Molecular structure of diphenylbis(9,10-phenanthrenesemiquinonate)tin(iv), an organometallic diradical complex

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The title compound, formed in the reaction between hexaphenylditin and 9,10-phenanthrenequinone, is shown to be an organotin(IV) diradical; its X-ray structure and EPR spectra are reported.

Substituted *ortho*-quinones can oxidize main-group elements or their low-oxidation state compounds, yielding semiquinone or catecholate complexes, characterised chemically and crystallographically.[1] The oxidation has been shown to proceed *via* successive one-electron transfer reactions,[2] involving semiquinone derivatives as important intermediates, conveniently detectable by electron paramagnetic resonance (EPR) spectroscopy. Some more unusual products were isolated, *e.g.* an oxygen-bridged tetrachlorocatecholate derivative $[(Cl_4C_6O_2)\text{-}TePh]_2O$ from the reaction between Ph_2Te and $Cl_4C_6O_2$.[3]

The present work is a part of our study of reactions of Sn_2Ph_6 with various *o*-quinones and of Ph_2SnCl_2 or Ph_3SnCl with sodium semiquinonates,[4] and of the redistribution processes which follow these reactions. The resulting systems comprise $SnPh_4$ and various radical and diradical species, identified by their EPR spectra. In particular, the reaction between equimolar amounts of Sn_2Ph_6 and 9,10-phenanthrenequinone (pq) in refluxing dichloromethane (1 h) yielded a brown solid, identified as $Ph_3Sn(psq)$ (psq = 9,10-phenanthrenesemiquinone). The residual solution (strongly EPR active) after about 5 days at room temperature deposited dark brown shiny crystals suitable for an X-ray diffraction study,† which proved them to be $Ph_2Sn(psq)_2$ **1**.‡ On the available evidence we believe that the primary reaction is given by eqn. (1), and the subsequent

$$Sn_2Ph_6 + pq \rightarrow Ph_3Sn(psq) + Ph_3Sn^{\cdot} \qquad (1)$$

processes include ligand redistribution to give the diradical.

The tin atom in **1** has a distorted *cis*-octahedral coordination (Fig. 1). The sensitive indicators of the oxidation state of the chelating ligand are known[2,5] to be the lengths of the C–O bonds (av. 1.23, 1.29 and 1.35 Å for the *o*-benzoquinone, *o*-semiquinone and catecholate) and the intervening C–C bond (1.53, 1.44 and 1.40 Å, respectively). Thus, the corresponding C–O and C–C distances in **1** [mean 1.291(6) and 1.44(1) Å] characterise it unequivocally as a semiquinone complex of tin(iv). The Sn–C distances in **1** (2.16 Å) are essentially equal and within the range (2.09–2.19 Å) observed in other $R_2Sn(O\text{–}O)_2$ complexes, *viz*. R = Me, O–O = tropolonate (**2**);[6,7] R = Me, O–O = kojate (6-hydroxymethyl-4*H*-pyran-4-on-3-olate) (**3**);[7] R = Me, O–O = maltolate (3-hydroxy-2-methyl-4*H*-pyran-4-oate) (**4**)[8] and R = Ph, O–O = maltolate (**5**).[8] On the other hand, Sn–O bonds formed by each semiquinone ligand show considerable non-equivalence (Δ) in length. Formally, such a ligand forms one covalent and one dative bond, and their unequal contribution can explain this difference. As Haaland[9] pointed out, a dative bond can have half the enthalpy of the corresponding covalent one and be 0.2 Å (or more) longer. Its length is also very sensitive to inductive effects of other ligands, increasing with their electron donating ability. Indeed, Δ in diphenyl complexes (0.08 Å in **1**, 0.16 Å in **4**) is much smaller than in dimethyl ones (0.34 Å in **3**, 0.28 Å in **5**) in accordance with the values of σ_I, −0.01 for Me and 0.12 for Ph.[10] However, in both polymorphs of **2**, Δ is only 0.04 Å, probably due to electron-poor character of the tropilium ring itself. It is noteworthy that the shorter Sn–O bonds are invariably in *trans*-positions to the less polar (Sn–C) ones, while exactly the opposite is observed in psq complexes of transition metals,[11] in accordance with the view[12] that in Sn complexes, less electronegative ligands exercise *cis*-influence, rather than *trans* (as for d elements).

