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The oxidation of diphenyl ditelluride by substituted orthobenzoquinones, and the molecular structure of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ *

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Abstract

The reaction between tetrahalogeno-*ortho*-benzoquinones ($X_4C_6O_2$-*o*; X = Cl, Br) and diphenyl ditelluride gives the unusual tellurium(IV) derivatives $[(X_4C_6O_2)TeC_6H_5]_2O$. Crystallographic studies show that tellurium is coordinated by a substituted catecholate, a phenyl group, and a bridging oxygen. The mechanism of the reaction probably involves initial formation of a semiquinone-tellurium-phenyl species, since ESR spectroscopy identifies the presence of *o*-semiquinone radicals. A similar reaction was observed with $(C_6H_5)_2Te_2$ and 3,5-di-tert-butyl-*ortho*-benzoquinone.

1. Introduction

Recent papers from this laboratory have reported the results of preparative and spectroscopic investigations of the reaction between substituted *ortho*-benzoquinones and a variety of Main Group elements, or the low oxidation state compounds of such elements. The tellurium system [1] is quite typical of such investigations, in that oxidation of the element by an *o*-quinone yields the corresponding bis-catecholato-tellurium(IV) species $Te(CAT)_2$, while the analogous reaction with organo-tellurium(II) compounds TeR_2 gives $R_2Te(CAT)$. While the detailed mechanism of these reactions is not completely clear, it has been established that semiquinone species are involved as intermediates, since the characteristic electron spin resonance spectra have been identified in these, and related [2], reactions.

We have now extended these investigations to the oxidation of diphenyl ditelluride, in which tellurium is formally in the +1 oxidation state. Reaction occurs between this compound and tetrahalogeno-*o*-benzoquinones ($X_4C_6O_2$; X = Cl, Br) to give $[(X_4C_6O_2)TeC_6H_5]_2O$, and the structure of the tetrachlorocatecholate derivative has been established crystallographically. The reaction between Ph_2Te_2 and 3,5-di-tert-butyl-*ortho*-benzoquinone gives an apparently related product, but in each case the reaction mechanism is clearly complicated, and the only certain feature is that paramagnetic species are observed, implying the involvement of free radicals in the electron transfer process.

2. Experimental section

2.1. General

All reagents, including elemental tellurium (Aldrich), were reagent grade, or better, and were used as supplied. Solvents were dried by conventional methods, and stored over drying agents. All reactions were carried out under dry nitrogen.

Infrared spectra were recorded as KBr discs on a Nicolet 5DX instrument, and ^1H and ^{13}C nuclear magnetic resonance spectra on a Bruker AC-300L spectrometer. Mass spectroscopy involved a Finnigan 400 GC-MS instrument. Microanalysis was performed by Canadian Microanalytical Services Ltd., and tellurium analysis was by atomic absorption, using an IL-251 spectrophotometer.

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* This paper is dedicated to Mike Lappert on the occasion of his sixty-fifth birthday, in acknowledgement of his immeasurable contributions to the organometallic chemistry of Main Group elements.

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Electron spin resonance (ESR) spectra were recorded on a Bruker ESP300E instrument. The frequencies were calibrated with a Hewlett-Packard frequency counter, and the field strength with an NMR gaussmeter.

2.2. *Preparation of diphenyl ditelluride*

The preparation followed the method of Irgolic [3,4], in which phenylmagnesium bromide is treated with tellurium, to give a product presumed to be C_6H_5-TeMgBr, which on reaction with gaseous oxygen forms $(C_6H_5)_2Te_2$ in 70% yield. Gram quantities were prepared by this route. The mass spectrum showed significant clusters of peaks centred at $m/e = 410$ ($Ph_2Te_2^+$), 284 (Ph_2Te^+), 207 ($PhTe^+$), 154 (Ph_2^+) and 77 (Ph^+); in each case, the isotopic distribution agreed with the calculated values within experimental error. ^{1}H NMR (d_6-dmso) 7.8, 2H, 7.2, m, 3H; ($CDCl_3$), 7.78, 7.81, 2H, 7.2 m, 3H (all in ppm; $Me_4Si = 0$). ^{13}C NMR ($CDCl_3$) 137.6, 129.3, 128.1, 107.9 ppm ($Me_4Si = 0$). ^{125}Te NMR ($CDCl_3$) 421.8 ppm ($Me_2Te = 0$).

