The Reaction of Some Substituted *ortho*-Benzoquinones with Elemental Tellurium and with Tellurium(II) Compounds*

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The oxidation of elemental tellurium by three *ortho*-benzoquinones (RO_2: R = Cl_4C_6, Br_4C_6 or 3,5-$Bu^t_2H_2C_6$) is a direct route to the corresponding tellurium(IV) catecholates $Te(O_2R)_2$. The analogous reaction with organotellurium(II) TeR'_2 [R' = Me_2, Et_2, Ph(Et) or Ph(Br)] gives the products $Te(O_2R)R'_2$. The reactions proceed in each case by one-electron transfer, since the presence of the semiquinone radical $RO_2^{\bullet}$ in the reaction mixture has been demonstrated by ESR spectroscopy. The $Te(O_2R)_2$ species resist further oxidation, and also show weak donor and acceptor properties. The structure of the compound $Te(O_2C_6H_2Bu^t_2\text{-}3,5)_2(bipy)$ **1** (bipy = 2,2'-bipyridine) has been determined by X-ray crystallography. Crystal parameters: triclinic, space group $P\bar{1}$, a = 10.388(2), b = 14.468(3), c =15.820(3) Å, α = 106.00(1), β = 115.98(2), γ = 94.98(2)°, Z = 2 and R = 0.0424 for 3424 reflections. For $Te(O_2C_6Cl_4)\cdot$18-crown-6 **2** (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane), the crystal parameters are: monoclinic, space group $P2_1/n$, a = 10.809(4), b = 18.571(7), c = 19.287(9) Å, β = 91.53(4)°, Z = 4 and R = 0.057 for 3768 reflections. In **1** the bipy is co-ordinated by weak Te–N interactions, with clear evidence for a stereochemically active lone pair, while in **2** the cryptand ring is situated around the axis of the presumed lone pair.

Recent papers from this laboratory have established that the oxidation of indium(I) and tin(II) halides by substituted *ortho*-quinones gives rise to the corresponding halide-catecholate derivatives. The transitory presence of the semiquinone in the reaction mixture, as demonstrated by electron spin resonance (ESR) spectroscopy, implies that two successive one-electron transfers are involved in the formation of these indium(III) and tin(IV) products.[1–4] We have also shown that *ortho*-quinones oxidize a number of metallic (In, Ga, Sn, Zn, Cd, Mg, Ba)[5–7] and non-metallic (P, Sb)[8] elements, and here again stable catecholate or semiquinone derivatives have been characterized.

This research has now been extended to the reactions of both elemental tellurium and a number of tellurium(II) compounds, for which the products are of the type $Te(O_2R)_2$ or $Te(O_2R)R'_2$ (R = substituted phenylene ring; R' = Me, Et or Ph). We have also investigated the donor–acceptor chemistry of $Te(O_2R)_2$, and the structures of two novel derivatives of these tellurium(IV) species.

Experimental

Tellurium (Aldrich) and dialkyl tellurides (Alfa) were used as supplied, as were donor ligands [2,2'-bipyridine(bipy), *N,N,N',N'*-tetramethylethane-1,2-diamine (tmen)] and *o*-quinones. Solvents were dried by standard methods, and stored over appropriate drying agents. All experiments were carried out in an atmosphere of dry nitrogen, using the conventional methods for handling air-sensitive poisonous substances.

Tellurium analysis was by atomic absorption spectrophotometry, using an IL-251 instrument, and microanalysis was performed by Canadian Microanalytical Services Ltd. Infrared spectra were run as CsI discs on a Nicolet 5DX instrument over the range 200–4000 cm^{-1}; ^1H, ^{13}C and ^{125}Te NMR spectra were recorded on Varian EM 360 or Bruker AC-300L spectrometers at 300, 75 and 63 MHz respectively. Electron spin resonance spectra were obtained by the techniques described earlier[3] on a Varian E12 instrument.

In this paper, we follow earlier practice and identify the triad of species based on 3,5-di-*tert*-butyl-1,2-benzoquinone as dbbq, dbsq$^{\bullet-}$ and dbc^{2-} respectively.

Reaction of Tellurium with o-*Quinones*.—Tellurium powder (0.128 g, 1 mmol) was suspended in a solution of $Y_4C_6O_2$-*o* (Y = Cl, 0.504 g, 2.05 mmol; Y = Br, 0.869 g) in toluene (20 cm^3), and the mixture stirred mechanically at room temperature. After *ca.* 12 h the solution became pale yellow, and the solid phase was perceptibly yellow. When the tellurium had reacted completely (*ca.* 24 h), as shown by its dissolution, the volume of the solution was reduced by 80%, and light petroleum (b.p. 35–60 °C) (30 cm^3) added. After further stirring (30 min) the pale yellow final product was collected, washed with *n*-hexane, and dried *in vacuo*. The yields of $Te(O_2C_6Y_4)$ were almost quantitative. Analytical results for all products are given in Table 1.

The analogous reaction between tellurium (1 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.441 g, 2 mmol) in toluene (20 cm^3) required reflux conditions in order to achieve a reasonable rate of reaction. After 24 h, the initially dark red solution was dark brown. The mixture was filtered hot, and the filtrate evaporated *in vacuo* to give a residue which was recrystallized from light petroleum as an orange solid; yield of $Te(dbc)_2$, 85%.

Dialkyl Tellurides + o-*Quinones*.—In each experiment, a solution of 1 mmol of TeR'_2 (R' = Me or Et) in toluene (15 cm^3) was added dropwise to an equimolar quantity of *o*-quinone in the same solvent (15 cm^3) cooled to −78 °C in an acetone–solid CO_2 bath. The mixture was stirred for 2 h and then allowed to warm to room temperature. The resultant solution was pale yellow ($Y_4C_6O_2$-*o*) or pale green (dbbq). In the case of $Y_4C_6O_2$, the volume of the solution was reduced by

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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

Compound	C	H	Te
$Te(O_2C_6Cl_4)_2$	23.9 (23.6)		21.0 (20.5)
$Te(O_2C_6Br_4)_2$			13.0 (13.0)
$Te(dbc)_2$	59.3 (59.2)	6.55 (7.10)	22.5 (22.5)
$Te(O_2C_6Br_4)Me_2$			22.0 (22.0)
$Te(dbc)Me_2$			34.5 (34.0)
$Te(O_2C_6Cl_4)Et_2$	27.6 (27.8)	2.45 (2.35)	30.0 (29.5)
$Te(O_2C_6Br_4)Et_2$	25.4 (25.2)	1.55 (1.50)	20.0 (21.0)
$Te(dbc)Et_2$			31.0 (31.5)
$Te(O_2C_6Cl_4)Ph(Et)$			27.0 (26.5)
$Te(O_2C_6Br_4)Ph(Et)$	20.2 (20.4)	0.90 (0.70)	19.0 (19.5)
$Te(dbc)_2Ph(Et)$			28.0 (28.0)
$Te(O_2C_6Cl_4)Ph(Br)$			23.0 (24.0)
$Te(O_2C_6Br_4)Ph(Br)$	20.2 (20.4)	0.90 (0.70)	18.0 (18.0)
$Te(dbc)Ph(Br)$[a]			25.0 (25.5)
$Te(dbc)_2(bipy){\cdot}0.5C_7H_8$[b]	64.5 (64.7)	6.90 (6.80)	—
$Te(dbc)_2(tmen)$			18.5 (18.5)
$Te(O_2C_6Cl_4)_2{\cdot}18\text{-crown-}6{\cdot}C_7H_8$	39.0 (38.2)	3.50 (3.30)	13.0 (13.0)
$Te(O_2C_6Cl_4)_2{\cdot}BCl_3$			17.4 (17.3)

[a] Br 15.3 (15.8)%. [b] N 3.65 (3.60)%.

ca. 90%, after which light petroleum (30 cm^3) was added to precipitate a pale yellow solid which was collected, washed and dried *in vacuo*. For the dbbq experiments, the solution was taken to dryness, and the product recrystallized from light petroleum. Each reaction gave products of the type $Te(O_2R)R'_2$ (RO_2 = substituted catecholate) in almost quantitative yield.

