Oxidation of Elemental Antimony by Substituted *ortho*-Benzoquinones*

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The oxidation of elemental antimony by the *o*-quinones $Y_4C_6O_2$-*o* (Y = Cl or Br) in diethyl ether gives the unusual antimony(V) products $Sb(O_2C_6Y_4)_{2.5}\cdot nEt_2O$ (Y = Cl, *n* = 1.5; Y = Br, *n* = 1). The same quinones, and 3,5-di-*tert*-butyl-1,2-benzoquinone, upon treatment with Sb + $\frac{1}{2}X_2$ (X = Br or I) in toluene, give the antimony(III) derivatives Sb(cat)X (cat = substituted catecholate anion). The oxidations are shown by electron spin resonance spectroscopy to proceed *via* the *o*-semiquinone intermediates. Adducts of Sb(cat)I with bidentate neutral donors have been prepared. The structure of Sb(dbc)I(bipy) (dbc = 3,5-di-*tert*-butylcatecholate, bipy = 2,2′-bipyridine) has been shown to be that of a pseudo-octahedral molecule with a stereochemically active lone pair of electrons. Crystal parameters for Sb(dbc)I(bipy)·0.5bipy: triclinic, space group $P\bar{1}$, *a* = 9.779(4), *b* = 18.554(7), *c* = 8.944(3) Å, α = 100.94(3), β = 115.11(3), γ = 86.82(4)°, *Z* = 2 and *R* = 0.044 for 3307 unique reflections.

The oxidation of low-oxidation state compounds of main-group elements, and of the elements themselves, by *ortho*-benzoquinones has been the subject of a number of recent investigations in this laboratory. Both metallic (Zn, Cd, Ga, In, Te, Sn, Mg, Ba)[1–4] and non-metallic (P, Te)[5,6] elements react to yield the corresponding semiquinonate or catecholate derivatives, depending on the particular metal and substituted *o*-quinone couple in question. The results with phosphorus[5] and tellurium[6] are of special relevance to the present work, which involves the same *o*-quinones, namely $Y_4C_6O_2$-*o* (Y = Cl or Br) and 3,5-di-*tert*-butyl-1,2-benzoquinone (dbbq), used previously. The reaction of any of these compounds with a mixture of P_4 and Br_2 gave the phosphorus(V) species $P(cat)_2Br$, (cat^{2-} = substituted catecholate) but no reaction occurred in the absence of elemental bromine. In contrast, tellurium reacts in refluxing toluene to yield $Te(cat)_2$, and these tellurium(IV) products resist further oxidation by halogen (Br_2, I_2). Similarly, phosphorus(III) compounds such as PPh_3 are readily oxidised[5,7,8] to $P(cat)Ph_3$, whereas TeR_2 (R = Me, Et, *etc*) can only be oxidised to $Te(cat)R_2$.

It therefore seemed logical to investigate the reaction between *o*-quinones and elemental antimony, or triphenylantimony. In the event, we find some aspects of these systems which are similar to those involving phosphorus, but equally others in which the better analogy is to tellurium.

Experimental

All reagents, including elemental antimony (Aldrich) and triphenylantimony (Aldrich) were reagent grade or better, and used as supplied. Solvents were purified by standard procedures. Reactions were carried out in an atmosphere of dry nitrogen, using conventional techniques for handling potentially air-sensitive materials.

Microanalysis was carried out by Canadian Microanalytical Services Ltd., and antimony analysis was by flame photometry, using an IL-251 instrument. Infrared spectra were obtained with KBr discs using a Nicolet 5DX spectrometer and ^1H and ^{13}C NMR spectra were run on a Bruker AC-300L instrument. Electron spin resonance (ESR) spectroscopy used the techniques previously described[9] with a Varian E-12 spectrometer calibrated against an NMR spectrometer; the Klystron frequency was standardised against diphenyldipicrylhydrazyl.