2.3. *Reaction of diphenyl ditelluride with o-quinones*

(i) Diphenyl ditelluride (0.205 g, 0.5 mmol) was dissolved in toluene (15 ml), and a solution of $X_4C_6O_2$-*o* (X = Cl, 0.37 g, 1.5 mmol; X = Br, 0.64 g, 1.5 mmol) in the same solvent (15 ml) added dropwise at 0°C over 10 min. Reaction began as soon as the reactants were in contact, as shown by the discharge of the red-orange colour of the initial mixture. The resultant yellow solution was allowed to reach room temperature (~ 20°C) over 1 h, with stirring. The volume of the solution was reduced by about 80% *in vacuo*; addition of mixed hexanes (20 ml) caused the precipitation of a pale yellow solid, which was collected by filtration, washed with hexanes (2 × 5 ml) and dried *in vacuo* for 24 h. The yields of $[(X_4C_6O_2)TeC_6H_5]_2O$, were almost quantitative, based on the quantity of $(C_6H_5)_2Te_2$ used.

These compounds are air-stable, pale yellow solids, soluble in dimethylformamide, dimethylsulphoxide, tetrahydrofuran, diethyl ether, and toluene.

Analysis for $[(Cl_4C_6O_2)TeC_6H_5]_2O$; found C 31.6; H 1.18; Te 27.5; calculated for $C_{24}H_{10}O_5Cl_8Te_2$ C 31.4; H 1.10; Te 27.8%. ^{1}H NMR (d_6-dmso) 7.7, 3H, 8.4, 2H. ^{13}C NMR (d_6-dmso) 144.8, 116.8, 113.9 ($Cl_4C_6O_2$) 131.5, 129.2, 109.8 (C_6H_5). ^{125}Te(d_6-dmso) 1620.30 ppm.

Analysis for $[(Br_4C_6O_2)TeC_6H_5]_2O$; found C 23.0; H 0.90; Te 20.0; calculated for $C_{24}H_{10}O_5Br_8Te_2$ C 22.6; H 0.79; Te 20.1%. ^{1}H NMR (d_6-dmso) 7.6, 3H, 8.2 br, 2H. ^{13}C NMR (d_6-dmso) 149.0, 116.3, 109.8 ($Br_4C_6O_2$) 131.5, 129.2, 109.8 (C_6H_5). ^{125}Te (d_6-dmso) 1546.6 ppm.

A sample of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ was recrystallized from tetrahydrofuran (THF) for X-ray analysis (see below); the resultant crystals proved to be $[(Cl_4C_6O_2)TeC_6H_5]_2O.2THF$. Found C 36.2; H 2.20: calculated for $C_{32}H_{26}O_7Cl_4Te_2$ C 36.2; H 2.47%. ^{1}H NMR (d_6-dmso) 8.2 br, 2H, 7.6 3H (C_6H_5) 3.60 4H, 1.75 4H (THF). The presence of the THF molecules in the lattice was also confirmed by X-ray crystallography.

(ii) As in the above experiments, a solution of 3,5-di-tert-butyl-*ortho*-benzoquinone (TBQ) (0.33 g, 1.55 mmol) in toluene (15 ml) was added dropwise over 10 min to a solution of $(C_6H_5)_2Te_2$ (0.205 g, 0.5 mmol, 15 ml toluene). The work-up of the solution followed the procedures outlined above, except that the reaction solution was taken to dryness, and the residue recrystallized from light petroleum. Yield 0.44 g, 82%, based on initial quantities taken.

The ^{125}Te NMR resonance at 1620.8 ppm confirmed that the tellurium had been oxidized to the +IV state. Microanalysis identified the compound as $[(C_{14}H_{20}O_2)TeC_6H_5]_2O \cdot \frac{1}{2}C_7H_8$ (Found C 57.6; H 6.30. Calcd. for $C_{43.5}H_{54}O_5Te$ C 57.3; H 5.97%). No further structural studies of this compound were performed.

