Fourier difference map. The structure was refined using a blocked-matrix least-squares method, with Sn and O(1) in both blocks; one block also contained O(2), O(3), N(1), N(2), and C(1)—C(12), and the other C(21)—C(66), O(4), O(5), and N(3), N(4). The atoms Sn, O(1), O(2), N(1), N(2), and C(1)—C(12) were refined anisotropically, and the remainder isotropically. Hydrogen atoms were included in later cycles in ideal positions (C–H 0.95 Å, CCH 109.5 or 120° as appropriate). The function $\Sigma w(|F_o| - |F_o|)^2$ was minimized, and in the final cycles the weighting scheme $w = 1/[\Sigma\sigma^2(F) + pF]^2$ was employed, with $p = 0.0001$. No evidence was found for secondary extinction. Sources of scattering factors and computer programs were those given previously.[4]

The refinement converged at $R = 0.0699$. The final atomic co-ordinates for non-hydrogen atoms are given in Table 3, and important interatomic distances and angles in Table 4. Figure 1 shows the molecular structure of (**1**) and Figure 2 the unit-cell packing with the dmf molecules. From the thermal parameters there is some evidence for disorder in one of these dmf molecules [C(66)].

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

E.S.R. Spectroscopy.—Spectra were recorded on a Varian E12 spectrometer which was calibrated with an n.m.r. gaussmeter. The klystron frequency was determined from the e.s.r. spectrum of diphenylpicrylhydrazide. Spectra run at 77 K involved solids frozen on a liquid-nitrogen cold-finger Dewar vessel. The Varian cooling system was used in the variable-temperature studies.

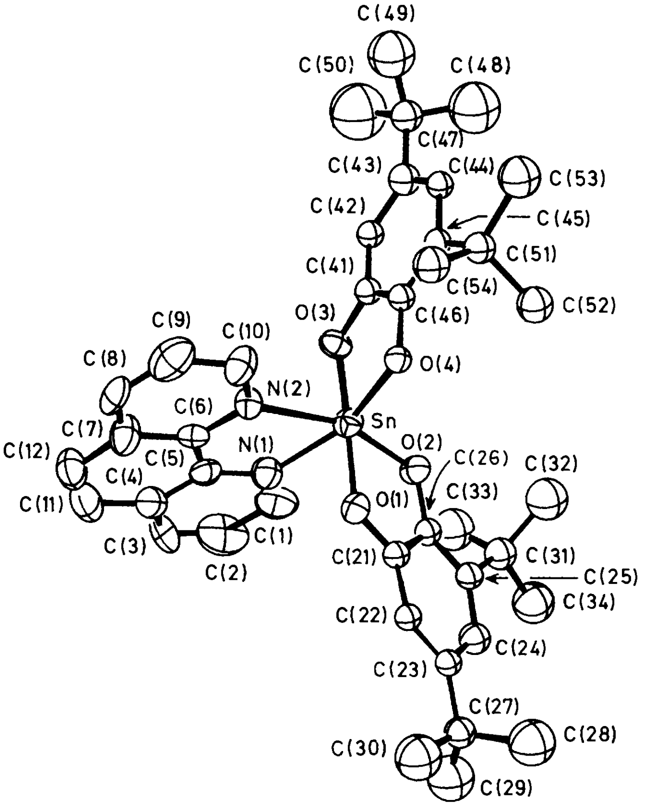


Figure 1. ORTEP diagram of bis(3,5-di-t-butylcatecholato)tin(IV) 1,10-phenanthroline (**1**) with atoms shown as 30% probability ellipsoids. Hydrogen atoms are omitted for clarity

Table 4. Bond lengths (Å) and angles (°) for Sn(dbc)$_2$·phen·2 dmf, with standard deviations in parentheses

