Bis-(8-oxo quinoline)diorgano tellurium(IV) compounds; structural and spectroscopic studies

Anatoly G. Maslakov [a], Elizabeth Gresham [a], Thomas A. Hamor [b], William R. McWhinnie [a], Michael C. Perry [a] and Nirmala Shaikh [a]

[a] *Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET (UK)*
[b] *School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT (UK)*

Abstract

Three new compounds of the type $R_2Te(OR')_2$ are reported in which R' bears a potentially co-ordinating group: bis-(8-hydroxo quinoline)dimethyltellurium (I) bis-(8-oxo-2-methyl quinoline)dimethyltellurium (II), and bis-(8-oxo-quinoline) di-(*p*-tolyl)tellurium (III). The crystal structures of II and III have been determined. The primary geometry around tellurium in both cases can be described as Ψ-trigonal bipyramidal but long Te $\cdots$ N contacts in the range 2.840(6)–2.899(4) Å which lie well within the van der Waals distance imply extension of the co-ordination sphere. Variable temperature multi-nuclear (^{1}H, ^{13}C, [125]Te) studies of the compounds I, II, and III in solution indicate the presence of a single species over the range 216–343 K. The data do not distinguish between the presence of a single 14-Te-6 pertellurane seen in the crystallographic studies, or that of such a species in equilibrium, rapid on the ^{1}H and [125]Te timescales, with the 10-Te-4 tellurane.

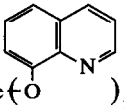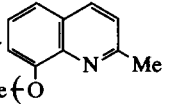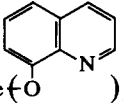*Key words:* Tellurium; Crystal structure

1. Introduction

Intra-molecular coordination is now a well established method of stabilising a range of otherwise reactive organotellurium compounds [1,2]. To date, the most frequently encountered donor atoms are O [3] and N [1,2] and, particularly in the case of nitrogen donors, a considerable body of structural data is available. It has been noted that the length (and so strength?) of the Te ← N contact is dependent on the nature of the atom *trans* to N, *i.e.* there is a *trans*-influence: C ≫ Te > S, O, halogen.

More structural information is available for Te[(II)] than for Te[(IV)] compounds, although it is well established that RTeX₃ (X = halogen) is monomeric when R carries a donor group [4], in contrast to the polymeric structures (*e.g.* (*p*-EtO.C₆H₄)TeBr₃ [6]) observed when R is a simple organic group. On substitution of a second organic group to give R_2TeX_2, the

Lewis acidity of the tellurium atom falls significantly, although in the solid state secondary bonding interactions [7] can even be sufficiently important for distinct clusters to form as is the case for tetrameric phenoxatellurin-10,10-dichloride [8]. Few examples are known in which the organic group attached to tellurium carries a donor group. In one case that has been examined, chloro(*p*-ethoxyphenyl) (2-(2'-pyridyl)phenyl)tellurium(IV) trichloro-mercurate(II) [9], the intra-molecular coordination of the 2-pyridyl-nitrogen atom maintains the Ψ-trigonal bipyramidal geometry in a novel telluronium species. Another example is provided by 2-dichloro(butyl)tellurobenzaldehyde, in which a long (2.848(4) Å) intra-molecular Te $\cdots$ O contact confers a distorted Ψ-octahedral geometry on tellurium [10]. An alternative approach is to select "X" in R_2TeX_2 to be a potentially bidentate anionic group. Minkin *et al.* have used this approach with X = –O.C₆H₄.H=CH.C₆H₄R-*m*, and have produced a range of diorganotellurium(IV) compounds [11]. The structure of Me₂Te (O · C₆H₄.N=CH · C₆H₄NO₂)₂ has been reported [11]

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* Correspondence to: Prof. W.R. McWhinnie.