2.4. *Crystallographic studies*

A yellow block crystal of recrystallized $[(Cl_4C_6O_2)TeC_6H_5]_2O.2THF$ was mounted in a glass capillary in the beam of a Rigaku AFCGS diffractometer, using Mo Kα radiation ($\lambda = 0.71069$ Å) at 23°C. Cell constants, and an orientation matrix, were obtained from 12 strong reflections in the range $25.18 < 2\theta < 28.47°$. The systematic absences $h0l: h + l \neq 2n$, $0k0$, $k \neq 2n$

TABLE 1. Summary of crystal data, intensity collection and structural refinement for $[(Cl_4C_6O_2)TeC_6H_5]_2O.2THF$, $C_{32}H_{26}O_7Cl_8Te_2$

Cell constants	*a* 10.88(1) Å, *b* 22.69(3) Å, *c* 15.724(6) Å, β 103.43(6)°
Cell volume (Å^3)	3777(8)
Space group	$P2_1/n$ (No. 14)
Z	4
F(000)	2056
ρ(calc.) (g cm^{-3})	1.866
Abs. coeff. (cm^{-1})	21.63
Min./max. abs. correction	0.82/1.09
Crystal dimensions (mm)	0.3 × 0.3 × 0.2
Total reflections measured	7211
2θ(°)	4.5–50
h, *k*, *l* (max, min)	0–12, 0–26, −18–17
Unique av. data [$I \geqslant 3\sigma(I)$]	3497
Number of parameters	442
$R = (\Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma \lvert F_o\rvert)$	0.055
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w F_o^2)^{1/2}$	0.068
Max. shift/error in final cycle	0.14
$\Delta\rho$(max, min) (e Å^{-3})	0.77, −0.93

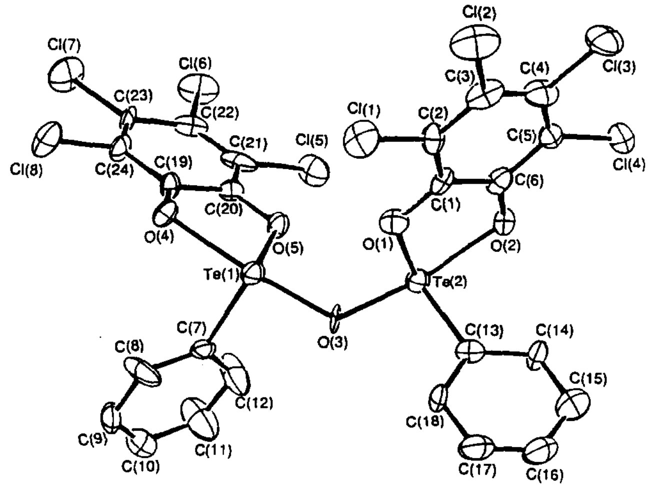


Fig. 1. The molecular structure of $[(Cl_4C_6O_2)Te(C_6H_5)]_2O$, shown as an ORTEP diagram, with 30% probability of ellipsoids. Hydrogen atoms have been omitted for clarity.

indicated the space group $P2_1/n$ (no. 14), and the subsequent successful solution and refinement confirmed this. Details of the data intensity collection are given in Table 1. The intensities of three representative reflections measured after every 150 reflections declined by 0.30%, and a linear correction factor was therefore applied in the calculations. An empirical absorption correction (DIFABS [5]) was applied in view of the significant absorption coefficient (21.6 cm^{-1}). The data were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods [6], with non-hydrogen atoms being refined anisotropically. The refinement converged on the values $R = 0.055$ and $R_w = 0.068$. The programs and other data used in this solution are listed in refs [7–11].

The structure of the molecule is shown in Fig. 1, the positional parameters in Table 2, and the important bond distances and angles in Table 3. Other material which has been deposited includes the hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms, least square planes, and tables of observed and calculated structure factors.