Sn–O(1)	1.995(8)	O(1)–Sn–O(2)	82.6(3)
Sn–O(2)	2.019(8)	O(1)–Sn–O(3)	177.6(3)
Sn–O(3)	2.008(7)	O(2)–Sn–O(3)	97.9(3)
Sn–O(4)	2.010(7)	O(1)–Sn–O(4)	98.5(3)
		O(2)–Sn–O(4)	106.6(3)
		O(3)–Sn–O(4)	83.6(3)
Sn–N(1)	2.25(1)	O(1)–Sn–N(1)	89.2(3)
		O(1)–Sn–N(1)	89.2(3)
		O(2)–Sn–N(1)	89.8(4)
		O(3)–Sn–N(1)	88.5(3)
		O(4)–Sn–N(1)	162.6(3)
Sn–N(2)	2.26(1)	O(1)–Sn–N(2)	85.5(3)
		O(2)–Sn–N(2)	160.0(4)
		O(3)–Sn–N(2)	93.4(3)
		O(4)–Sn–N(2)	91.0(4)
		N(1)–Sn–N(2)	74.0(4)
O(1)–C(21)	1.38(1)	Sn–O(1)–C(21)	111.3(7)
O(2)–C(26)	1.35(1)	Sn–O(2)–C(26)	111.2(7)
O(3)–C(41)	1.35(1)	Sn–O(3)–C(41)	110.4(7)
O(4)–C(46)	1.36(1)	Sn–O(3)–C(41)	110.4(7)
O(4)–C(46)	1.36(1)	Sn–O(4)–C(46)	111.4(7)
N(1)–C(1)	1.34(2)	Sn–N(1)–C(1)	126(1)
N(1)–C(5)	1.36(2)	Sn–N(1)–C(5)	115(1)
		C(1)–N(1)–C(5)	119(1)
N(2)–C(6)	1.36(2)	Sn–N(2)–C(6)	115(1)
N(2)–C(10)	1.32(2)	Sn–N(2)–C(10)	125(1)
		C(6)–N(2)–C(10)	120(1)
Rings 1,10-phenanthroline			
mean C–C	1.40(5)	C(23)–C(27)	1.51(2)
mean C–C–C/N–C–C	120(5)	C(25)–C(31)	1.58(2)
		O(1)–C(21)–C(22)	122(1)
Ring C(21)—C(26)		O(1)–C(21)–C(26)	117(1)
mean C–C	1.39(5)	O(2)–C(26)–C(21)	118(1)
mean C–C–C	120(6)	O(2)–C(25)–C(21)	124(1)
		C(22)–C(23)–C(27)	122(1)
Ring C(41)—C(46)		C(24)–C(25)–C(31)	124(1)
mean C–C	1.39(4)	C(26)–C(25)–C(31)	119(1)
mean C–C–C	120(4)	C(43)–C(47)	1.52(2)
		C(45)–C(51)	1.57(2)
t-Butyl group C(27)—C(30)		O(3)–C(41)–C(42)	122(1)
mean C–C	1.51(3)	O(3)–C(41)–C(46)	118(1)
mean C–C–C	110(2)	O(4)–C(46)–C(41)	116(1)
		O(4)–C(46)–C(45)	124(1)
t-Butyl group C(31)–C(34)		C(42)–C(43)–C(47)	121(1)
mean C–C	1.49(3)	C(44)–C(43)–C(47)	121(1)
mean C–C–C	109(2)	C(44)–C(45)–C(51)	122(1)
		C(46)–C(45)–C(51)	120(1)
t-Butyl group C(47)—C(50)			
mean C–C	1.49(3)		
mean C–C–C	109(5)		
t-Butyl group C(51)—C(54)			
mean C–C	1.53(2)		
mean C–C–C	110(2)		

Estimated standard deviations on mean values have been calculated with the use of the scatter formula $\sigma = [\Sigma(d_i - \bar{d})^2/(N - 1)]^{\frac{1}{2}}$, where d_i is the ith and $\bar{d}$ is the mean of N equal measurements.