TABLE 1. Analytical Data for New Tellurium(IV) Compounds

No.	Compound	C% (calc.)	H% (calc.)	N% (calc.)	m.p.
I	Me₂Te⁺O [quinoline structure] ₂	54.1 (53.9)	4.00 (4.10)	6.25 (6.25)	93
II	C₆H₆· Me₂Te⁺O [quinoline-Me structure] ₂	58.9 (60.9)	4.80 (5.10)	5.20 (5.10)	142
III	(p-tol)₂Te⁺O [quinoline structure] ₂	64.5 (66.9)	4.40 (4.10)	4.55 (4.35)	188

and shows long Te · · · N contacts of 2.92 and 2.96 Å. It is interesting that the material is very stable under normal laboratory conditions whereas more simple diorganotellurium(IV) dialkoxides (or diaryloxides) are much more reactive [11]; whether this is due to "stabilisation" by the weak Te · · · N interactions or to a reduced reactivity arising from the bulk of the group attached to the oxygen atom is a matter for debate [12]. ¹²⁵Te NMR solution data for Me₂Te(O · C₆H₄.N=CH · C₆H₄ · NO₂)₂ and related compounds often show two
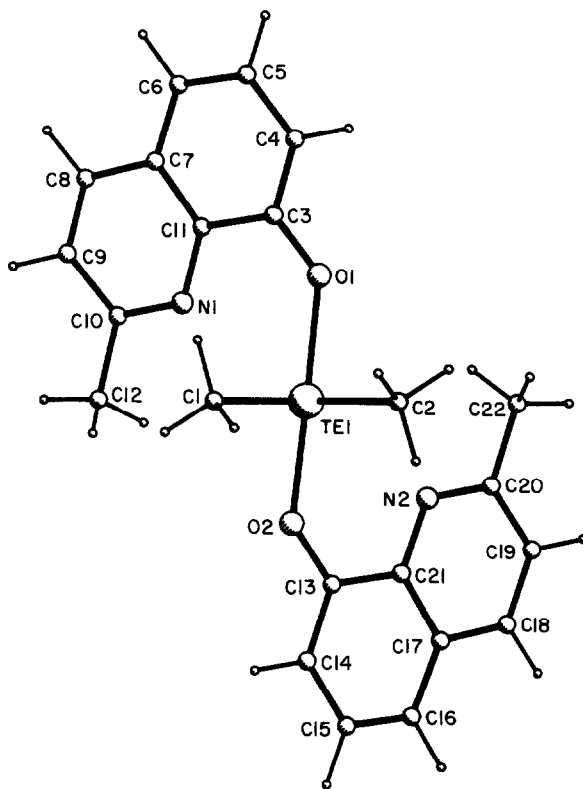

Fig. 1. The molecular structure of compound II showing the atom numbering.

TABLE 2. Some NMR Data for New Tellurium(IV) Compounds

¹H NMR (ppm vs. TMS)

Compound	Solvent	T(K)	CH₃–Te	CH₃ (p-tol)	CH₃ (Me quinoline)
I	CDCl₃	297	2.97 (J(H–Te) = 21.4 Hz)	–	–
II	CDCl₃	297	2.85 (J(H–Te) = 19.0 Hz)	–	2.58
	DMF(d₇)	343	3.34		3.12
		333	3.38		3.18
		297	3.40		3.22
III	C₆D₆	297	–	1.94	–

¹²⁵Te NMR (ppm vs. Me₂Te)

Compound	Solvent	T(K)	δ (¹²⁵Te)	Temperature Dependence (ppm K⁻¹)
I	CDCl₃	297 228	1152.5 1159.2	0.10
II	CDCl₃	297 [a] 216	1149.7 1156.3	0.08
III	CDCl₃	297 [b] 238	1139.7 1142.3	0.06

I, II, and III shows a single resonance close to above values at 343 K in DMF (d₇).
[a] Proton coupled spectrum gives J(H–Te) = 21.4 Hz (septet).
[b] J(¹³C–¹²⁵Te) = 2.99 Hz.

resonances which have been attributed to co-ordinated (Te · · · N) and uncoordinated anionic ligands.

In this short paper this area of tellurium chemistry is extended to include studies of diorganotellurium(IV) derivatives of the familiar 8-hydroxyquinoline system, thus extending the range of readily isolable and stable examples of $R_2Te(OR')_2$.