The EPR spectra of the solution obtained finally in the reaction of Sn_2Ph_6 and pq show the presence of three species. The room temperature solution spectrum which shows hyperfine structure is predominantly that of the primary reaction product identified as the $Ph_3Sn(psq)$ monoradical, but the frozen solution spectrum showed, in addition to the $S = 1/2$ resonance ($g = 2.07$), both a fine structure and a resonance at half-field, indicating the presence of diradical species. The fine structure of the central resonance showed the presence of two such species, with $D = 63$ and 104×10^{-4} cm^{-1} respectively. The lower D value is very close to that of *trans*-$Cl_2(dbsq)SnSn(dbsq)Cl_2$ ($dbsq^{\cdot-}$ = 3,5-di-*tert*-butylorthosemiquinonate anion)[1a] and is presumably from the analogous $Ph_2(psq)SnSn(psq)Ph_2$ compound with a Sn–Sn bond. The higher D value can be assigned to **1**. It is of the same order as those observed for $Cd(dbsq)_2L$ (L = py, tmen, bipy) and related

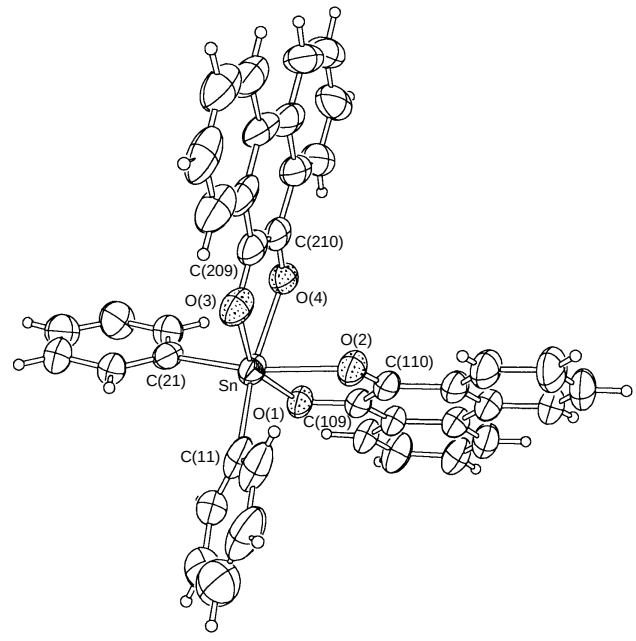

Fig. 1 Molecular structure of $Ph_2Sn(psq)_2$ **1**, showing 50% probability ellipsoids. Selected bond distances (Å) and angles (°): Sn–O(1) 2.127(5), Sn–O(2) 2.210(5), Sn–O(3) 2.137(5), Sn–O(4) 2.214(5), Sn–C(11) 2.160(9), Sn–C(21) 2.157(7), O(1)–C(109) 1.298(8), O(2)–C(110) 1.284(9), O(3)–C(209) 1.296(10), O(4)–C(210) 1.287(9), C(109)–C(110) 1.446(10), C(209)–C(210) 1.430(12); O(1)–Sn–O(2) 75.8(2), O(3)–Sn–O(4) 76.0(2), C(11)–Sn–O(4) 164.7(3), C(21)–Sn–O(2) 163.8(3).

molecules,[13] but slightly smaller; the difference may be due to the larger size of psq$^{\cdot-}$ compared with dbsq$^{\cdot-}$.

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Footnotes

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† The diffraction experiment at T = 150 K on a Siemens three-circle diffractometer with a CCD area detector (graphite-monochromated Mo-Kα radiation, $\bar{\lambda}$ = 0.71073 Å, ω scan mode, $2\theta \leqslant 52°$); structure solution by Patterson method, refinement against F^2 of all data (SHELXTL software). The structure contains large cavities with highly disordered solvent of crystallisation, approximated by arbitrary C atoms at electron density peaks; no chemically sensible model could be found. *Crystal data* (neglecting the solvent): $C_{40}H_{26}O_4Sn$, M = 689.3, monoclinic, space group $C2/c$ (no. 15), a = 31.962(1), b = 12.402(1), c = 20.838(1) Å, β = 120.20(1)°, U = 7138.9(7) Å^3, Z = 8, D_c = 1.28 g cm^{-3}, μ = 7.5 cm^{-1}, crystal size 0.35 × 0.2 × 0.2 mm, 15612 reflections total, 6026 unique, 4224 observed, R_{int} = 0.068, 459 variables, final $R(F$, obs. data) = 0.066, $R(F^2$, all data) = 0.188, goodness-of-fit 1.14, max. residual $\Delta\rho$ = 0.84 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/399.

‡ Elemental analysis. Calc. for $C_{40}H_{26}O_4Sn$, C 69.7, H 3.8. Found C 69.8, H 4.0%. Yield *ca.* 9%.

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