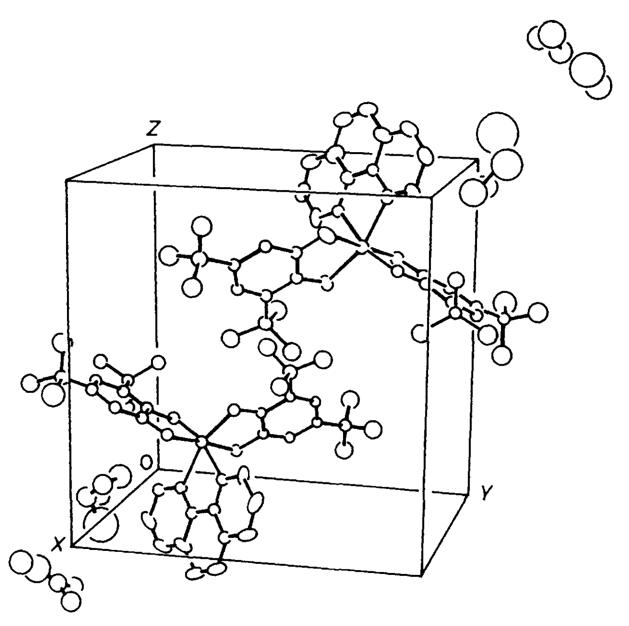
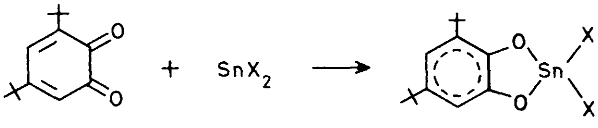


Figure 2. Unit-cell packing of compound (**1**), also showing the position of the dimethylformamide molecule(s) drawn about $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Atoms are drawn as 20% probability ellipsoids

Solutions for e.s.r. spectroscopy were prepared in a special three-arm cell. A solution of SnX$_2$ (1 mg) in dry tetrahydrofuran (thf) (5 cm^3) was thoroughly degassed by a series of three freeze–evacuate–thaw cycles in one arm of the cell, and an equimolar quantity of the *o*-quinone in thf (5 cm^3) placed in a second separate compartment, where it too was degassed. Reaction was initiated by opening the stopcocks and tilting the apparatus to allow the solutions to mix. After mild agitation, part of the reaction mixture was allowed to flow into the third chamber which could then be inserted into the cavity of the e.s.r. spectrometer.

Results and Discussion

Preparative.—The compounds listed in Table 1 are evidently the result of adduct formation by the (catecholato)dihalogenotin(IV) species, whose genesis must lie in the overall oxidative-addition reaction, *e.g.* equation (1). To this extent, the



(1)

reactions are identical to those identified in the SnX$_2$–tetrahalogeno-*o*-benzoquinone system,[1] although the e.s.r. studies discussed below reveal important features not accessible in the earlier work.

In addition to the crystallographic evidence discussed below, the vibrational and n.m.r. spectra confirm the formulation of the final products as catecholatotin(IV) species. The most significant feature of the i.r. spectra is the absence of ν(C=O), which is observed at 1 661s + 1 662(sh) cm^{-1} for dbbq, and at 1 673s + 1 648(sh) cm^{-1} for pq; the corresponding *o*-diolato derivatives do not exhibit these vibrations, and ν(C–O) modes appear at 1 468s + 1 414s cm^{-1} for SnX$_2$(dbc) and at 1 453s + 1 443s cm^{-1} for SnX$_2$(pd). The i.r. spectra also confirm the presence of co-ordinated bipy or phen in the adducts.

The ^{1}H n.m.r. spectra equally confirm the presence of the appropriate *o*-diolato and bidentate nitrogen ligands. The results are summarized in Table 1. The assignments for bipy and phen are based on the previous work of Castellano *et al.*[5] and Dove and Hallett[6] respectively, and those for the anionic ligands by comparison with the spectra of the relevant *o*-quinone and diol. For dbbq in (CD$_3$)$_2$SO solution we found ^{1}H resonances at 6.97 (m, 1 H, assigned as H^4), 6.13 (m, 1 H, H^6),

Table 5. Carbon-13 n.m.r. spectra of tin(IV) derivatives in $(CD_3)_2SO$; values in p.p.m. relative to $SiMe_4$