Table 1 Analytical results (%), with calculated values in parentheses

Compound	Sb	C	H
$Sb(O_2C_6Cl_4)_{2.5}\cdot 1.5Et_2O$	13.9 (14.4)	30.0 (29.8)	2.10 (1.80)
$Sb(O_2C_6Br_4)_{2.5}\cdot Et_2O$	10.0 (9.70)	17.9 (18.2)	1.15 (0.80)
$Sb(O_2C_6Cl_4)Br$	26.7 (27.2)	—	—
$Sb(O_2C_6Br_4)Br$	18.8 (19.5)	—	—
$Sb(O_2C_6Cl_4)I$	25.6 (24.6)	15.0 (14.6)	—
$Sb(O_2C_6Br_4)I\cdot 0.5Et_2O$	16.8 (17.2)	13.4 (13.5)	0.70 (0.70)
Sb(dbc)I	26.2 (26.0)	—	—
Sb(dbc)I(bipy)[a]	19.7 (19.5)	—	—
Sb(dbc)I(phen)[b]	18.0 (18.8)	—	—
$Sb(dbc)Ph_3$	21.8 (21.2)	66.4 (67.0)	6.45 (6.15)
$Sb(O_2C_6Cl_4)Ph_3$	21.3 (20.3)	—	—
$Sb(O_2C_6Br_4)Ph_3$	16.4 (15.9)	—	—

[a] bipy = 2,2′-Bipyridine. [b] phen = 1,10-Phenanthroline.

Reaction of Antimony with o-*Quinones*.—There was no identifiable reaction when antimony powder was refluxed with $Y_4C_6O_2$-*o* (Y = Cl or Br), or $3,5\text{-}Bu^t{}_2H_2C_6O_2$-*o* (dbbq) in toluene, nor when a suspension of the element in diethyl ether was treated with dbbq at room temperature. When antimony powder (0.061 g, 0.5 mmol) was added to a stirred solution of $Y_4C_6O_2$-*o* (Y = Cl, 0.369 g, 1.5 mmol; Y = Br, 0.636 g, 1.5 mmol) in Et_2O (25 cm^3), a slow reaction ensued. After *ca.* 10 h, the antimony was consumed, and the solid product remaining (colourless for Y = Cl, yellow for Br) was collected by filtration, washed with *n*-hexane (2 × 10 cm^3) and dried *in vacuo*.

The products were identified by elemental analysis (Table 1) as $Sb(O_2C_6Cl_4)_{2.5}\cdot 1.5Et_2O$ and $Sb(O_2C_6Br_4)_{2.5}\cdot Et_2O$. In each case the infrared spectrum showed the absence of ν(C=O) of the parent *o*-quinone. The ^1H NMR spectra in $(CD_3)_2SO$ confirmed the presence of Et_2O [δ 1.07 (t, 3 H), 3.36 (q, 2 H), relative to $SiMe_4$ (δ = 0)], as did the ^{13}C spectra [δ 64.85, 15.0, relative to $SiMe_4$ (δ = 0)]. In addition, the ^{13}C spectra had features found in other tetrahalogenocatecholate complexes;[5,9] for Y = Cl, these were at δ 142.4 ($C^{1,2}$), 121.8 ($C^{3,6}$), 116.9 ($C^{4,5}$); and for Y = Br at δ 144.1 ($C^{1,2}$), 117.4 ($C^{3,6}$) and 110.1 ($C^{4,5}$).

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

Reaction of Antimony + Bromine + o*-Quinones*.—(*i*) Bromine (0.240 g, 1.5 mmol Br_2) was weighed into a Schlenk flask containing diethyl ether (30 cm^3), the contents cooled to −78 °C, and antimony powder (0.365 g, 3 mmol) and $Cl_4C_6O_2$-*o* (0.738 g, 3 mmol) added under nitrogen. The mixture was stirred at this temperature; after *ca.* 5 min the formation of a white solid was apparent, and after 6 h all the antimony had been consumed. The mixture was allowed to reach ambient temperature, and the product collected by filtration, washed twice with diethyl ether and dried *in vacuo*. The yield of $Sb(O_2C_6Cl_4)Br$ was quantitative, as was that of $Sb(O_2C_6Br_4)Br$ in an identical experiment. The ^{13}C NMR resonances of these products in $(CD_3)_2SO$ were at δ 143.0, 122.4 and 117.4 for Y = Cl, and δ 145.9, 117.7 and 110.9 for Y = Br, and the infrared spectrum confirmed the presence of the substituted catecholate ligand.