3. Results and discussion

3.1. The structure of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ (1)

The product of the reaction between $(C_6H_5)_2Te_2$ and $Cl_4C_6O_2$-*o* is the compound **1**, whose structure reveals a number of interesting features. The substance is an oxide, in which the oxygen atom bridges two identical moieties containing tellurium(IV) atoms with $r(Te–O) = 1.965(9)$ Å (av.) and Te–O–Te = 126.5(5)°; very similar values were reported for the related molecule $[(C_6H_5)_2TeNCS]_2O$ [12], for which $r(Te–O) = 1.985(4)$ Å, and Te–O–Te = 121.7(4)°. The Te-phenyl interaction ($r(Te–C) = 2.10(1)$ Å) is close to that in other organotellurium(IV) molecules; in $[p\text{-}PhOC_6H_4TeCl_3]_2$, for example, $r(Te–C) = 2.110(6)$ Å [13]. Equally, the $TeO_2C_6Cl_4$ part of the molecule is

TABLE 2. Atomic coordinates and thermal parameters for non-hydrogen atoms of $[(Cl_4C_6O_2)TeC_6H_5]_2O$

Atom	x	y	z	B_{eq}
Te(1)	0.6083(1)	0.57375(4)	1.07195(7)	3.27(4)
Te(2)	0.7895(1)	0.70102(4)	1.13556(7)	3.32(4)
Cl(1)	0.5765(5)	0.6841(2)	0.8229(3)	6.9(3)
Cl(2)	0.6723(5)	0.7755(3)	0.7023(3)	8.4(3)
Cl(3)	0.8936(6)	0.8602(2)	0.7844(3)	7.9(3)
Cl(4)	1.0079(5)	0.8570(2)	0.9876(3)	6.1(2)
Cl(5)	1.0701(4)	0.5515(2)	1.1579(3)	5.3(2)
Cl(6)	1.1656(4)	0.4241(2)	1.1219(3)	6.1(2)
Cl(7)	0.9700(4)	0.3308(2)	1.0287(4)	6.7(3)
Cl(8)	0.6846(4)	0.3630(2)	0.9716(3)	6.0(2)
O(1)	0.7064(9)	0.6932(4)	1.0086(6)	3.8(5)
O(2)	0.8873(8)	0.7659(4)	1.0779(7)	3.6(5)
O(3)	0.6526(9)	0.6456(4)	1.1417(7)	3.9(5)
O(4)	0.6310(8)	0.4858(4)	1.0196(6)	3.5(5)
O(5)	0.7946(8)	0.5651(4)	1.0974(6)	3.6(5)
O(6)	0.565(2)	0.160(1)	0.142(1)	14(2)
O(7)	0.414(3)	0.024(2)	0.066(3)	21(3)
C(1)	0.744(1)	0.7326(6)	0.954(1)	2.9(6)
C(2)	0.694(1)	0.7330(6)	0.866(1)	3.8(7)
C(3)	0.741(2)	0.7735(8)	0.812(1)	4.7(8)
C(4)	0.836(2)	0.8114(7)	0.850(1)	4.8(9)
C(5)	0.889(1)	0.8094(6)	0.939(1)	3.7(7)
C(6)	0.840(1)	0.7692(6)	0.992(1)	3.4(7)
C(7)	0.587(1)	0.5309(6)	1.186(1)	3.3(7)
C(8)	0.498(2)	0.490(1)	1.189(1)	7(1)
C(9)	0.492(2)	0.4593(7)	1.263(1)	6(1)
C(10)	0.576(2)	0.474(1)	1.339(1)	6(1)
C(11)	0.668(2)	0.513(1)	1.338(1)	9(1)
C(12)	0.670(2)	0.5456(9)	1.262(1)	7(1)
C(13)	0.682(1)	0.7701(6)	1.170(1)	3.3(7)
C(14)	0.736(1)	0.8250(7)	1.186(1)	4.3(8)
C(15)	0.670(2)	0.8694(9)	1.216(1)	8(1)
C(16)	0.551(2)	0.860(1)	1.227(1)	7(1)
C(17)	0.496(2)	0.808(1)	1.209(1)	6(1)
C(18)	0.561(2)	0.7612(7)	1.180(1)	4.5(8)
C(19)	0.750(1)	0.4697(6)	1.043(1)	3.1(6)
C(20)	0.838(1)	0.5127(6)	1.0827(9)	2.9(6)
C(21)	0.966(1)	0.4977(8)	1.109(1)	4.3(8)
C(22)	1.008(1)	0.4435(7)	1.091(1)	3.8(7)
C(23)	0.922(1)	0.3994(6)	1.051(1)	4.0(7)
C(24)	0.793(1)	0.4141(6)	1.025(1)	3.6(7)
C(25)	0.553(3)	0.175(2)	0.045(2)	12(2)
C(26)	0.668(3)	0.201(1)	0.039(2)	12(2)
C(27)	0.736(2)	0.214(1)	0.129(2)	10(2)
C(28)	0.672(1)	0.1899(7)	0.1847(8)	2.6(6)
C(29)	0.283(4)	−0.047(1)	0.104(3)	16(3)
C(30)	0.398(6)	−0.026(2)	0.094(4)	22(5)
C(31)	0.218(3)	0.010(1)	0.095(2)	12(2)
C(32)	0.304(3)	0.055(1)	0.074(2)	10(2)