Compound	dbbq, dbc, pq, pd	bipy	phen
dbbq	180.5 (C^2), 179.7 (C^1) 162.5 (C^3), 148.9 (C^5) 133.4 (C^4), 121.7 (C^6) 35.7 (C^7), 35.0 (C^8) 29.0 (C^9), 27.5 (C^{10})		
H_2dbc	144.3 (C^2), 141.4 (C^1) 140.0 (C^3), 134.5 (C^5) 113.1 (C^4), 110.2 (C^6) 34.4 (C^7), 33.8 (C^8) 31.5 (C^9), 29.5 (C^{10})		
bipy		155.2 (C^3), 149.2 (C^1) 137.2 (C^4), 124.1 (C^6) 120.4 (C^5)	
phen			149.7 (C^2, C^9) 145.4 (C^{4b}, C^{6b}) 135.3 (C^3, C^8) 128.1 (C^4, C^7) 126.4 (C^{4a}, C^{6a}) 123.0 (C^5, C^6)
$SnCl_2$(dbc)·bipy	148.3 (C^1, C^2) 112.6 (C^3, C^5) 110.9 (C^4, C^6) 34.4 (C^7), 33.8 (C^8) 31.7 (C^9), 29.6 (C^{10})	150.4 (C^3) 147.6 (C^1) 140.6 (C^4) 126.0 (C^6) 122.4 (C^5)	
$SnBr_2$(dbc)·phen	149.4 (C^1, C^2) 110.0 (C^3, C^5) 109.8 (C^4, C^6) 35.0 (C^7), 34.7 (C^8) 31.8 (C^9), 29.8 (C^{10})		144.7 (C^2, C^9) 141.6 (C^{4b}, C^{6b}) 139.0 (C^3, C^8) 128.2 (C^4, C^7) 127.0 (C^{4a}, C^{6a}) 125.0 (C^5, C^6)
pq	179.0 (C^9, C^{10}) 135.5 (C^{11}, C^{14}) 135.3 (C^{12}, C^{13}) 131.2 (C^1, C^8) 129.3 (C^4, C^5) 129.1 (C^3, C^6) 124.4 (C^2, C^7)		
$SnCl_2$(pd)·bipy	145.5 (C^9, C^{10}) 139.1 (C^{11}, C^{14}) 129.2 (C^{12}, C^{13}) 126.9 (C^1, C^8) 125.8 (C^4, C^5) 124.3 (C^3, C^6) 121.5 (C^2, C^7)	154.9 (C^3) 149.1 (C^1) 137.5 (C^4) 122.5 (C^6) 120.7 (C^5)	
SnI_2(pd)·phen	147.3 (C^9, C^{10}) 138.9 (C^{11}, C^{14}) 128.8 (C^{12}, C^{13}) 128.2 (C^1, C^8) 125.7 (C^4, C^5) 124.1 (C^3, C^6) 121.3 (C^2, C^7)	141.7 (C^2, C^9) 137.1 (C^4, C^6) 129.3 (C^3, C^8) 127.3 (C^4, C^7) 124.1 (C^{49}, C^{69}) 122.5 (C^5, C^6)	

and 1.18 (s, 18 H, Bu^t); for the corresponding diol, in the same solvent, the values are 8.00 (br, 2 H, OH), 6.74 (m, 2 H, H^4, H^6), 1.32 (s, 9 H, Bu^t at C^5), and 1.21 (s, 9 H, Bu^t at C^3). The resonances for pq are at 8.31(m), 8.05(m), 7.75(m), and 7.45(m), each 2 H; the corresponding lines in the spectra of pd complexes could not be individually integrated or assigned. Finally, the ^{13}C n.m.r. spectra of the products clearly demonstrate the presence of aromatic rather than quinonoid ring systems. Data for the starting materials, the corresponding *o*-diols, the neutral ligands, and certain typical products are shown in Table 5. The values for phen are taken from ref. 1. While some of the assignments are tentative, there is no doubt that the high-field resonances identified as C=O of dbbq and pq disappear on formation of the tin(IV) species, and that these same changes are observed on comparing dbbq and H_2dbc. In summary, the spectroscopic evidence shows unambiguously that the final products are tin(IV) derivatives of aromatic *o*-diolato ligands.