Reaction of Antimony + Iodine + o*-Quinones*.—(*i*) *Tetrahalogeno-*o*-quinones*. Antimony powder (0.121 g, 1 mmol) was suspended in a solution of $Y_4C_6O_2$-*o* (Y = Cl, 0.246 g, 1 mmol; Y = Br, 0.424 g, 1 mmol) in diethyl ether (30 cm^3), and solid iodine (0.127 g, 0.5 mmol as I_2) added. After about 5 min the colour of the solution changed to light red and the suspension turned pale yellow. After 10 h at room temperature, with mechanical agitation, the antimony had dissolved; the volume of the now pale yellow solution was then reduced to *ca.* 10 cm^3 *in vacuo*, and the resultant pale yellow precipitate collected by filtration and washed with *n*-hexane (2 × 5 cm^3). The product, $Sb(O_2C_6Y_4)I$, was obtained in yields of 83% (Y = Cl) and 92% (Y = Br). The ^{13}C NMR spectra had resonances at δ 150.2, 118.5 and 116.8 (Y = Cl) and δ 151.0, 114.2 and 110.6 (Y = Br); in addition the latter also had the characteristic features of Et_2O (δ 64.9, 15.2).

(*ii*) *dbbq*. The procedure was essentially identical to that just described, except that the period to the detectable onset of the reaction (30 min) and the total time required (24 h) indicated a more sluggish reaction. It was necessary to reduce the volume of the final solution to *ca.* 5 cm^3 and to add *n*-hexane (30 cm^3) in order to precipitate the product completely. The pale yellow solid was dried *in vacuo* for 2 d, and identified as Sb(dbc)I (dbc = 3,5-di-*tert*-butylcatecholate anion). Yield: 80%. In this compound, the ^{13}C NMR spectrum identified each of the benzenoid carbon atoms (δ 151.4, 147.9, 140.5, 135.1, 112.6 and 110.5; see ref. 5 for assignments) and those of the *tert*-butyl groups (δ 34.5, 34.2, 32.0 and 29.8).

(*iii*) *Adducts of* Sb(dbc)I. A solution of Sb(dbc)I in diethyl ether was prepared, and an equimolar quantity of solid 2,2′-bipyridine (bipy) added. The mixture was stirred for 8 h at room temperature, during which time a yellow precipitate formed. This was collected and dried *in vacuo*, and identified as Sb(dbc)I(bipy); ^1H NMR (relative to $SiMe_4$) δ 8.81 (d, 2 H), 8.55 (d, 2 H), 8.24 (t, 2 H), 7.72 (t, 2 H) (bipy); 6.71, 6.62 (2 H, $H^{4,6}$ of dbc); 1.40, 1.23 (q, 18 H, Bu^t of dbc). The yield was quantitative. The structure of this compound was subsequently the subject of an X-ray crystallographic study. An analogous adduct with 1,10-phenanthroline was also prepared by the same method.

Reaction of Triphenylantimony with o*-Quinones*.—(*i*) In each experiment $SbPh_3$ (0.353 g, 1 mmol) in toluene (20 cm^3) was added dropwise to an equimolar solution of the *o*-quinone ($Y_4C_6O_2$ or dbbq) in the same solvent (20 cm^3). A colour change was apparent within a few seconds for $Y_4C_6O_2$-*o*, and a few minutes for dbbq. After 4 h of mechanical stirring, the volume was reduced to *ca.* 5 cm^3 *in vacuo* and light petroleum (30 cm^3) added to precipitate a colourless solid which was collected and dried *in vacuo*. The yields of $Sb(dbc)Ph_3$, *etc.* were essentially quantitative.

(*ii*) Other experiments were not as successful as those just described. When equimolar quantities of $SbPh_3$ and anthraquinone were mixed in toluene at room temperature, a pale yellow solution resulted; this quickly became dark green and then yellow over a period of 12 h. The mixture was refluxed for 30 min, toluene removed *in vacuo* (90%) and *n*-hexane added. The resultant yellow precipitate could not be identified; the infrared spectrum showed the presence of C=O groups. For the reaction between $SbPh_3$ and benzil, the material isolated after refluxing in toluene included unreacted diketone. None of these systems was investigated further.

Crystallographic Studies.—A sample of Sb(dbc)I(bipy) was dissolved in *N*,*N*-dimethylformamide (dmf) and allowed to recrystallise by slow evaporation of the solvent in air. The subsequent structure determination showed that the product of this procedure was in fact Sb(dbc)I(bipy)·0.5bipy **1**, with one molecule of 2,2′-bipyridine and two molecules of Sb(dbc)I(bipy) in the unit cell.