Phenyl Ethyl Telluride + o-*Quinones*.—Diphenyl ditelluride was prepared by the method of Haller and Irgolic,[9] in which phenylmagnesium bromide is treated with an equimolar quantity of tellurium powder in tetrahydrofuran. The final orange-red product was recrystallized from 95% ethanol. A portion of this material (4.09 g, 10 mmol) in absolute ethanol was treated with successive quantities of $NaBH_4$ to a total of 0.85 g (22.4 mmol). When the reduction of NaTePh was complete, as judged by the evolution of hydrogen and the formation of a homogeneous mixture, EtBr (2.07 g, 19 mmol) was slowly added. The mixture was stirred at room temperature for 4 h, followed by 30 min reflux, and then cooled, mixed with water (100 cm^3), and the product extracted into Et_2O (3 × 25 cm^3). Diethyl ether was removed *in vacuo* and the product, TePh(Et), purified by column chromatography on silica gel [hexane, then 9:1 hexane–Et_2O (3 × 25 cm^3)]. Treatment of this material with $Y_4C_6O_2$-*o* following the methods described above gave $Te(O_2C_6Y_4)Ph(Et)$. Similar reactions lead to Te(dbc)Ph(Et), and in both cases the yields, based on TePh(Et), were almost quantitatve.

Phenyltellurium Bromide + o-*Quinones*.—A solution of TePh(Br) was prepared by treating Te_2Ph_2 (0.21 g, 0.5 mmol) in Et_2O (10 cm^3), cooled to −78 °C, with Br_2 (0.08 g, 0.5 mmol as Br_2) in the same solvent (10 cm^3). The solution was stirred for *ca.* 15 min, after which $Cl_4C_6O_2$-*o* (0.24 g, 1.0 mmol) in toluene (10 cm^3) was added dropwise, and the resultant mixture allowed to reach room temperature with stirring over 1 h. Evaporation *in vacuo* removed Et_2O, and the addition of light petroleum (30 cm^3) to the residual mixture precipitated $Te(O_2C_6Cl_4)Ph(Br)$ as a yellow solid. The procedure with dbbq was essentially identical except that *n*-hexane was used in the final precipitation.

Adducts of Tellurium(IV) *Derivatives*.—(*i*) A solution of $Te(dbc)_2$ (0.57 g, 1 mmol) and either 2,2′-bipyridine (0.155 g, 1 mmol) or *N,N,N′,N′*-tetramethylethane-1,2-diamine (0.115 g, 1 mmol) in toluene (30 cm^3) was refluxed for 4 h, during which time the colour changed from orange to pale yellow; toluene was then removed by evaporation *in vacuo*, and the residue treated with light petroleum (5 cm^3). The resultant solution deposited crystals of $Te(dbc)_2(bipy){\cdot}0.5C_7H_8$, or $Te(dbc)_2(tmen)$, in almost quantitative yield after 12 h at 0 °C.

(*ii*) Tellurium powder (0.13 g, 1 mmol) was suspended in a solution of $Cl_4C_6O_2$-*o* (0.49 g, 2 mmol), and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (0.26 g, 1 mmol) in toluene (50 cm^3) added. This mixture was refluxed for 24 h, filtered hot, and the volume of the filtrate reduced *in vacuo*. The resultant solid was recrystallized from toluene, and identified as $Te(O_2C_6Cl_4)_2{\cdot}18\text{-crown-}6{\cdot}C_7H_8$, obtained in almost quantitative yield.

Reaction between $Te(O_2C_6Cl_4)_2$ *and* BCl_3.—When a suspension of $Te(O_2C_6Cl_4)_2$ (0.31 g, 0.5 mmol) in toluene (20 cm^3) was treated dropwise with a solution of BCl_3 in *n*-hexane (0.5 cm^3 of a 1 mol dm^{-3} solution) the initially yellow mixture became green-yellow. Over a period of 24 h, during which the reaction mixture was stirred at room temperature, the solid dissolved almost completely to give an orange-yellow solution. Small traces of residual solid were removed by filtration, and the volume reduced *in vacuo*; addition of light petroleum produced a pale yellow precipitate which was collected and dried *in vacuo*. The composition and properties of this material corresponded to those predicted for $Cl_3B{\cdot}Te(O_2C_6Cl_4)_2$, but re-analysis after a period of 15 d showed that BCl_3 had been lost to give a residue of $Te(O_2C_6Cl_4)_2$.

Attempted Oxidation of $Te(O_2C_6Cl_4)_2$ *by* Br_2.—When $Te(O_2C_6Cl_4)_2$ (0.31 g, 0.5 mmol) in toluene (20 cm^3) was treated with Br_2 (0.08 g, 0.5 mmol) the reaction mixture became orange. The mixture was stirred at room temperature for 12 h, and separated by filtration into a pale yellow solid (A) and a dark orange solution, which on evaporation of solvent yielded a dark brown solid (B). The solid A contained Te (26.9%), while B was almost free of this element (Te 2.7%). For comparison, we note that $Te(O_2C_6Cl_4)_2Br_2$ has 10.4% Te (calc.), and $Te(O_2C_6Cl_4)Br_2$ 23.9% Te. We find that $Te(O_2C_6Cl_4)_2$ does not decolorize a solution of I_2 in toluene.