We note finally that there are significant differences in the

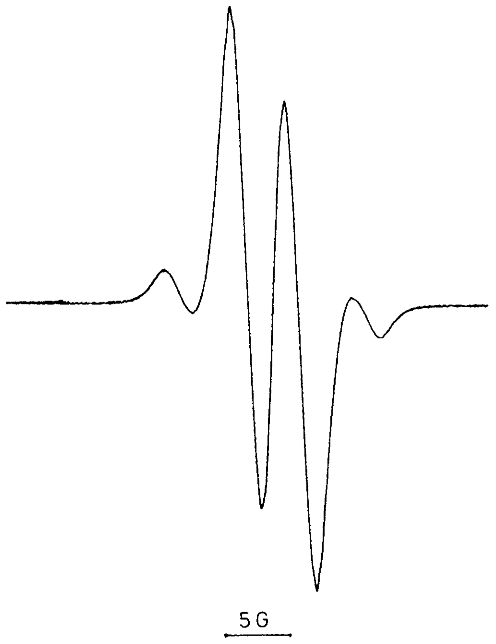


Figure 3. E.s.r. spectrum of a tetrahydrofuran solution of $SnCl_2$ + dbbq at room temperature

solubility of the adducts of $SnX_2(dbc)$, with the chloride precipitating spontaneously from the reaction mixture and the bromide requiring addition of diethyl ether. The iodo derivative is the most soluble, and apparently may undergo rearrangement by reaction (2). The existence of such an equilibrium is

$$2SnI_2(dbc) \rightleftharpoons Sn(dbc)_2 + SnI_4 \qquad (2)$$

demonstrated by the identification of $Sn(dbc)_2$·phen and SnI_4·bipy as the products of two similar reactions (see Experimental section). Such rearrangements are a common feature of tin(IV) solution chemistry, and a very similar process has been reported for germanium.[7] It seems probable that the detailed course of the reaction between dbbq and SnI_2 is solvent and temperature dependent, but we have not investigated this point in detail.

E.S.R. Spectroscopy.—Figure 3 shows the e.s.r. spectrum of a solution prepared by treating SnX_2 ($X = Cl$) with dbbq in tetrahydrofuran at room temperature. Although the spectrum is not well resolved, the most obvious feature is the presence of the spectrum of the semiquinone $dbbsq^{\bullet}$. The splitting due to one aromatic hydrogen atom is clearly observed, as is that due to the magnetic isotopes of tin, but the separate resonances due to ^{117}Sn and ^{119}Sn could not be resolved because of the large linewidth ($\nu_{\frac{1}{2}} = 1.34$ G). The coupling constants $a_H = 3.4$ G and $a_{Sn} = 10.3$ G allowed the spectrum to be computer-simulated to a satisfactory agreement. These values are similar to those reported by Davies and Hawari[8] for the semiquinone–tin radical $[SnX_3(O_2C_6H_2Bu^t{}_2)]^{\bullet}$ formed in the reaction of SnX_3R (R = Me, Bu, or C_5H_5) with 3,6-di-t-butyl-1,2-benzoquinone. The hyperfine constants for hydrogen are also close to those found for the InX–dbbq system,[2] implying a similar distribution of the unpaired electron density on the aromatic rings of all these semiquinone systems.

A significant result was obtained on recording the e.s.r. spectrum of a solution obtained by heating a mixture of dbbq + $SnCl_2$ + $\frac{1}{2}I_2$ at *ca.* 100 °C until the colour of iodine was completely discharged (4 h). The spectrum of this solution was significantly sharper than those discussed above and the derived

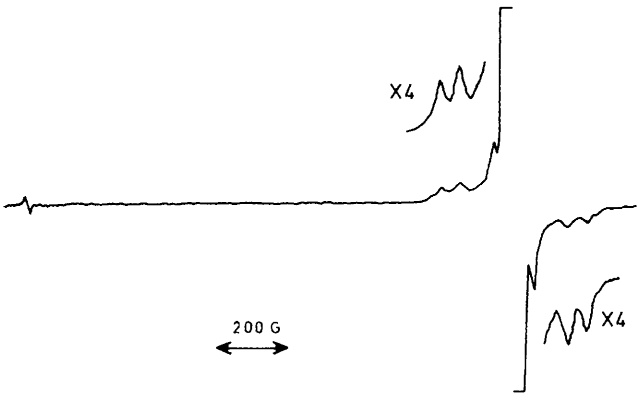


Figure 4. E.s.r. spectrum of a frozen solution of $SnCl_2$ + dbbq in thf at 77 K

coupling constants were $a_H = 3.4$ G and $a_{Sn} = 8.6$ G. This spectrum is undoubtedly that of $SnCl_2I(dbbsq)$ formed by

$$\text{dbbq} + SnCl_2 + \tfrac{1}{2}I_2 \longrightarrow SnCl_2I(\text{dbbsq}) \qquad (3)$$