An orange crystal of **1** was mounted on a glass fibre in a Rigaku AFC6S diffractometer, equipped with Mo-Kα radiation (λ = 0.710 69 Å) and a rotating anode. Cell constants, and an orientation matrix, were obtained using 25 strong reflections in the range $30.67 < 2\theta < 34.27°$. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. No decay corrections were needed since the intensity of three representative reflections remained constant throughout the data collection, but analytical absorption corrections were applied and the data were also corrected for Lorentz and polarization effects. The relevant experimental details are given in Table 2. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically; hydrogen atoms on carbon were initially included in ideal positions, and subsequently refined isotropically. The programs and other data used are listed in refs. 10–15. The convergence minimised the function $\Sigma w(|F_o| - |F_c|)^2$, and a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$ was used in the final cycles. The atomic coordinates are presented in Table 3, and the important interatomic distances for the Sb(dbc)I(bipy) molecule are in Table 4. Fig. 1 shows the structure of this unit, and Fig. 2 the arrangement of Sb(dbc)I(bipy) and bipy in the unit cell.

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

Results and Discussion

Synthetic Methods.—The interaction of elemental antimony with substituted *o*-quinones makes an interesting contrast with the case of phosphorus, which reacts only in the presence of bromine to give $P(cat)_2Br$.[5] Although antimony is unaffected by any of the three quinones examined in refluxing toluene (111 °C), there is a slow reaction with $Y_4C_6O_2$-*o* (Y = Cl or Br) in diethyl ether at room temperature (*ca.* 23 °C). The cause of this marked solvent effect is not clear, but may be due to a slight solubility of the element in diethyl ether.[16] The products of the reaction are antimony(V) compounds whose structure has not been determined, but which can be written tentatively as the ionic species $[Sb(O_2C_6Y_4)_2L_n]^+[Sb(O_2C_6Y_4)_3]^-$ (L = Et_2O; Y = Cl, *n* = 2; Y = Br, *n* = 1). This formulation is in keeping with earlier work by Hall and Sowerby[17] on the compound $[SbPh_3(O_2C_6H_4\text{-}o)(H_2O)][SbPh_3(O_2C_6H_4\text{-}o)]$, which demonstrated that antimony(V) species of differing co-ordination number can co-exist in a crystalline lattice. Another possibility would be a polymer linked by bridging $Y_4C_6O_2^{2-}$ groups. Further work on this problem is planned.

In the presence of bromine, the reaction products are the antimony(III) compounds Sb(cat)X (X = Br or I), different again from the corresponding phosphorus reaction which yielded $Pb(cat)_2Br$ for each of the *o*-quinones in question.[5] The +5 state of antimony is generally stable and accessible, and the isolation of these lower oxidation species may be due to the

Table 2 Summary of crystal data, intensity collection and structure refinement for Sb(dbc)I(bipy)·0.5bipy **1**

Formula	$C_{29}H_{32}IN_3O_2Sb$
M	703.25
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	9.779(4)
b/Å	18.554(7)
c/Å	8.944(3)
α/°	100.94(3)
β/°	115.11(3)
γ/°	86.82(4)
U/Å^3	1442(2)
Z	2
D_c/g cm^{-3}	1.62
Crystal dimensions/mm	0.3 × 0.3 × 0.1
μ/cm^{-1}	20.49
2θ/°	50.5
Total reflections measured	5402
Unique data used [$I \geqslant 3\sigma(I)$]	3307
Number of parameters	325
$F(000)$	694
T/°C	23
R	0.044
R'	0.053
Maximum shift/error in final cycle	0.03
Maximum, minimum peaks in final difference map/e Å^{-3}	1.22, −0.91