Crystallographic Studies.—In the crystallographic study of $Te(dbc)_2(bipy)$ **1** the crystal was sealed in a glass capillary and mounted along its longest dimension on a four-circle Syntex $P2_1$ automated diffractometer, equipped with graphite-monochromatized Mo-Kα radiation. The initial orientation matrices and the crystal system were obtained from 15 machine-centred reflections chosen from a rotation photograph. The cell parameters were measured, checked for dimensions and

Table 2 Summary of crystal data, intensity collection and structure refinement

Compound	1	2
Chemical formula	$C_{38}H_{48}N_2O_4Te{\cdot}0.5C_7H_8$	$C_{24}H_{24}Cl_8O_{10}Te{\cdot}C_7H_8$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
M	770.46	975.83
a/Å	10.388(2)	10.809(4)
b/Å	14.468(3)	18.571(7)
c/Å	15.820(3)	19.287(9)
α/°	106.00(1)	—
β/°	115.98(2)	91.53(4)
γ/°	94.98(2)	—
U/Å^3	1994(1)	3870(3)
Z	2	4
F(000)	798	1944
D_c/g cm^{-3}	1.28	1.63
D_m/g cm^{-3}	1.30	1.67
Crystal dimensions/mm	0.2 × 0.2 × 0.4	0.4 × 0.3 × 0.3
μ/cm^{-1}	7.11	13.8
2θ/°	4–45	4–50
Total reflections measured	4010	7437
Unique data used [$I \geqslant 3\sigma(I)$]	3424	3768
T/°C	24	23
No. of parameters	435	407
R	0.0424	0.057
R'	0.0439	0.066

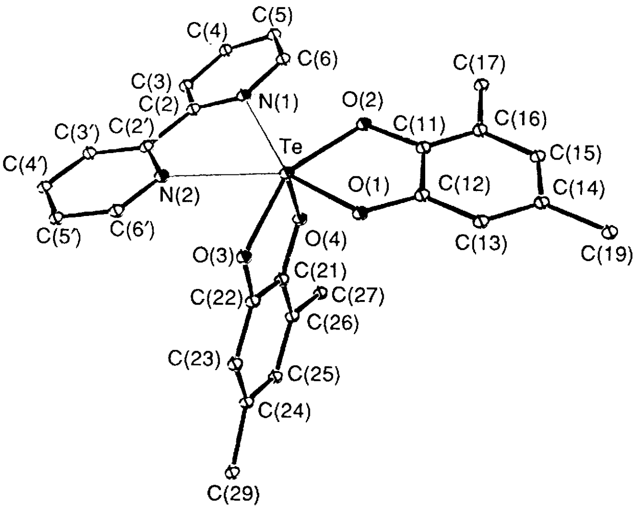


Fig. 1 An ORTEP[12b] diagram of the bis(3,5-di-*tert*-butylcatecholato)tellurium(IV) 2,2′-bipyridine adduct **1**, with atoms shown as 30% probability ellipsoids. Hydrogen atoms, and the methyl groups of the *tert*-C_4H_9 are omitted for clarity

symmetry from axial photographs, and refined from data from 45 strong reflections in the range $15 < 2\theta < 25°$. Data were collected by the procedures described previously.[10] The intensities of three monitor reflections did not change significantly during the time required for data collection. The appropriate corrections were made for Lorentz and polarization effects; no absorption corrections were used due to the low absorption coefficient. Computation was carried out using the SHELX 76 program package;[11] refinement involved blocked-matrix least-squares techniques, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ and in the final cycles the weighting scheme $w = 1/[\Sigma\sigma^2(F) + \rho F]^2$ was employed, with $\rho = 0.000\,01$. Atomic scattering factors and anomalous dispersion[12a] were taken from the standard sources. Hydrogen atoms were fixed at idealized positions [r(C–H) 0.95 Å] and assigned isotropic thermal parameters 10% higher than those of the bonding carbon atoms. Pertinent crystal and experimental data are given in Table 2. The density was measured by the flotation method using mixtures of carbon tetrachloride and benzene.

No symmetry or extinctions were observed and the crystal was assigned the centrosymmetric space group $P\bar{1}$, which was subsequently taken to be correct in view of the successful refinement. The tellurium atom site was determined from a three-dimensional Patterson map, and the phases derived from the refinement of this atom were used to locate all the non-hydrogen atoms of the structure. Anisotropic thermal parameters were assigned, first to the tellurium atom and then to all non-hydrogen atoms, and after several least-squares refinement convergence was achieved with $R = 0.053$, $R' = 0.063$. At this stage, the Fourier difference map revealed the presence of toluene in the crystal lattice about an inversion centre, in keeping with the analytical results which indicated the presence of half a molecule of toluene. Several attempts were made to establish a disordered model for the toluene, but none led to convergence, and the structure was finally refined with half occupancy for all the atoms of this molecule. The entire structure refined to $R = 0.0424$, and $R' = 0.0439$; the largest peak in the final Fourier difference map was 0.76 e Å^{-3}. The final positional parameters are given in Table 3, and selected bond lengths and angles in Table 4; Fig. 1 shows the molecular structure of **1**.

In the case of $Te(O_2C_6Cl_4)_2{\cdot}$18-crown-6 **2**, a suitable crystal on a glass fibre was mounted in a Rigaku AFC6S diffractometer, equipped with Mo-Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using 25 centred reflections in the range $28.1 < 2\theta < 34.5°$. From the systematic absences $h0l$: $h + l \neq 2n$; $0k0$: $k \neq 2n$, the space group was identified as $P2_1/n$ (no. 14), and this was confirmed by the subsequent solution and refinement of the structure. Details of the data intensity collection are given in Table 2. The density was measured with carbon tetrachloride–ethyl iodide mixtures. The intensities of three representative reflections, which were measured after every 150 reflections, declined by 2.0%, and a linear correction factor was applied in the calculations. The data were also corrected for Lorentz, polarization and absorption effects.

The structure was solved by a combination of Patterson and direct methods, with non-hydrogen atoms being refined anisotropically. The exceptions to this were C(21) and C(22) of the 18-crown-6 ring; these atoms exhibited unusually high thermal

Table 3 Final positional coordinates for non-hydrogen atoms of Te(dbc)$_2$(bipy) **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Te	0.576 26(4)	0.453 25(3)	0.123 89(3)	C(17)	0.523 0(7)	0.237 5(5)	−0.205 0(5)
O(1)	0.566 1(4)	0.384 8(3)	−0.012 1(3)	C(18A)	0.590 3(7)	0.333 7(5)	−0.208 9(5)
O(2)	0.360 5(4)	0.393 8(3)	0.037 4(3)	C(18B)	0.642 2(7)	0.205 2(6)	−0.128 2(6)
O(3)	0.634 4(4)	0.335 7(3)	0.150 2(3)	C(18C)	0.464 8(8)	0.156 9(5)	−0.308 0(5)
O(4)	0.513 2(4)	0.455 2(3)	0.230 6(3)	C(19)	−0.018 9(7)	0.150 8(6)	−0.292 0(6)
N(1)	0.125 4(6)	0.521 3(4)	0.842 8(5)	C(20A)	−0.042 4(10)	0.094 1(12)	−0.386 0(8)
N(2)	0.169 2(6)	0.458 4(4)	0.681 9(4)	C(20B)	−0.066 2(13)	0.081 9(9)	−0.248 7(10)
C(2)	0.009 7(7)	0.503 4(4)	0.751 8(5)	C(20C)	−0.121 4(10)	0.216 5(8)	−0.300 9(8)
C(3)	−0.123 0(8)	0.521 5(6)	0.744 4(6)	C(21)	0.528 6(6))	0.373 6(5)	0.256 6(4)
C(4)	−0.141 3(9)	0.554 8(6)	0.826 6(6)	C(22)	0.595 7(6)	0.309 2(4)	0.215 3(4)
C(5)	−0.023 3(8)	0.571 3(6)	0.919 1(6)	C(23)	0.619 8(6)	0.223 1(4)	0.236 2(4)
C(6)	0.106 1(7)	0.552 9(6)	0.922 3(5)	C(24)	0.568 5(7)	0.204 2(5)	0.299 9(5)
C(2′)	0.032 2(7)	0.460 3(5)	0.665 1(5)	C(25)	0.499 6(6)	0.264 3(5)	0.341 6(4)
C(3′)	−0.085 4(8)	0.420 5(6)	0.567 2(6)	C(26)	0.481 5(6)	0.351 2(5)	0.320 2(4)
C(4′)	−0.059 5(10)	0.376 2(7)	0.490 1(6)	C(27)	0.694 5(8)	0.154 3(5)	0.189 6(5)
C(5′)	0.078 5(10)	0.372 1(6)	0.508 3(6)	C(28A)	0.605 8(10)	0.121 1(5)	0.074 7(6)
C(6′)	0.191 5(8)	0.415 6(6)	0.605 3(6)	C(28B)	0.849 7(8)	0.206 5(6)	0.224 3(6)
C(11)	0.319 8(7)	0.329 5(4)	−0.056 8(5)	C(28C)	0.694 5(13)	0.058 9(7)	0.214 0(8)
C(12)	0.431 9(7)	0.320 6(4)	−0.082 9(4)	C(29)	0.437 1(8)	0.236 6(6)	0.405 1(5)
C(13)	0.401 9(7)	0.254 0(5)	−0.175 5(5)	C(30A)	0.270 3(9)	0.215 4(7)	0.348 3(7)
C(14)	0.254 4(7)	0.200 6(5)	−0.240 1(5)	C(30B)	0.472 0(11)	0.142 3(8)	0.425 0(8)
C(15)	0.141 1(7)	0.210 5(5)	−0.216 7(5)	C(30C)	0.491 7(13)	0.317 5(8)	0.502 7(7)
C(16)	0.175 8(7)	0.276 0(5)	−0.123 2(5)				