2. Experimental section and results

2.1. Synthesis

The compounds prepared for this study were: bis-(8-oxoquinoline)dimethyltellurium(IV) (I), bis-(8-oxo-2-methylquinoline)dimethyltellurium(IV) (II), and bis-(8-oxoquinoline) di-(p-tolyl)tellurium(IV) (III). Preparations followed the procedure developed by Minkin et al. [11], and an example is given below.

Dimethyltellurium(IV) dichloride (8.23 g, 20 mmol) in dry toluene (50 ml) was treated with stirring with a solution of NaOMe (Na (0.95 g, 40 mmol) in methanol (30 ml)). After completion of the addition methanol was distilled off until the vapour temperature was 110°C and crystals of NaCl separated. The crystals were filtered off and the filtrate was added with stirring to 8-hydroxyquinoline (5.80 g, 40 mmol) in dry toluene (50 ml). The bulk of the toluene was removed under vacuum and the concentrated residue was treated with an equal volume of ethanol and the mixture was cooled to −5°C to give crystals of the product, which

Fig. 2. The molecular structure of compound III showing the atom numbering.

TABLE 3. Fractional atomic coordinates ($\times 10^4$), Te ($\times 10^5$) with e.s.d.'s in parentheses for compound II (top) and compound III (bottom)

	x	y	z
Te(1)	−1293(3)	−27199(2)	−23949(2)
O(1)	1377(3)	−3390(3)	−1175(3)
O(2)	−1845(3)	−1907(3)	−3124(3)
N(1)	2937(4)	−1621(3)	−1893(3)
N(2)	−2288(4)	−4204(3)	−4532(3)
C(1)	272(5)	−1166(4)	−1017(4)
C(2)	−1605(5)	−3735(5)	−1751(4)
C(3)	2825(4)	−3088(4)	−771(4)
C(4)	3556(6)	−3657(5)	15(4)
C(5)	5100(7)	−3339(6)	478(5)
C(6)	5911(6)	−2460(6)	188(5)
C(7)	5207(5)	−1859(4)	−614(4)
C(8)	5941(5)	−928(5)	−979(5)
C(9)	5196(6)	−394(5)	−1752(5)
C(10)	3669(5)	−775(4)	−2219(4)
C(11)	3667(4)	−2161(4)	−1098(3)
C(12)	2839(8)	−206(7)	−3099(7)
C(13)	−2921(5)	−2307(4)	−4161(4)
C(14)	−3833(5)	−1568(4)	−4519(4)
C(15)	−4969(6)	−1947(5)	−5592(5)
C(16)	−5188(5)	−3030(5)	−6315(4)
C(17)	−4300(4)	−3823(4)	−6000(4)
C(18)	−4447(6)	−4983(5)	−6682(4)
C(19)	−3581(6)	−5704(5)	−6287(4)
C(20)	−2481(5)	−5293(4)	−5190(4)
C(21)	−3162(4)	−3473(4)	−4905(3)
C(22)	−1499(6)	−6070(4)	−4739(5)
C(100)	−382(10)	−3459(6)	−8190(7)
C(200)	−1072(9)	−3193(9)	−7367(10)
C(300)	−708(11)	−2081(11)	−6633(9)
C(400)	330(9)	−1250(7)	−6723(6)
C(500)	1071(7)	−1497(6)	−7538(7)
C(600)	708(9)	−2638(8)	−8299(6)
Te(1)	11295(5)	29853(2)	−8791(3)
O(1)	323(5)	3767(2)	−1830(4)
O(2)	2060(5)	2368(2)	290(3)
N(1)	−1734(6)	2951(4)	−1420(5)
N(2)	2680(6)	1925(3)	−1554(5)
C(1)	439(7)	3442(3)	340(5)
C(2)	579(8)	4112(3)	530(5)
C(3)	94(9)	4383(4)	1347(6)
C(4)	−534(10)	4011(4)	2007(6)
C(5)	−697(9)	3355(4)	1806(6)
C(6)	−218(8)	3065(4)	988(6)
C(7)	−1016(15)	4326(6)	2928(9)
C(8)	2992(7)	3506(4)	−746(5)
C(9)	4107(8)	3303(4)	−99(6)
C(10)	5345(9)	3623(5)	−26(7)
C(11)	5506(8)	4162(4)	−604(6)
C(12)	4390(9)	4381(4)	−1237(6)
C(13)	3138(8)	4057(4)	−1339(6)
C(14)	6864(9)	4495(5)	−582(8)
C(15)	−780(8)	3662(4)	−2532(6)
C(16)	−860(11)	3959(5)	−3458(6)
C(17)	−2080(14)	3890(6)	−4178(8)
C(18)	−3154(12)	3528(6)	−3931(8)
C(19)	−3083(10)	3203(5)	−3042(8)
C(20)	−4113(10)	2810(6)	−2751(10)
C(21)	−3940(11)	2507(6)	−1847(10)
C(22)	−2741(10)	2587(5)	−1197(8)
C(23)	−1866(8)	3266(4)	−2314(7)