Table 3 Final positional coordinates for the non-hydrogen atoms of Sb(dbc)I(bipy)·0.5 bipy **1**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
I	1.14 350(8)	0.01 355(4)	0.31 448(9)
Sb	0.86 132(6)	0.08 336(3)	0.36 389(7)
O(1)	1.0 016(6)	0.1 477(3)	0.5 817(6)
O(2)	0.8 891(6)	0.1 675(3)	0.2 692(6)
N(1)	0.6 625(7)	0.1 439(4)	0.4 114(8)
N(2)	0.6 261(7)	0.0 876(4)	0.0 997(8)
N(3)	0.685(1)	0.4 901(7)	0.657(2)
C(1)	0.520(1)	0.1 436(5)	0.288(1)
C(2)	0.684(1)	0.1 699(5)	0.571(1)
C(3)	0.569(1)	0.1 958(5)	0.615(1)
C(4)	0.426(1)	0.1 943(6)	0.491(2)
C(5)	0.402(1)	0.1 664(6)	0.328(1)
C(6)	0.504(1)	0.1 174(4)	0.115(1)
C(7)	0.621(1)	0.0 621(6)	−0.051(1)
C(8)	0.491(1)	0.0 666(6)	−0.197(1)
C(9)	0.367(1)	0.0 967(6)	−0.183(1)
C(10)	0.370(1)	0.1 219(5)	−0.025(1)
C(11)	1.0 452(8)	0.2 108(5)	0.553(1)
C(12)	0.9 869(8)	0.2 207(4)	0.387(1)
C(13)	1.0 270(9)	0.2 834(5)	0.349(1)
C(14)	1.127(1)	0.3 341(5)	0.485(1)
C(15)	1.1 840(9)	0.3 241(5)	0.651(1)
C(16)	1.1 416(9)	0.2 609(5)	0.683(1)
C(17)	0.961(1)	0.2 957(5)	0.166(1)
C(18)	1.292(1)	0.3 830(6)	0.791(1)
C(19)	1.017(1)	0.3 698(7)	0.157(1)
C(20)	1.431(2)	0.392(1)	0.771(2)
C(21)	1.338(3)	0.367(2)	0.957(2)
C(22)	1.227(2)	0.455(1)	0.791(4)
C(23)	1.005(1)	0.2 371(7)	0.057(1)
C(24)	0.789(1)	0.2 992(7)	0.097(1)
C(25)	0.558(1)	0.4 716(6)	0.516(1)
C(26)	0.780(2)	0.376(1)	0.595(3)
C(27)	0.792(2)	0.442(1)	0.691(3)
C(28)	0.534(1)	0.4 056(7)	0.411(1)
C(29)	0.650(2)	0.3 539(8)	0.452(2)

Table 4 Bond lengths (Å) and angles (°) for Sb(dbc)I(bipy) and uncoordinated bipy in **1**, with e.s.d.s in parentheses*