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

Te–O(1)	2.057(5)	O(1)–C(12)	1.374(6)
Te–O(2)	1.992(3)	O(2)–C(11)	1.371(7)
Te–O(3)	1.945(4)	O(3)–C(22)	1.385(9)
Te–O(4)	2.055(5)	O(4)–C(21)	1.353(9)
Te–N(1)	2.877(6)	N(1)–C(2)	1.344(8)
Te–N(2)	2.858(4)	N(1)–C(6)	1.334(12)
		N(2)–C(2′)	1.332(10)
		N(2)–C(6′)	1.342(12)
O(1)–Te–O(2)	79.1(2)	C(12)–O(1)–Te	113.4(5)
O(3)–Te–O(1)	83.5(2)	C(11)–O(2)–Te	115.0(4)
O(3)–Te–O(2)	97.6(2)	C(22)–O(3)–Te	114.7(4)
O(3)–Te–O(4)	81.0(2)	C(21)–O(4)–Te	111.8(4)
O(4)–Te–O(1)	151.3(2)	C(12–C(11)–O(2)	116.4(5)
O(4)–Te–O(2)	79.2(2)	C(11)–C(12)–O(1)	114.3(5)
N(1)–Te–N(2)	56.1(2)	C(21)–C(22)–O(3)	115.6(6)
N(1)–Te–O(1)	72.8(2)	C(22)–C(21)–O(4)	116.4(7)
N(1)–Te–O(2)	151.6(2)	C(2)–C(2′)–N(2)	118.3(3)
N(1)–Te–O(3)	75.4(2)	C(2′)–C(2)–N(1)	116.2(7)
N(1)–Te–O(4)	125.4(2)		
N(2)–Te–O(1)	128.7(2)		
N(2)–Te–O(2)	150.8(2)		
N(2)–Te–O(3)	79.4(1)		
N(2)–Te–O(4)	71.6(2)		

2,2′-Bipyridine rings		*tert*-Butyl group C(17)C(18A–C)	
Mean C–C	1.37(2)	Mean C–C	1.53(1)
Mean C–C–C/N–C–C	120(3)	Mean C–C–C	108(1)
Ring C(11)–C(16)		*tert*-Butyl group C(19)C(20A–C)	
Mean C–C	1.39(1)	Mean C–C	1.46(2)
Mean C–C–C	120(3)	Mean C–C–C	107(4)
Ring C(21)–C(26)		*tert*-Butyl group C(27)C(28A–C)	
Mean C–C	1.39(1)	Mean C–C	1.52(2)
Mean C–C–C	120(3)	Mean C–C–C	108(2)
		tert-Butyl group C(29)C(30A–C)	
		Mean C–C	1.51(2)
		Mean C–C–C	108(3)

vibrations, and the resultant C–C bond length [1.33(2) Å] is anomalously small. A similar result emerged for C(15)–C(16), although these atoms did refine anisotropically. Such behaviour has been reported previously for some crown ether complexes,[13,14] and various locations were tested in an unsuccessful bid to model this disorder. Problems were also encountered with the toluene molecule which is situated in the lattice. This is disordered, but we were unable to model the molecule satisfactorily (*cf.* refs. 15 and 16). The resultant bond lengths *etc.* are unsatisfactory, but the effect of this on the overall structure refinement is small.

After several cycles of refinement, the structure converged to $R = 0.057$ and $R' = 0.066$. The maximum shift/estimated standard deviation on any of the parameters in the final cycles in each structure was 0.01. A final Fourier difference map calculation showed no peaks of chemical significance; the maximum and minimum peaks corresponded to 1.61 and −0.80 e Å^{-3} respectively. In these calculations, neutral-atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in the calculations;[18] the values for $\Delta f'$ and $\Delta f''$ were those published by Cromer.[19] The TEXSAN[20] crystallographic software package was used in the refinement of **2**. Table 5 gives the positional parameters, Table 6 the interatomic distances and angles, and the structure is shown in Fig. 2.

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

Results and Discussion

Oxidation Reactions.—The reaction between tellurium and three representative *ortho*-benzoquinones provides a direct one-pot high-yield synthesis of the corresponding bis(catecholato)tellurium(IV) compounds. The preparative route used in earlier work on Te(O$_2$R)$_2$ or Te(OR)$_4$ species involved the treatment of TeCl$_4$ with R(OH)$_2$ or ROH in the presence of base,[21] and other reported methods for alkoxides are based on the reaction between TeCl$_4$ and NaOR,[22–25] so that the use of elemental tellurium offers advantages both in simplicity and in avoiding the use of the moisture-sensitive tetrachloride.