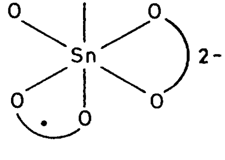
reaction (3) and is essentially identical to those spectra reported by Davies and Hawari.[8]

The e.s.r. spectrum of a frozen solution at 77 K is shown in Figure 4. In addition to the spectrum of the $SnX_n(dbbsq)$ species, we observe a pair of spin-triplet features, indicating the presence of two diradical species. These would not be observed in the solution spectra because of the averaging effect of molecular motion. Although the amplitude of the first-derivative spectrum of the diradicals is in total about 20 times smaller than that of the semiquinone species, the signal from the latter is isotropic and only a few gauss wide, while the highly anisotropic diradical spectra range over about 500 G. We estimate that the total concentration of these diradicals is of the same order as that of $SnX_2(dbbsq)$, although it was not possible to integrate the spectra to establish this ratio exactly. The e.s.r. parameters of the two diradicals are $g_y = g_z = 2.0037$, $|D| = 0.0228$ cm^{-1}, $E = 0.0035$ cm^{-1}, g_x not accessible (**A**) and $g_z = 2.0037$, $|D| = 0.0065$ cm^{-1}, g_x, g_y, E not accessible (**B**). The zero-field splitting parameters D and E may be assumed in the present systems to arise uniquely from the magnetic dipole–dipole interactions between the two unpaired electrons, and the parameter D in particular can then be used to estimate r, the effective distance between the two electrons, using the formula[9] (4). The above results then give interelectronic distances of 4.9 Å

$$D_{\text{dipole}} = -(3/2)g^2\beta^2/r^3 \qquad (4)$$

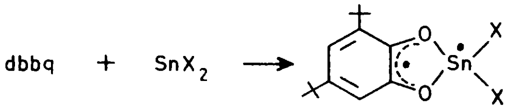
for (**A**) and 7.4 Å for (**B**), although some uncertainty may arise if the electrons are highly delocalized. The addition of iodine to a solution of $SnX_2(dbbsq)$, followed by freezing, causes the e.s.r. spectrum identified as (**A**) to disappear, while that of (**B**) is unaffected; a time of 5 min for the former reaction to go to completion in dilute solution is typical.

The reaction of tin (dissolved in mercury) with 3,6-di-t-butyl-1,2-benzoquinone has also been studied by e.s.r. spectroscopy.[10] In addition to features identifying the semiquinone ligand bonded to tin, the spectra also reveal the presence of diradicals in the frozen solution, and these have been assigned by Prokof'ev *et al.*[10] to the structure shown below, identified as a



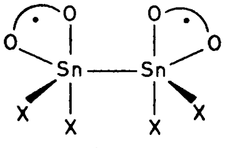
six-co-ordinate tin(IV) complex, and reduction of this diradical with tin amalgam is reported.

We offer a different interpretation based on the present results. The first step in the reaction between dbbq and SnX_2 is believed to be (5) in which the product is a short-lived reactive intermediate with two unpaired electrons, one delocalized on the semiquinone bidentate ligand and the other on the tin atom. The e.s.r. spectrum of this species was not detected in the present work, which is not surprising since its steady-state concentration is probably very low. Tin-centred radicals have been reported for a number of SnR_3 species by Lappert and co-workers,[11,12] and by Lloyd and Rogers;[13] these authors reported *g* factors close to the free-spin value, and very large hyperfine constants. The proposed intermediate species formed *via* equation (5) would have two electrons which would probably be paired to give a singlet ground state because of a strong exchange interaction. The thermally accessible triplet state would be e.s.r. active, but a broad spectrum would be expected by effects arising from large zero-field interactions. For these reasons then, the detection of this intermediate by e.s.r. spectroscopy would be difficult even at high concentrations.