TABLE 3. Interatomic distances (Å) and angles (°), with esd's in parentheses

Te(1)–O(3)	1.961(9)	C(2)–C(3)	1.42(2)
Te(1)–O(4)	2.195(9)	C(3)–C(4)	1.37(2)
Te(1)–O(5)	1.983(9)	C(4)–C(5)	1.39(2)
Te(1)–C(7)	2.10(1)	C(5)–C(6)	1.42(2)
Te(2)–O(1)	1.999(9)	C(7)–C(8)	1.35(2)
Te(2)–O(2)	2.138(9)	C(7)–C(12)	1.36(2)
Te(2)–O(3)	1.969(9)	C(8)–C(9)	1.37(2)
Te(2)–C(13)	2.10(1)	C(9)–C(10)	1.37(2)
Cl(1)–C(2)	1.71(2)	C(10)–C(11)	1.34(2)
Cl(2)–C(3)	1.72(2)	C(11)–C(12)	1.41(3)
Cl(3)–C(4)	1.72(2)	C(13)–C(14)	1.38(2)
Cl(4)–C(5)	1.72(2)	C(13)–C(18)	1.38(2)
Cl(5)–C(21)	1.72(2)	C(14)–C(15)	1.38(2)
Cl(6)–C(22)	1.73(1)	C(15)–C(16)	1.36(2)
Cl(7)–C(23)	1.71(1)	C(16)–C(17)	1.33(2)
Cl(8)–C(24)	1.73(2)	C(17)–C(18)	1.40(2)
O(1)–C(1)	1.37(2)	C(19)–C(20)	1.41(2)
O(2)–C(6)	1.33(2)	C(19)–C(24)	1.40(2)
O(4)–C(19)	1.32(1)	C(20)–C(21)	1.40(2)
O(5)–C(20)	1.32(1)	C(21)–C(22)	1.36(2)
O(6)–C(25)	1.54(3)	C(22)–C(23)	1.41(2)
O(6)–C(28)	1.38(2)	C(23)–C(24)	1.40(2)
O(7)–C(30)	1.24(5)	C(25)–C(26)	1.40(3)
O(7)–C(32)	1.42(3)	C(26)–C(27)	1.46(3)
C(1)–C(2)	1.37(2)	C(27)–C(28)	1.36(3)
C(1)–C(6)	1.36(2)	C(29)–C(30)	1.38(6)
		C(29)–C(31)	1.46(4)
		C(31)–C(32)	1.46(3)
O(3)–Te(1)–O(4)	158.6(4)	Cl(2)–C(3)–C(4)	122(2)
O(3)–Te(1)–O(5)	82.1(4)	C(2)–C(3)–C(4)	120(2)
O(3)–Te(1)–C(7)	88.2(5)	Cl(3)–C(4)–C(3)	119(1)
O(4)–Te(1)–O(5)	77.7(3)	Cl(3)–C(4)–C(5)	120(1)
O(4)–Te(1)–C(7)	86.8(4)	C(3)–C(4)–C(5)	120(2)
O(5)–Te(1)–C(7)	95.4(5)	Cl(4)–C(5)–C(4)	121(1)
O(1)–Te(2)–O(2)	78.0(4)	Cl(4)–C(5)–C(6)	119(1)
O(1)–Te(2)–O(3)	79.7(4)	C(4)–C(5)–C(6)	120(1)
O(1)–Te(2)–C(13)	100.0(5)	O(2)–C(6)–C(1)	119(1)
O(2)–Te(2)–O(3)	156.6(4)	O(2)–C(6)–C(5)	122(1)
O(2)–Te(2)–C(13)	87.5(5)	C(1)–C(6)–C(5)	119(2)
O(3)–Te(2)–C(13)	89.6(5)	Te(1)–C(7)–C(8)	125(1)
Te(2)–O(1)–C(1)	116.0(8)	Te(1)–C(7)–C(12)	117(1)
Te(2)–O(2)–C(6)	111.0(9)	C(8)–C(7)–C(12)	119(2)
Te(1)–O(3)–Te(2)	126.5(5)	C(7)–C(8)–C(9)	124(2)
Te(1)–O(4)–C(19)	109.8(8)	C(8)–C(9)–C(10)	118(2)
Te(1)–O(5)–C(20)	116.5(8)	C(9)–C(10)–C(11)	119(2)
C(25)–O(6)–C(28)	104(2)	C(10)–C(11)–C(12)	122(2)
C(30)–O(7)–C(32)	104(4)	C(7)–C(12)–C(11)	118(2)
O(1)–C(1)–C(2)	122(1)	Te(2)–C(13)–C(14)	119(1)
O(1)–C(1)–C(6)	116(1)	Te(2)–C(13)–C(18)	122(1)
C(2)–C(1)–C(6)	122(1)	C(14)–C(13)–C(18)	119(1)
Cl(1)–C(2)–C(1)	119(1)	C(13)–C(14)–C(15)	120(2)
Cl(1)–C(2)–C(3)	122(1)	C(14)–C(15)–C(16)	121(2)
C(1)–C(2)–C(3)	119(1)	C(15)–C(16)–C(17)	121(2)
Cl(2)–C(3)–C(2)	119(1)	C(16)–C(17)–C(18)	120(2)
C(13)–C(18)–C(17)	120(1)	O(7)–C(32)–C(31)	105(2)
O(4)–C(19)–C(20)	117(1)	Cl(7)–C(23)–C(22)	122(1)
O(4)–C(19)–C(24)	123(1)	Cl(7)–C(23)–C(24)	119(1)
C(20)–C(19)–C(24)	120(1)	C(22)–C(23)–C(24)	119(1)
O(5)–C(20)–C(19)	118(1)	Cl(8)–C(24)–C(19)	119(1)
O(5)–C(20)–C(21)	123(1)	Cl(8)–C(24)–C(23)	121(1)
C(19)–C(20)–C(21)	119(1)	C(19)–C(24)–C(23)	121(1)
Cl(5)–C(21)–C(20)	118(1)	O(6)–C(25)–C(26)	107(2)
Cl(5)–C(21)–C(22)	121(1)	C(25)–C(26)–C(27)	106(2)
C(20)–C(21)–C(22)	121(1)	C(26)–C(27)–C(28)	109(2)
Cl(6)–C(22)–C(21)	122(1)	O(6)–C(28)–C(27)	112(2)
Cl(6)–C(22)–C(23)	117(1)	C(30)–C(29)–C(31)	97(3)
C(21)–C(22)–C(23)	121(1)	O(7)–C(30)–C(29)	124(5)
		C(29)–C(31)–C(32)	109(3)