There is an important difference between the present results and those for elemental phosphorus,[8] in that the reaction product is not in the highest oxidation state of the element. Moreover, the Te(O$_2$R)$_2$ compounds obtained in this way are stable against oxidation by excess *o*-quinone or iodine, and while some reaction occurs on prolonged treatment with bromine, the product is clearly not Te(O$_2$R)$_2$Br$_2$. Similarly, oxidation reactions between dialkyl tellurides or phenyl-

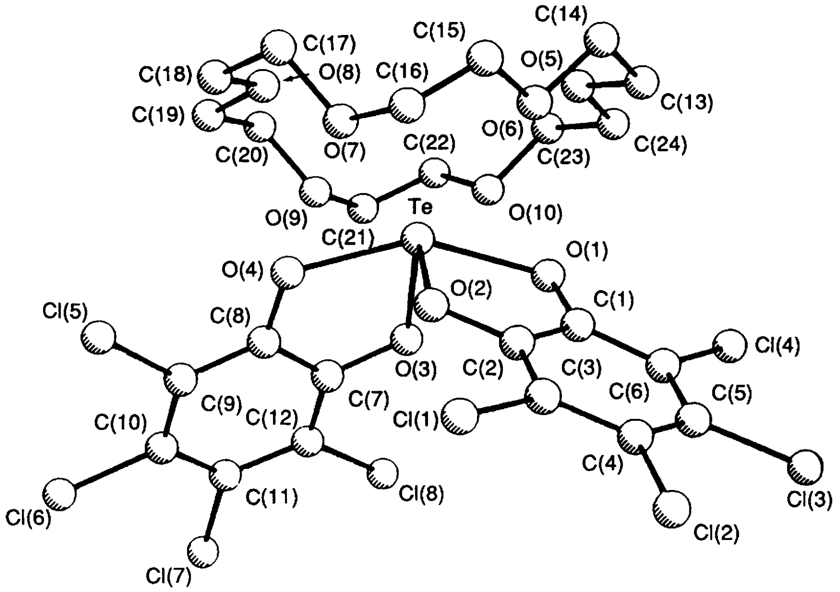


Fig. 2 An ORTEP diagram of the bis(tetrachlorocatecholato)tellurium(IV)–18-crown-6 ether adduct **2**, with atoms shown as 30% probability ellipsoids. Hydrogen atoms are omitted for clarity

Table 5 Final positional parameters for non-hydrogen atoms of Te($O_2C_6Cl_4$)$_2$·18-crown-6 **2**, with e.s.d.s

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Te	0.261 14(7)	0.106 13(4)	0.147 58(4)	C(7)	0.155(1)	0.110 8(6)	0.279 3(5)
Cl(1)	−0.086 9(3)	0.244 2(2)	0.042 0(2)	C(8)	0.083(1)	0.059 5(5)	0.243 1(5)
Cl(2)	−0.023 0(3)	0.407 5(2)	0.021 8(2)	C(9)	−0.014(1)	0.027 0(6)	0.276 1(5)
Cl(3)	0.238 7(3)	0.464 5(2)	0.068 0(2)	C(10)	−0.039(1)	0.042 6(6)	0.344 5(6)
Cl(4)	0.434 2(3)	0.357 0(2)	0.133 5(2)	C(11)	0.038(1)	0.090 9(6)	0.381 5(5)
Cl(5)	−0.102 9(3)	−0.034 5(2)	0.230 2(2)	C(12)	0.134(1)	0.126 4(6)	0.347 8(6)
Cl(6)	−0.160 0(3)	0.002 5(2))	0.384 8(2)	C(13)	0.530(1)	0.168 2(8)	0.013 8(9)
Cl(7)	0.012 6(3)	0.109 4(2)	0.467 2(1)	C(14)	0.453(2)	0.130(1)	−0.037 7(8)
Cl(8)	0.228 0(3)	0.187 5(2)	0.390 4(2)	C(15)	0.257(2)	0.082(1)	−0.059(1)
O(1)	0.341 0(6)	0.205 9(4)	0.138 8(4)	C(16)	0.150(1)	0.061(1)	−0.034 7(7)
O(2)	0.119 9(6)	0.160 2(4)	0.105 4(4)	C(17)	0.180(1)	−0.055 7(8)	0.020 1(7)
O(3)	0.244 5(7)	0.143 3(4)	0.242 6(4)	C(18)	0.176(1)	−0.092 8(6)	0.088 1(8)
O(4)	0.115 2(6)	0.044 6(4)	0.178 6(3)	C(19)	0.277(1)	−0.105 3(8)	0.195 8(8)
O(5)	0.551 9(8)	0.122 2(5)	0.071 4(5)	C(20)	0.382(2)	−0.080(1)	0.237 1(8)
O(6)	0.331(1)	0.123 2(5)	−0.012 0(5)	C(21)	0.468(2)	0.023(1)	0.296(1)
O(7)	0.160 4(7)	0.018 9(5)	0.029 3(4)	C(22)	0.567(1)	0.050 8(6)	0.266 8(6)
O(8)	0.280 0(8)	−0.073 7(5)	0.129 0(4)	C(23)	0.640(1)	0.109 0(9)	0.182(1)
O(9)	0.369(1)	−0.006 8(7)	0.251 3(5)	C(24)	0.624(1)	0.157 8(8)	0.122 0(9)
O(10)	0.525(1)	0.105 3(6)	0.216 8(5)	C(25)	0.305(3)	0.242(2)	0.787(2)
C(1)	0.262(1)	0.254 8(6)	0.113 1(5)	C(26)	0.319(2)	0.272(1)	0.846(1)
C(2)	0.143(1)	0.231 5(5)	0.094 4(5)	C(27)	0.214(3)	0.283(1)	0.884(1)
C(3)	0.056 8(9)	0.277 3(5)	0.066 1(5)	C(28)	0.092(2)	0.267(1)	0.870(1)
C(4)	0.086(1)	0.351 1(6)	0.057 2(6)	C(29)	0.092(2)	0.230(1)	0.803(1)
C(5)	0.202(1)	0.375 3(5)	0.078 3(5)	C(30)	0.185(2)	0.217 6(9)	0.765 8(9)
C(6)	0.290(1)	0.328 7(6)	0.106 7(5)	C(31)	0.386(2)	0.228(1)	0.741(1)

tellurium bromide and *o*-quinones again produce the appropriate tellurium(IV) species Te(O_2R)R'_2. No attempt was made to study the further oxidation of these compounds. Similar results have been obtained with antimony, in that Q + Sb + $\frac{1}{2}Br_2 \longrightarrow$ Sb^{III}(cat)Br, but Q + SbPh$_3 \longrightarrow$ SbPh$_3$(cat) (cat = catecholate); the comparison of the behaviour of these elements will be discussed elsewhere.[26]

In earlier discussions of the oxidation of Main Group elements, or their low-oxidation state complexes, by *o*-quinones, we stressed the importance of the semiquinone intermediate, and the identification of these radical anion ligands bonded to the element in question has been a crucial part of the mechanistic evidence.[1–6] We have now shown by ESR spectroscopy that the oxidation of TeEt$_2$ by dbbq in toluene at room temperature involves the formation of Te–dbsq$^{\bullet}$ species. The spectrum of a freshly prepared mixture consists of a central resonance, which leads to a hyperfine coupling constant A_{H4} = 2.63 G (G = 10^{-4} T), and additional fine structure due to interaction with the Bu^t group at C^5 of the ring. This constant is significantly lower than those found for various indium-(I) and -(III) derivatives of this ligand.[3,4] The spectrum also shows a pair of resonances due to coupling with tellurium, with hyperfine constants of 33.2 (^{123}Te) and 38.5 G (^{125}Te); the ratio of 0.86 can be compared with that of 0.829 calculated from the nuclear magnetic moments, and the agreement seems reasonable in view of the low intensity of these features. The spin density at the tellurium atom is 0.2% of the total. We also observed ESR-active species in the heterogeneous reaction between tellurium and dbbq indicating the presence of dbsq$^{\bullet-}$, but no detailed information could be obtained from this experiment.