I–Sb	3.148(2)	C(7)–C(8)	1.40(1)
Sb–O(1)	2.033(6)	C(8)–C(9)	1.35(1)
Sb–O(2)	1.994(6)	C(9)–C(10)	1.38(1)
Sb–N(1)	2.345(6)	C(11)–C(12)	1.39(1)
Sb–N(2)	2.513(6)	C(11)–C(16)	1.36(1)
O(1)–C(11)	1.37(1)	C(12)–C(13)	1.39(1)
O(2)–C(12)	1.362(9)	C(13)–C(14)	1.40(1)
N(1)–C(1)	1.36(1)	C(13)–C(17)	1.55(1)
N(1)–C(2)	1.34(1)	C(14)–C(15)	1.39(1)
N(2)–C(6)	1.34(1)	C(15)–C(16)	1.38(1)
N(2)–C(7)	1.32(1)	C(15)–C(18)	1.54(1)
C(1)–C(5)	1.38(1)	C(17)–C(19)	1.54(1)
C(1)–C(6)	1.46(1)	C(17)–C(23)	1.49(1)
C(2)–C(3)	1.38(1)	C(17)–C(24)	1.53(1)
C(3)–C(4)	1.37(1)	C(18)–C(20)	1.46(2)
C(4)–C(5)	1.37(1)	C(18)–C(21)	1.44(2)
C(6)–C(10)	1.39(1)	C(18)–C(22)	1.44(2)
I–Sb–O(1)	89.8(2)	C(7)–C(8)–C(9)	118.6(9)
I–Sb–O(2)	87.4(2)	C(8)–C(9)–C(10)	120.1(9)
I–Sb–N(1)	175.5(2)	C(6)–C(10)–C(9)	118.6(9)
I–Sb–N(2)	116.0(2)	O(1)–C(11)–C(12)	116.9(7)
O(1)–Sb–O(2)	81.4(2)	O(1)–C(11)–C(16)	121.0(7)
O(1)–Sb–N(1)	86.3(2)	C(12)–C(11)–C(16)	122.1(8)
O(1)–Sb–N(2)	142.0(2)	O(2)–C(12)–C(11)	116.7(7)
O(2)–Sb–N(1)	89.7(2)	O(2)–C(12)–C(13)	123.3(7)
O(2)–Sb–N(2)	73.1(2)	C(11)–C(12)–C(13)	120.0(8)
N(1)–Sb–N(2)	66.3(2)	C(12)–C(13)–C(14)	116.7(7)
Sb–O(1)–C(11)	111.6(4)	C(12)–C(13)–C(17)	120.4(7)
Sb–O(2)–C(12)	113.3(5)	C(14)–C(13)–C(17)	122.9(8)
Sb–N(1)–C(1)	122.5(6)	C(13)–C(14)–C(15)	123.1(8)
Sb–N(1)–C(2)	118.3(5)	C(14)–C(15)–C(16)	118.2(8)
C(1)–N(1)–C(2)	118.4(7)	C(14)–C(15)–C(18)	119.4(9)
Sb–N(2)–C(6)	117.8(5)	C(16)–C(15)–C(18)	122.5(8)
Sb–N(2)–C(7)	122.0(6)	C(11)–C(16)–C(15)	119.9(7)
C(6)–N(2)–C(7)	120.2(7)	C(13)–C(17)–C(19)	110.6(8)
N(1)–C(1)–C(5)	119.8(8)	C(13)–C(17)–C(23)	111.5(7)
N(1)–C(1)–C(6)	116.2(7)	C(13)–C(17)–C(24)	109.8(8)
C(5)–C(1)–C(6)	124.0(8)	C(19)–C(17)–C(23)	107.8(9)
N(1)–C(2)–C(3)	123.3(8)	C(19)–C(17)–C(24)	106.5(8)
C(2)–C(3)–C(4)	118.4(9)	C(23)–C(17)–C(24)	110.5(8)
C(3)–C(4)–C(5)	118.7(9)	C(15)–C(18)–C(20)	111.6(9)
C(1)–C(5)–C(4)	121.3(9)	C(15)–C(18)–C(21)	113(1)
N(2)–C(6)–C(1)	116.0(7)	C(15)–C(18)–C(22)	112(1)
N(2)–C(6)–C(10)	120.9(8)	C(20)–C(18)–C(21)	107(2)
C(1)–C(6)–C(10)	123.1(8)	C(20)–C(18)–C(22)	105(2)
N(2)–C(7)–C(8)	121.5(9)	C(21)–C(18)–C(22)	108(2)
2,2′-bipyridine			
N(3)–C(25)	1.34(1)	C(25)–N(3)–C(27)	117(1)
N(3)–C(27)	1.30(2)	N(3)–C(25)–C(25′)	115(1)
C(25)–C(25′)	1.48(2)	N(3)–C(25)–C(28)	124(1)
C(25)–C(28)	1.36(1)	C(25′)–C(25)–C(28)	121(1)
C(26)–C(27)	1.35(2)	C(27)–C(26)–C(29)	120(2)
C(26)–C(29)	1.38(2)	N(3)–C(27)–C(26)	124(2)
C(28)–C(29)	1.41(2)	C(25)–C(28)–C(29)	118(1)
		C(26)–C(29)–C(28)	117(1)

* Prime indicates atoms related by the symmetry operation 1 − *x*, 1 − *y*, 1 − *z*.

precipitation of a stable oligomeric species which resists further oxidation; such species are an important feature of antimony(III) chemistry.[18] Reaction with the neutral bidentate donors 2,2′-bipyridine and 1,10-phenanthroline give 1 : 1 adducts, and the structure of Sb(dbc)I(bipy), discussed below, is clearly that of a monomer. On the other hand, the processes which give rise to crystals of this compound require more than mere dissolution and recrystallisation from dmf, since the overall change is, at the simplest, represented by equation (1).

$$2\mathrm{Sb(dbc)I(bipy)} \longrightarrow \underset{\mathbf{1}}{\mathrm{Sb(dbc)I(bipy)\cdot 0.5bipy}} + 0.5\ \mathrm{bipy} + [\mathrm{Sb(dbc)I}]_n \qquad (1)$$