structurally very similar to the same unit in $Te(O_2C_6Cl_4)_2 \cdot$ 18-crown-6 in which the average Te–O bond distance at the tetrachlorocatecholate ligand is 2.014(7) Å, and the r(C–O) value is 1.34(1) Å [1]. Here, as in the present compound, for which the average r(C–O) is 1.34(2) Å, this bond length confirms the formulation of the ligand as being a catecholate derived from the *o*-quinone by reduction at the initial tellurium(I) centre.

The stereochemistry at the $TeCO_2O'$ kernel can be regarded as identifying the tellurium(IV) MX_3YE unit predicted by valence shell electron pair repulsion theory, and the vertical axis of this structure is then O(3)–Te(1)–O(4) in the left-hand moiety of the molecule as portrayed in Fig. 1, (angle = 158.6(4)°), with the equatorial plane being occupied by Te–C(7) and Te–O(5) bonds, and the presumed lone pair of electrons. The C(7)–Te(1) bond is approximately orthogonal to the plane Te–O(3)–O(4)–O(5), illustrated by the angles of 88.2(5)° for C(7)–Te(1)–O(3), 95.4(5)° for C(7)–Te(1)–O(5) and 86.8(4)° for C(7)–Te(1)–O(4). The other feature of interest is that the equatorial Te(1)–O(5) bond (1.983(9) Å) is substantially shorter than the apical Te(1)–O(4) bond (2.195(9) Å) of the catecholate ligand. Allowing for the distortion from idealized AX_4E stereochemistry caused by the presence of the bidentate ligand(s), the structures of this molecule, of $Te(O_2C_6H_4)_2$ [14], and of $Te(O_2C_6Cl_4)_2 \cdot$ 18-crown-6 [1], are all in reasonable agreement.