In a subsequent experiment, dilute (*ca.* 10^{-6} mol dm^{-3})

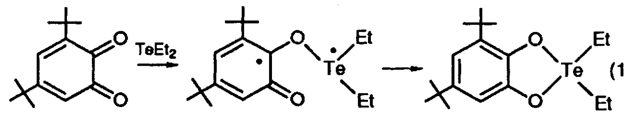
Table 6 Bond lengths (Å) and angles (°) for $Te(O_2C_6Cl_4)_2 \cdot$18-crown-6 **2**, with e.s.d.s in parentheses

Te–O(1)	2.054(7)	O(2)–C(2)	1.36(1)	O(10)–C(22)	1.46(1)	C(11)–C(12)	1.40(1)
Te–O(2)	1.983(6)	O(3)–C(7)	1.35(1)	O(10)–C(23)	1.43(2)	C(13)–C(14)	1.46(2)
Te–O(3)	1.972(7)	O(4)–C(8)	1.33(1)	C(1)–C(2)	1.39(1)	C(15)–C(16)	1.32(2)
Te–O(4)	2.050(6)	O(5)–C(13)	1.42(2)	C(1)–C(6)	1.41(1)	C(17)–C(18)	1.48(2)
Cl(1)–C(3)	1.72(1)	O(5)–C(24)	1.40(1)	C(2)–C(3)	1.37(1)	C(19)–C(20)	1.45(2)
Cl(2)–C(4)	1.71(1)	O(6)–C(14)	1.43(2)	C(3)–C(4)	1.42(1)	C(21)–C(22)	1.33(2)
Cl(3)–C(5)	1.72(1)	O(6)–C(15)	1.43(2)	C(4)–C(5)	1.38(1)	C(23)–C(24)	1.48(2)
Cl(4)–C(6)	1.72(1)	O(7)–O(16)	1.47(2)	C(5)–C(6)	1.39(1)	C(25)–C(26)	1.27(3)
Cl(5)–C(9)	1.72(1)	O(7)–C(17)	1.41(1)	C(7)–C(8)	1.41(1)	C(25)–C(30)	1.43(3)
Cl(6)–C(10)	1.71(1)	O(8)–C(18)	1.40(1)	C(7)–C(12)	1.38(1)	C(25)–C(31)	1.30(3)
Cl(7)–C(11)	1.72(1)	O(8)–C(19)	1.42(1)	C(8)–C(9)	1.38(1)	C(26)–C(27)	1.38(2)
Cl(8)–C(12)	1.72(1)	O(9)–C(20)	1.40(2)	C(9)–C(10)	1.39(1)	C(27)–C(28)	1.37(3)
O(1)–C(1)	1.33(1)	O(9)–C(21)	1.46(2)	C(10)–C(11)	1.40(1)	C(28)–C(29)	1.45(3)
						C(29)–C(30)	1.27(2)
O(1)–Te–O(2)	80.2(3)	C(18)–O(8)–C(19)	112(1)	Cl(2)–C(4)–C(5)	122.0(8)	C(7)–C(8)–C(9)	119(1)
O(1)–Te–O(3)	79.1(3)	C(20)–O(9)–C(21)	114(1)	C(3)–C(4)–C(5)	119.0(9)	Cl(5)–C(9)–C(8)	118.2(8)
O(1)–Te–O(4)	148.8(3)	C(22)–O(10)–C(23)	95(1)	Cl(3)–C(5)–C(4)	119.6(8)	Cl(5)–C(9)–C(10)	120.6(9)
O(2)–Te–O(3)	96.6(3)	O(1)–C(1)–C(2)	117.4(9)	Cl(3)–C(5)–C(6)	119.2(8)	C(8)–C(9)–C(10)	121(1)
O(2)–Te–O(4)	79.2(3)	O(1)–C(1)–C(6)	124.2(9)	C(4)–C(5)–C(6)	121.2(9)	Cl(6)–C(10)–C(9)	121(1)
O(3)–Te–O(4)	80.4(3)	C(2)–C(1)–C(6)	118.3(9)	Cl(4)–C(6)–C(1)	117.6(8)	Cl(6)–C(10)–C(11)	119.8(9)
Te–O(1)–C(1)	112.3(6)	O(2)–C(2)–C(1)	115.7(9)	Cl(4)–C(6)–C(5)	122.4(8)	C(9)–C(10)–C(11)	119(1)
Te–O(2)–C(2)	114.3(6)	O(2)–C(2)–C(3)	122.5(9)	C(1)–C(6)–C(5)	119.9(9)	Cl(7)–C(11)–C(10)	120.7(9)
Te–O(3)–C(7)	114.5(6)	C(1)–C(2)–C(3)	121.7(9)	O(3)–C(7)–C(8)	115.9(9)	Cl(7)–C(11)–C(12)	119.4(9)
Te–O(4)–C(8)	112.3(6)	Cl(1)–C(3)–C(2)	119.2(8)	O(3)–C(7)–C(12)	123(1)	C(10)–C(11)–C(12)	119.9(9)
C(13)–O(5)–C(24)	110(1)	Cl(1)–C(3)–C(4)	121.1(8)	C(8)–C(7)–C(12)	121(1)	Cl(8)–C(12)–C(7)	118.7(9)
C(14)–O(6)–C(15)	109(1)	C(2)–C(3)–C(4)	119.7(9)	O(4)–C(8)–C(7)	116.6(9)	Cl(8)–C(12)–C(11)	121.7(9)
C(16)–O(7)–C(17)	115(1)	Cl(2)–C(4)–C(3)	119.0(8)	O(4)–C(8)–C(9)	124(1)	C(7)–C(12)–C(11)	120(1)
O(5)–C(13)–C(14)	109(1)	O(8)–C(18)–C(17)	110(1)	O(10)–C(23)–C(24)	109(1)	C(25)–C(26)–C(27)	117(2)
O(6)–C(14)–C(13)	109(1)	O(8)–C(19)–C(20)	109(1)	O(5)–C(24)–C(23)	108(1)	C(26)–C(27)–C(28)	131(2)
O(6)–C(15)–C(16)	114(2)	O(9)–C(20)–C(19)	110(1)	C(26)–C(25)–C(30)	119(3)	C(27)–C(28)–C(29)	105(2)
O(7)–C(16)–C(15)	114(1)	O(9)–C(21)–C(22)	119(2)	C(26)–C(25)–C(31)	130(3)	C(28)–C(29)–C(30)	127(2)
O(7)–C(17)–C(18)	110(1)	O(10)–C(22)–C(21)	108(1)	C(30)–C(25)–C(31)	111(3)	C(25)–C(30)–C(29)	120(2)

Table 7 Tellurium-125 NMR resonances, relative to neat $TeMe_2$ (δ 0) at *ca.* 30 °C