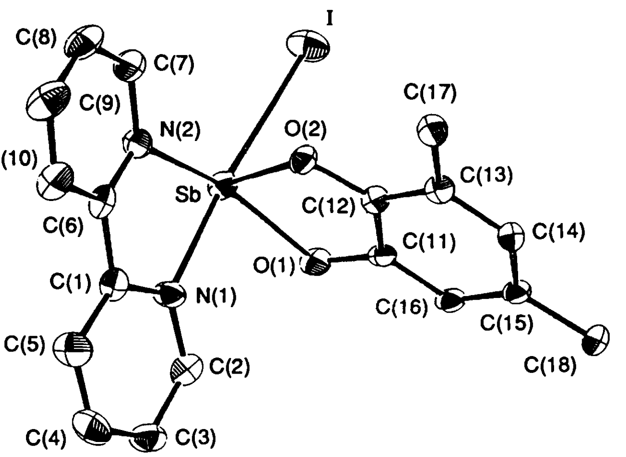

Fig. 1 The structure of Sb(dbc)I(bipy); ORTEP diagram[15] with atoms represented as 30% probability ellipsoids. All hydrogen atoms, and the C atoms of the CH_3 groups of Bu^t have been omitted for clarity; C(19), C(23) and C(24) ride on C(17) and C(20)–(22) on C(18)

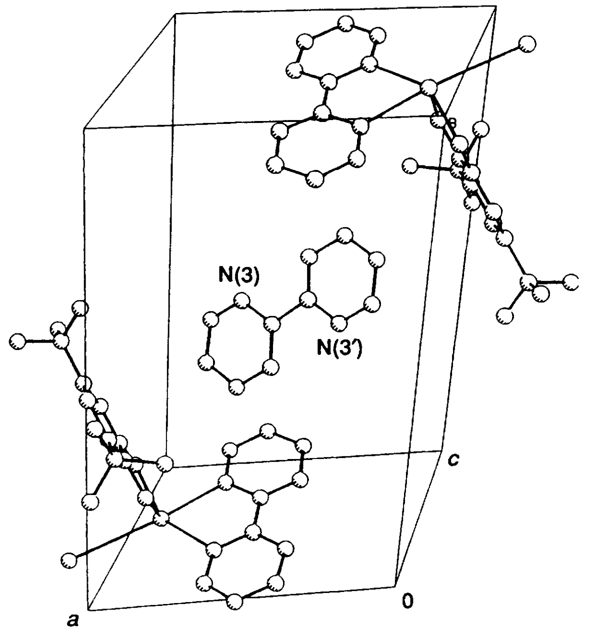

Fig. 2 Cell diagram for Sb(dbc)I(bipy)·0.5bipy **1**; hydrogen atoms have been omitted. Carbon atoms of unco-ordinated bipy are C(25)–C(29)

We also observed the precipitation of a non-crystalline material, in addition to the crystals of **1**, and presume this to be the oligomer of the uncomplexed Sb(dbc)I, similar to that formed in the reaction between Sb + *o*-quinones + X_2. Thus it seems that the reaction products from such reactions are defined in some measure by the solid-state chemistry of antimony(III), rather than by any simple consideration of ionisation energies. Finally we note that the oxidation of $SbPh_3$ by *o*-quinones leads to the antimony(V) analogues of $P(cat)Ph_3$ species reported earlier,[5,7,8] and the mechanism of this reaction is discussed below.

Reaction Mechanism.—The ESR spectrum of the heterogeneous reaction mixture Sb + 2 dbbq + $\frac{1}{2}Br_2$ in toluene at room temperature gave a clear ESR signal, with the classical features of the 3,5-di-*tert*-butyl-1,2-benzosemiquinone radical, with $g = 2.0019$. No fine structure was detected, and hence no coupling constants are available. Similar results emerged from the system Sb + $Cl_4C_6O_2$-*o* in diethyl ether at room temperature. Frozen samples (77 K) showed some fine structure, with $g = 2.0067$, but the quality of the spectra did not allow quantitative analysis.

The reaction between $SbPh_3$ and *o*-quinones in toluene at room temperature is too rapid for study, but we were able to detect a weak ESR signal when solutions of the individual reactants were mixed at 77 K and allowed to warm slowly. For $SbPh_3$ + $Cl_4C_6O_2$-*o*, this resonance yielded $g = 2.0043$. From these results we conclude that semiquinone species are involved in these reactions, and by extension generally in the oxidation of antimony, or $SbPh_3$, by *o*-benzoquinones.