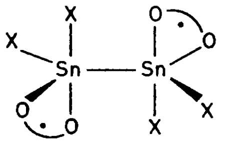


(5)

The species $SnX_2(dbbsq)$ can be oxidized by $\frac{1}{2}I_2$ to $SnX_2I(dbbsq)$, but in the absence of this equivalent of oxidant the proposed fate of the diradical is dimerization by Sn–Sn bonding to give a different type of diradical, namely (dbbsq)-X_2SnSnX_2(dbbsq) (*cf.* ref. 14). This latter species would require tin to be five-co-ordinate and would therefore give rise to two isomers (**A**) and (**B**). We identify these as the species whose e.s.r. parameters are discussed above. The interelectronic distances, estimated from models using reasonable bond lengths and angles, are 5.5 Å in (**A**) and 7.1 Å in (**B**), in remarkably good agreement with the distances estimated earlier from the e.s.r. spectral data. The more rapid reaction of (**A**) with I_2 appears to be in keeping with the openness of this structure relative to that of (**B**) and the mechanism is probably similar to that involving the polar transition state proposed for the attack of I_2 at the Sn–Sn bond of organotin compounds.[15]

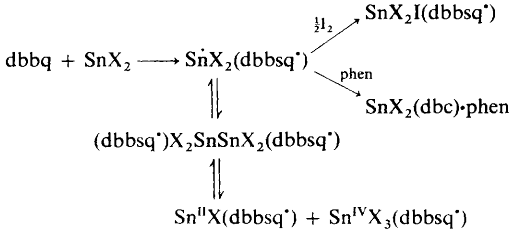


(A)



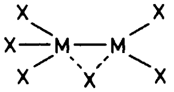
(B)

The overall reaction scheme is then as shown below. Under the conditions used, the only species whose e.s.r. spectrum would be observed with solutions of dbbq + SnX_2 using our instrument are $Sn^{II}X(dbbsq)$ and $SnX_3(dbbsq)$. Although the e.s.r. spectrum of the former has not been reported, it seems reasonable to assume that it would be very similar to that of $SnX_3(dbbsq)$, since the spectra of the series of such molecules studied by Davies and Hawari[8] show only a slight dependence on the nature of the other ligands attached to tin insofar as the spectrum of the dbbsq$^•$ moiety is concerned. We also note that the a_H values[2] for dbbsq$^•$ complexes to either indium(III) or indium(I) are similar to those for the tin(IV) radicals, again supporting the close identity proposed for the spectra of $SnX(dbbsq)$ and $SnX_3(dbbsq)$.



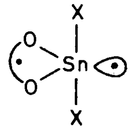
Scheme.

The disproportionation of the proposed Sn–Sn dimer is in keeping with the behaviour of Sn_2Cl_6, which above −65 °C goes to $SnCl_2$ and $SnCl_4$.[16] There are similar processes in the chemistry of indium(II), both in terms of the interaction of InX and InX_3,[17] and the disproportionation of $In_2X_6^{2-}$ anions to InX_2^- and InX_4^-.[18] All of these processes can be accommodated within a mechanism of halide transfer, in which the intermediate is (**C**). The detailed arguments for this process have been given elsewhere.[17,19]



(C)

Two final points should be made about the mechanism proposed in the Scheme. First, as already noted, the addition of 0.5 mol of I_2 converts $SnI_2(dbbsq^•)$ into $SnX_2I(dbbsq^•)$, thus oxidizing Sn^{III} to Sn^{IV}, rather than affecting the dbbsq$^•$ ligand, and this $SnX_2I(dbbsq^•)$ species is sufficiently stable in solution to permit e.s.r. investigation, and is not converted into the corresponding dbc derivative. Secondly, the preparative results show that when neutral bidentate donors are present in the reaction mixture, the products are derivatives of $SnX_2(dbc)$, so that under these conditions the final product is an adduct of $SnX_2(dbc)$, or a rearrangement product of the latter depending on the condition (see Experimental section). The effect of co-ordination of the neutral ligand can be understood in the following way. If the unpaired electron on tin in $\mathring{S}nX_2(dbbsq^•)$ is in a localized orbital, the structure can be written as the five-co-ordinated species (**D**). The question of whether this is trigonal bipyramidal or square pyramidal is not important at this stage. Co-ordination transfers negative charge to the tin, thereby favouring transfer of the unpaired electron to the dbbsq$^•$ ligand to give the corresponding catecholate. Furthermore, the adduct $SnX_2(dbbsq^•)$•bipy can only retain the localized electron by being seven-co-ordinate, whereas transfer to the dioxo ligand yields the six-co-ordinate complex, a stereochemistry of established stability in tin(IV) chemistry.