Compound	Solvent	δ
$Te(O_2C_6Cl_4)_2$	$(CD_3)_2SO$	1609.4
$Te(O_2C_6Br_4)_2$	$(CD_3)_2SO$	1591.5
$Te(dbc)_2$	$CDCl_3$	See text
$Te(O_2C_6Br_4)Me_2$	$(CD_3)_2SO$	1369.4
$Te(O_2C_6Cl_4)Et_2$	$(CD_3)_2SO$	1622.6
$Te(dbc)Et_2$	$CDCl_3$	1438.5
$Te(O_2C_6Cl_4)Ph(Et)$	$(CD_3)_2SO$	1470.9
$Te(O_2C_6Br_4)Ph(Et)$	$(CD_3)_2SO$	1480.6
$Te(dbc)_2(bipy)$	$CDCl_3$	1650.9
$Te(O_2C_6Cl_4)_2 \cdot$18-crown-6	$(CD_3)_2SO$	1599.4

solutions of $TeEt_2$ and dbbq in diethyl ether were mixed at room temperature. After 1 h the mixture gave an ESR spectrum with the features noted above, indicating the presence of dbsq$^{\bullet}$ bonded to tellurium. The intensity decreased over a period of 24 h, with some slight residual activity still detectable after 45 h. The existence of a tellurium–semiquinonate species in the reaction mixture identifies an important step in the mechanism as given by equation (1). As in other systems studied,[1–6] the



(1)

oxidation $Te^{II} \longrightarrow Te^{IV}$ by *o*-benzoquinones involves two successive one-electron transfer processes rather than the two-electron process implied by the stoichiometry of the reaction. It seems reasonable to conclude that successive one-electron transfers are a feature of all the redox reactions studied in this work.

Spectroscopic Results.—As in our earlier studies, we have confirmed the formation of the catecholate complexes by both infrared and NMR spectroscopic methods. The infrared spectra demonstrated the loss of ν(C=O) of the *o*-quinone, typically at 1600–1700 cm^{-1}, and its replacement by absorptions in the 1200–1400 cm^{-1} region. Similarly, the ^{13}C NMR spectra showed changes almost identical to those reported previously,[8] and in particular the reduction in resonance frequency at C^1 and C^2 from *ca.* δ 180 to *ca.* δ 150, and a lowering of *ca.* 20 ppm at the other ring carbon atoms of dbbq. The frequency changes for $Y_4C_6O_2$ species were also close to those found earlier, as were those in the ^1H NMR spectra of the compounds prepared.

In addition, we recorded the ^{125}Te NMR spectra of several of the products, with the results given in Table 7. The values are similar to those for other $Te(O_2R)_2$ and $Te(OR)_4$ compounds, for which chemical shifts between δ 1355 and 1601 have been reported.[21] Other compilations[27–29] of ^{125}Te NMR results demonstrate that the substitution of halogen in TeX_4 (X = Cl or Br) by alkyl or aryl groups causes large changes ($\approx$200 ppm) in δ(^{125}Te), and this is in general agreement with the present results. On the other hand, significant concentration and solvent effects have also been reported, and any detailed analysis of substitution effects in $Te(O_2R)_2$ compounds is not justified for the relatively small number of values recorded in this work.

The spectrum of $Te(dbc)_2$ in $CDCl_3$ shows two resonances at room temperature, and there is an interesting temperature dependence, which is illustrated in Fig. 3, along with the comparable results for $Te(O_2C_6Cl_4)_2$ and $Te(O_2C_6Br_4)_2$. The chemical shift clearly increases with temperature over the range 300–400 K for all three molecules. In the case of $Te(dbc)_2$, the resonance at δ 1621.5 is the more intense at 300 K (peak height

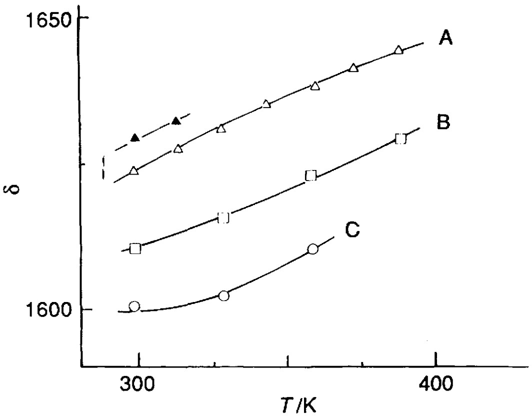
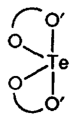
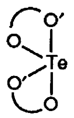


Fig. 3 Temperature dependence of ^{125}Te NMR resonances of $Te(O_2R)_2$ species in $(CD_3)_2SO$, relative to $TeMe_2$ (δ 0) (*cf.* Table 7); $Te(dbc)_2$ (A), $Te(O_2C_6Cl_4)_2$ (B) and $Te(O_2C_6Br_4)_2$ (C)

ratio *ca.* 2:1); as the temperature increases, the intensity rises (3:1 at 315 K, 4:1 at 330 K) until only one signal is seen, and the almost linear temperature dependence implies that the species responsible for this resonance is present over the whole temperature range studied. The slow exchange process indicated by the presence of two relatively sharp resonances would seem to rule out any explanation based on the presence of both trigonal bipyramidal (*TBPY*) and square pyramidal (*SPY*) isomers of $Te(dbc)_2$; exchange between these species can occur without bond breaking and would therefore be expected to be rapid at the temperatures involved. As further support of this argument, we note that only one signal is observed for $Te(O_2C_6Y_4)_2$ (Y = Cl or Br), and it therefore seems reasonable to seek an explanation based on the asymmetry of the dbc ligand (= O–O′), which in the case of a *TBPY* structure should give rise to three



IA



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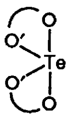
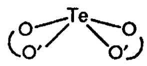
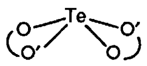


IC

isomers while in contrast only two stereoisomers are possible if the molecule is in the *SPY* form in solution. We therefore



IIA



IIB

conclude either that $Te(dbc)_2$ in solution has square-pyramidal stereochemistry, or that only two of the three possible trigonal-pyramidal forms are present below 330 K in the concentrations detectable by ^{125}Te NMR spectroscopy. For the present, the results are most simply explained in terms of a mixture of **IIA** and **IIB** below 330 K. Molecular models do not identify either of the two possible stereoisomers as being obviously more sterically hindered than the other, and so it is not possible to identify the more stable structure which is uniquely present above 350 K. The crystal structure[25] of $Te(O_2C_6H_4)_2$ shows significant intermolecular interactions between *TBPY* species in the solid state, so that the presence of the alternative *SPY* isomer in solution may simply reflect differing stabilizing factors in the two phases.

The ^{13}C NMR spectra of these compounds show only small changes with temperature over the range of these experiments. This result is not unexpected, since the postulated molecular rearrangements only involve changes in the shielding of the tellurium atom. Neither the C_6 rings nor the *tert*-C_4H_9 groups undergo reorganization as the result of these fluxional processes.