This study completes a set of investigations of the reactions of substituted *o*-quinones with the fourth-row elements Cd, In, Sn, Sn, Sb and Te, and with their low-oxidation compounds. In each case, the mechanism involves a one-electron process as the first step in the reaction and there can be no doubt of the generality of this conclusion, which also applies in the case of P, Ga and Tl. The *o*-quinones clearly are a favourable case for the identification of such processes, thanks to the thermodynamic stability of the *o*-semiquinones, and their ready spectroscopic identification. Few other oxidation reactions of main-group species present such favourable characteristics for the study of the mechanism of electron transfer, and the extension of the general conclusion to other redox processes is therefore moot in the absence of experimental evidence. One can however point to the increasing evidence of radical species[19] in the chemistry of such elements as N, P, S and Se as implying that the one-electron-transfer processes are not restricted to transition-metal chemistry, but can and do occur throughout the Periodic Table.

The Structure of Sb(dbc)I(bipy).—Of the compounds reported in the Experimental section, the only one which readily yielded crystalline material was Sb(dbc)I(bipy)·0.5bipy **1**, which can be viewed as the mononuclear 2,2'-bipyridine adduct of Sb(dbc)I in a lattice also containing uncomplexed 2,2'-bipyridine. It is interesting that Sb(dbc)I is a weak acceptor, as well as being an electron pair donor, and this dichotomy is presumably responsible for the oligomerisation which often occurs in antimony(III) compounds.

Electron pair repulsion theory predicts that a molecule with an SbO_2N_2I kernel and a lone pair of electrons will have a pseudo-octahedral AX_5E stereochemistry if the lone pair is sterically active, and distorted trigonal-bipyramidal or square-based pyramidal stereochemistry if it is not. This point has been discussed in terms of the atomic weight of the ligand involved for halide derivatives.[20] The present structure is most conveniently described as AX_5E, but with substantial distortion caused by the steric restrictions of the bidentate ligands.

The Sb–I bond distance of 3.148(2) Å is slightly larger than the average value for such bonds in crystalline SbI_3 (2.686, 3.313 Å)[21] and *r*(Sb–O) [average value = 2.014(6) Å] is well within the range of distances reported for a wide variety of antimony(III)–oxygen complexes.[18] The Sb–N bonds, in contrast, are substantially longer than would be predicted from the covalent radii, or by comparison with *r*(Sb–O), and this, together with the small N–Sb–N angle of 66.3(2)°, implies a weak donation from 2,2'-bipyridine to the antimony(III) centre. This is similar to the results[6] for $Te(dbc)_2(bipy)$, in which the bite angle is only 56.1(2)°, and both are lower than the value of *ca.* 78° usually found in complexes of this ligand. The remaining bond distances call for no comment, except to note that *r*(C–O) of the dbc^{2-} ligand [average value 1.366(9) Å] is typical of that for catecholato complexes,[22] as required by the formulation of this complex.

For the purposes of discussion, the I–Sb–N(1) axis [angle 175.5(2)°] can be regarded as passing through a rough plane defined by Sb, N(2), O(1) and O(2); the I–Sb–O(1) and I–Sb–O(2) angles [89.8(2), 87.4(2)°] are compatible with this description, but I–Sb–N(2) [116.0(2)°] shows that N(2) is well below this plane, in keeping with the small N(1)–Sb–N(2) bite angle. The large O(1)–Sb–N(2) angle, and the other features of the structure, indicate that a stereochemically active lone pair indeed occupies the vacant sixth position of the AX_5E kernel.

The features of the unco-ordinated 2,2′-bipyridine in the lattice in which the nitrogen atoms are in the *anti*-configuration are not significantly different from those previously reported.

Spectroscopic Results.—The ^{13}C NMR spectra of each of the compounds prepared confirm that all of these are based on substituted catecholate ligands, by comparison with the results for compounds with other elements. Equally important is that the ν(C–O) infrared frequencies are in the range 1200–1400 cm^{-1}, substantially lower than ν(C=O) in the original *o*-quinones. The numerical values, which are available on request, are close to those reported in previous papers from this laboratory.

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