(D)

It also follows from this argument that the essential difference in the behaviour of dbbq (and by analogy pq) and the tetrahalogeno-*o*-benzoquinones studied previously[1] lies in the redox properties of the two pairs of quinones. It is clear from measurements of the half-wave potentials[20,21] that the tetrahalogeno species are more easily reduced than the compounds used in the present work. In keeping with this, we observed a faster reaction in the earlier work,[1] with no evidence of stable semiquinone species as intermediates in those reactions.

Although the reaction of SnX_2 with pq appears to proceed in an identical fashion to that with dbbq, in terms of the preparative and other results, the interesting features seen in the e.s.r. spectrum of the latter are not observed with this quinone. Instead, we observed only a broad unresolved spectrum in tetrahydrofuran (thf), both at room temperature and at 77 K, with $g \approx 2.0023$, assigned to SnX(psq$^{\bullet}$) or SnX_3(psq$^{\bullet}$), or a mixture of these radicals. The breadth of this unresolved spectrum may be the consequence of the presence of a number of pairs of hydrogen atoms on the ring system of the semiquinone, each pair having different but similar hyperfine constants. This behaviour effectively hides the e.s.r. signal from any dimer species which may have been present. In this context, we note that the ^1H n.m.r. spectrum was equally not capable of resolution.

Structural Studies.—The structure of compound (**1**) confirms the conclusions reached from the n.m.r. and vibrational spectroscopic studies, namely that the isolated products are *o*-diolato derivatives of tin(IV), although (**1**) is in fact the product of the disproportionation reaction (2).

The SnO_4N_2 kernel has a strongly distorted octahedral geometry, due in part to the bite of the ligands being far from 90°. The bond distances in (**1**) are typical of those reported for other tin(IV) complexes. The average Sn–O bond distance is 2.008(8) Å, which is slightly less than the value of 2.062(3) Å found in $[Sn(O_2C_6Cl_4)_3]^{2-}$ ($O_2C_6Cl_4{}^{2-}$ = tetrachlorocatecholate anion), and the average value of 2.049(4) Å in the closely related $Sn(OCF_3)_2(dbc){\cdot}CH_3OH$ studied by Butters *et al.*[22] These distances are at the low end of the range reported for other tin(IV)–oxoligand species. (See ref. 1 for a comparison with some recent results, and ref. 21 for earlier determinations.) The C–O distances in the dbc ligand [average 1.36(1) Å] are typical of those in phenolates, and intermediate between the comparable values for $[Sn(O_2C_6Cl_4)_3]^{2-}$ [average 1.336(5) Å][1] and $Sn(OCF_3)_2(dbc){\cdot}CH_3OH$ [average 1.374(7) Å].[22] More importantly, the bonds are significantly longer than the average [1.29(5) Å] found for a variety of transition-metal complexes of the 3,5-di-t-butyl-*o*-benzosemiquinonato ligand.[24,25] The diolato ligand is essentially planar as far as the C_6O_2 atoms are concerned, and the C_6 ring is clearly aromatic, as evidenced by the C–C–C bond lengths and angles. The average bite angle of the ligand (*i.e.* O–Sn–O) is 83.1(4)°, slightly larger than the average reported for $[Sn(O_2C_6Cl_4)_3]^{2-}$ [O–Sn–O 81.5(4)°].

The average Sn–N bond distance in compound (**1**) is 2.26(2) Å, within the range for Sn^{IV}–N bonds in a variety of organotin compounds,[26] and slightly less than the average value in $Sn(SPh)_4{\cdot}$bipy [2.331(3) Å].[27] The bite of the ligand is 74.0(4)°, again in agreement with previous values,[28] and the phen ligand is essentially planar.

Acknowledgements

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