Donor Properties of $Te(O_2C_6Cl_4)_2$.—Valence-shell electron-pair repulsion theory predicts that a TeX_4 species will be of AX_4E type with a lone pair of electrons in an equatorial (*TBPY*) or apical (*SPY*) position. Such simple stereochemistry is in fact found only rarely in the tetrahalides, since halide cross-linking leads to oligomerization in the solid state,[30] but in β-TeO_2, and more importantly in $Te(O_2C_6H_4)_2$,[25] the TeO_4 kernel does indeed conform to the predicted *TBPY* form. On the other hand, the presumed lone pair of electrons is difficult, if not impossible to remove by oxidation with I_2 or Br_2 (see below), and it therefore seemed useful to investigate the possible donor properties of one of the $Te(O_2R)_2$ compounds synthesised in the present study.

The reaction between $Te(O_2C_6Cl_4)_2$ and BCl_3 gave a product whose tellurium content indicated the formation of a 1:1 adduct. The ^{125}Te NMR spectrum in $(CD_3)_2SO$ showed a chemical shift of δ 1640.2 [*cf.* 1609.4 for $Te(O_2C_6Cl_4)_2$], and the ^{11}B resonance in the same solvent was at δ 14.63 (relative to BF_3 in Et_2O, δ 0), a value which is in the range found for adducts with sulfur or selenium donors, and lower than the chemical shift of BCl_3 in non-donor solvents, which is in the range δ 42–47.[31] The ^{13}C NMR spectrum of the catecholato ligand showed little or no change from that in $Te(O_2C_6Cl_4)_2$. All this evidence indicates the formation of the 1:1 adduct, but this compound is apparently unstable, since re-analysis after 2 weeks showed that BCl_3 had been lost, so that $Te(O_2C_6Cl_4)_2$ is apparently only a weak Lewis base.

Acceptor Properties of $Te(O_2R)_2$.—One of the interesting properties of TeX_4 species is that in addition to any donor property they are also acceptors, and both neutral [*e.g.*, $TeF_4 \cdot L$, L = mono- or bi-dentate nitrogen donors,[32] and $TeCl_4 \cdot pyo$ (pyo = pyridine *N*-oxide)[33]] and anionic (*e.g.*, TeX_5^- [30,34]) derivatives have been reported. We have now prepared adducts of $Te(O_2R)_2$ with bidentate nitrogen donors and a crown ether, either by reaction between $Te(O_2R)_2$ and donor, or in the latter case by direct oxidation of elemental tellurium by $Cl_4C_6O_2$-*o* in the presence of 18-crown-6. The molecular structures of two of these compounds have been established by X-ray crystallography, and we note immediately that in each case the average C–O bond distances in the anionic ligands are indeed typical of C–O single bonds [1.37(1) Å for **1**, and 1.34(1) Å for **2**], confirming that substituted catecholates have been formed by the reduction of the appropriate *o*-quinone. The TeO_2C_2 rings are essentially planar in both molecules.

The reaction between $Te(dbc)_2$ and 2,2′-bipyridine gives $Te(dbc)_2(bipy) \cdot 0.5C_7H_8$ **1** in high yield, and the structure of this molecule is based on a TeO_4N_2 kernel. The Te–O bond distances (Table 4) are slightly larger in the apical direction [O(1), O(4), average value 2.056 Å] than in the equatorial (average value 1.969 Å), and in this respect the structure is similar to that of $Te(O_2C_6H_4)_2$ reported by Lindqvist[25] [comparable values 2.06(2), 1.98(2) Å]. The O–Te–O bite angles in the latter [average 81.2(1.0)°] are also close to those in **1**, as are the other O–Te–O angles, so that co-ordination of bipy has not apparently caused any great distortion from the solid-state structure of $Te(dbc)_2$, assuming the latter to be similar to that of $Te(O_2C_6H_4)_2$. Of the reported Te–N bonds, those in 2,6-diacetyl pyridine(*C*,*N*,*O*)tellurium trichloride[35] and 2-(2-pyridyl)phenyltellurium tribromide[36] both involve donation from a nitrogen heterocycle to a tellurium(IV) centre, but in each case the bond distances [2.402(3) and 2.244(14) Å respectively] are considerably smaller than the average value of 2.868 Å in **1**. This comparison clearly implies a weak ligand–metal interaction, and the other unusual feature, the small N–Te–N bite angle of 56.1(2)°, which is considerably lower than the values of *ca.* 78° found in the conventional complexes of this ligand, is in keeping with this conclusion. The Te–N(2)–C(2′)–C(2)–N(2) ring is planar (mean deviation from planarity 0.1 Å). The dihedral angles between the three five-membered rings at tellurium are [TeO(1)O(2)]–[TeO(3)O(4)] 91.1, [TeO(1)O(2)]–[TeN(1)N(2)] 163.9 and [TeO(3)O(4)]–[TeN(1)N(2)] 75.2°.

The overall effect is that the structure has a large and apparently unoccupied volume above the rough plane defined by Te, O(1), O(2), N(1), N(2) and O(3), and it seems reasonable to accept this as evidence of the presence of a stereochemically active lone pair of electrons implied by the AX_4E formulation. The stereochemistry of the interaction between this kernel and 2,2′-bipyridine does not correspond to any obvious co-ordination mode, and it may well be that this is a weak electrostatic interaction between the bipyridine nitrogens and the central tellurium atom.

In the case of $Te(O_2C_6Cl_4)_2$·18-crown-6 **2**, the stereochemistry of the tellurium–catecholate interaction is similar to that in **1**, and in $Te(O_2C_6H_4)_2$, with two Te–O bonds [O(1), O(4)] in the apical sites being significantly longer (av. 2.052 Å) than those in the equatorial plane (average 1.978 Å). The various O–Te–O angles are also close in value to those in the two previous structures, and the TeO_2C_2 rings are planar, with a dihedral angle of 86.4° between them.

The most striking feature of the stereochemistry of **2** is the very large distances between Te and the oxygen atoms of the cyclic polyether, ranging from 2.980(7) to 3.517(8) Å. The question of M–O distances in complexes with 18-crown-6 has been discussed by Drew and Nicholson,[37,38] who have calculated that for cationic heavy-element species the D_{3d} conformation of the ligand is at an energy minimum for M–O bond distances of ≈2.85 Å; distortion will then arise if the ions are either too small or too large, or if the polyether is forming a molecular adduct, as is the case with $BiCl_3$,[39] or with $SbCl_3$ and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane).[39] The compound **2** is clearly such an adduct, with considerable distortion of the cryptand ring, and a distribution of Te–O bond distances which is not very different from that in $BiCl_3$·18-crown-6. It has been argued that the structure of $BiCl_3$·18-crown-6, in which the bismuth is sandwiched between three Cl and six O, is evidence that the stereochemical activity of the lone pair is retained, and a parallel argument can clearly be made for $Te(O_2C_6Cl_4)_2$·18-crown-6. This approach is strengthened by the orientation of the cryptand. A plane defined by the oxygen atoms O(6), O(7), O(9) and O(10) makes dihedral angles of 45.9° with the TeO(1)O(2) ring, and 40.8° with TeO(3)O(4), implying that a vector through the presumed lone pair is almost normal to this O(6)–O(10) plane. Nevertheless, the large Te–O distances to these oxygen atoms brings into question the nature of the bonding interaction, as this is normally understood. Perhaps the only reasonable conclusion is that in this molecule, as in $Te(dbc)_2(bipy)$, the structure provides evidence of the stereochemical features expected from a molecule with a lone pair of electrons.

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