There remains the matter of the orientation of the two $(Cl_4C_6O_2)TeC_6H_5$ units with respect to each other, and to the bridging oxygen atom. The arrangement can be viewed as a balance between (i) the repulsive interactions between the presumed lone pair of one tellurium and the nearer catecholate oxygen of the other, and (ii) the attraction of each formally positive tellurium atom to the lone pair of its neighbour. The Te(1)–Te(2) distance in the molecule is 3.509(4) Å, which argues against the presence of any Te–Te bonding interaction. The Te(1)–O(1) and Te(1)–O(2) distances are 3.16(1) and 5.30(1) Å respectively.

The crystal lattice contains two molecules of tetrahydrofuran per molecule of $[(Cl_4C_6O_2)TeC_6H_5]_2O$.

These molecules are disordered, and show high thermal vibrational motion, which results in anomalous C–O distances (See Tables 2 and 3; C(30)–O(7) = 1.24(5), C(32)–O(7) = 1.42(3) Å). It was not possible to model the disorder, but fortunately the effect of this on the overall structure refinement is small. There is no interaction between THF and the tellurium atom of the title molecule; the closest approach is at a distance of 3.6 Å.

3.2. Spectroscopic studies

The ^1H and ^{13}C NMR spectra of both $[(X_4C_6O_2)TeC_6H_5]_2O$ (X = Cl, Br) compounds are essentially identical, the only significant differences being the ^{13}C resonances of the $X_4C_6O_2$ ring, and the frequencies in these two cases are similar to those found in previous studies [1,15] of related compounds. The ^{125}Te resonance of $(C_6H_5)_2Te_2$ in $CDCl_3$ is very close to that reported for this compound in CH_2Cl_2 (422 ppm from $Me_2Te=O$), and the values for the $[(X_4C_6O_2)TeC_6H_5]_2O$ compounds ae in the range for tellurium(IV) species [1,16,17]. The infrared spectra of the two products are also identical except for the C–X regions; more importantly, the ν(C=O) vibrations of the initial *o*-quinone in the 1600 cm^{-1} region are completely absent in the final products.

Dilute toluene solutions of $(C_6H_5)_2Te_2$ and $Cl_4C_6O_2$-*o* were mixed in an ESR tube at room temperature and the spectrum recorded immediately. The only feature was a weak broad signal, with $g = 2.006$. A similar experiment with $(C_6H_5)_2Te_2$ and $Bu_2H_2C_6O_2$-*o* gave a sharper and more intense resonance with no hyperfine structure ($g = 2.005$), and with a poorly resolved doublet, ascribed to coupling between the semiquinone radical and tellurium, with a coupling constant of 43 G. The value found for A_{Te} in the reaction between Et_2Te and this *o*-quinone is 38.5 G (for ^{125}Te) [1].

3.3. Reaction pathway

The overall reaction has three important features: the reduction of *o*-quinone to catecholate, the oxidation of tellurium from +I to +IV with the retention of the Te–C_6H_5 linkage, and the cleavage of the Te–Te bond of $(C_6H_5)_2Te_2$. As a starting point to a discussion of the reaction mechanism, we note that the thermolysis of R_2Te_2 (R = $Me_4{}^iPr$, ^tBu) has been shown [18] to proceed via the sequence

$$R_2Te_2 \longrightarrow Te + R_2Te \longrightarrow R^{\cdot} + RTe^{\cdot} \qquad (1)$$

in the temperature range 300–370 K. The concentration of radicals produced by eqn. (1) was low, according to the evidence of ESR spectroscopy, but tellurium mirrors were observed in photolytic experiments. This may be due to efficient recombination:

$$2\,RTe^{\cdot} \longrightarrow R_2Te + Te \qquad (2)$$

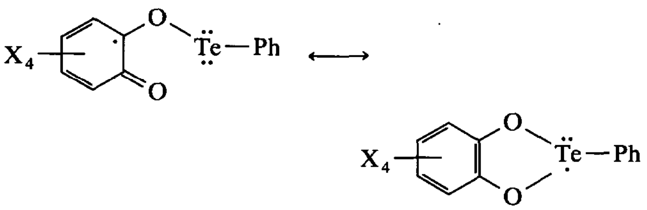
The preparative work described above was carried out in the temperature range 273–295 K, and reaction with $X_4C_6O_2$-*o* was essentially instantaneous under these conditions. Following the suggestion [18] that $RTe^{\cdot}$ radicals will add rapidly to alkenes, we suggest that the reaction pathway in these experiments involves the sequence:

$$Ph_2Te_2 \longrightarrow PhTe^{\cdot} \qquad (1a)$$

$$PhTe^{\cdot} + Q \longrightarrow (SQ^{\cdot})TePh \qquad (3)$$

$$(SQ^{\cdot})TePh \longrightarrow (CAT)Te^{\cdot}Ph \qquad (4)$$

in which the intramolecular electron transfer process (eqn. 4) is:



so that a tellurium(III) radical complex is formed. Internal rearrangements of this type are common in Q/SQ/CAT ligand systems.

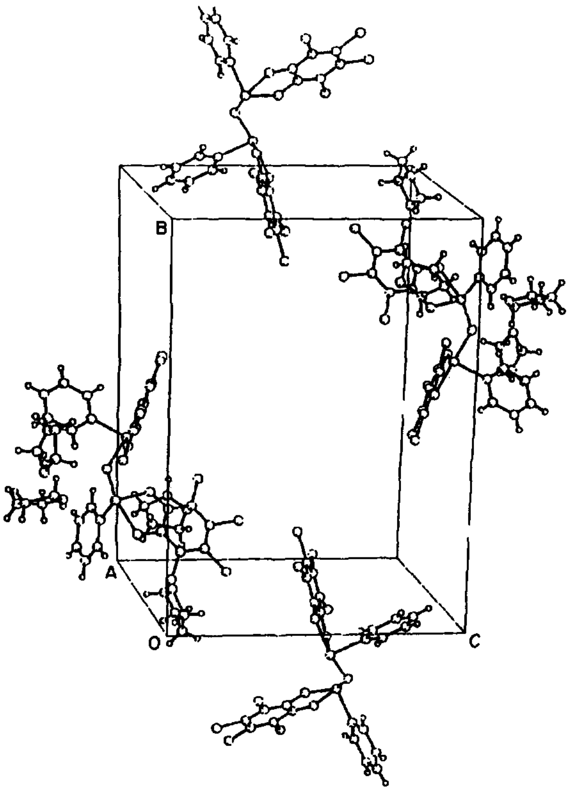


Fig. 2. The cell packing of $[(Cl_4C_6O_2)Te(C_6H_5)]_2O\cdot 2THF$.

Such processes reasonably account for the formation of the $(X_4C_6O_2)TeC_6H_5$ groups which are present in the final product, and to this point the mechanism is compatible with the ESR results, which confirm the presence of molecules in which the $Bu_2H_2C_6O_2$-*o* radical is bonded to tellurium. The reaction between $(C_6H_5)_2Te_2$ and $Cl_4C_6O_2$-*o* is much faster than with $Bu_2H_2C_6O_2$-*o*, and the weaker ESR signal observed is presumably a consequence of this rate difference, which is itself in keeping with the known stronger oxidizing power of the tetrahalogenoquinones. The general conclusion that one-electron transfer processes are involved in the reaction between $(C_6H_5)_2Te_2$ and *ortho*-quinones is in keeping with similar findings for other reactions of Main Group compounds.

The source of the oxygen atom in the final product poses a problem, since the high yields would appear to preclude oxygen or moisture impurities from providing this element in sufficient quantities under the experimental conditions used. On the other hand, there are severe mechanistic difficulties if the excess *ortho*-quinone is the source of the bridging oxygen. The reactions involved are evidently unclear at this point, and further investigations of this unusual reaction are planned.

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