TABLE 3 (continued)

	x	y	z
C(24)	2489(8)	1746(4)	191(6)
C(25)	2637(9)	1334(4)	1000(6)
C(26)	3111(11)	708(4)	921(8)
C(27)	3409(11)	453(5)	57(8)
C(28)	3290(9)	865(4)	−818(7)
C(29)	3593(10)	652(5)	−1755(7)
C(30)	3428(10)	1065(5)	−2546(7)
C(31)	2967(8)	1706(4)	−2427(6)
C(32)	2822(7)	1504(4)	−740(5)

was recrystallised from both hexane-benzene and CCl_4. Analytical data are given in Table 1.

2.2. Physical measurements

IR spectra were obtained for KBr discs (4000–400 cm^{-1}) and polythene discs (500–150 cm^{-1}) on a Bio-rad FTIR spectrometer. NMR spectra were measured with a Brüker AC-300 instrument operating at 300 MHz (^{1}H), 75.469 MHz (^{13}C), and 94.734 MHz (^{125}Te). Chemical shifts were recorded relative to TMS (^{1}H, ^{13}C) and Me_2Te (^{125}Te). Attempts to obtain solid state (MAS) spectra (^{125}Te) failed due to excessively long spin-lattice relaxation times; the facility to cross polarize when measuring solid state ^{125}Te spectra was not available. Some spectroscopic data are presented in Table 2.

2.3. Crystal structure determinations

Crystal Data: (II) $C_{22}H_{22}N_2O_2Te \cdot C_6H_6$, $M_r =$ 552.1, triclinic, space group $P\bar{1}$, $a = 9.643(3)$, $b =$

TABLE 4. Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses. Atom labels in square brackets refer to the labelling scheme for compound (III) as depicted in Fig. 2

	II	III
Te–O1	2.144(3)	2.122(5)
Te–O2	2.124(3)	2.112(5)
Te–C1	2.114(4)	2.088(7)
Te–C2[C8]	2.100(5)	2.125(7)
O1–C3[C15]	1.325(5)	1.351(8)
O2–C13[C24]	1.345(5)	1.352(8)
Te···N1	2.899(4)	2.840(6)
Te···N2	2.891(4)	2.886(6)
O1–Te–O2	162.1(1)	167.8(2)
O1–Te–C1	88.3(1)	89.6(2)
O1–Te–C2[C8]	80.1(2)	85.4(2)
O2–Te–C1	79.0(1)	81.2(2)
O2–Te–C2[C8]	88.6(2)	87.5(2)
C1–Te–C2[C8]	95.1(2)	95.8(3)
Te–O1–C3[C15]	130.3(3)	119.5(5)
Te–O2–C13[C24]	128.9(3)	126.6(5)
N1···Te–C2[C8]	143.0(2)	150.1(3)
N2···Te–C1	143.4(2)	146.9(3)

11.770(5), $c = 11.896(5)$ Å, $\alpha = 101.33(6)$, $\beta = 104.31(6)$, $\gamma = 98.94(5)$°, $U = 1253$ Å^3, $Z = 2$, $D_c = 1.464$ g cm^{-3}, $F(000) = 556$, $\mu(Mo$ K$\alpha) = 1.25$ mm^{-1}. (III) $C_{32}H_{26}N_2O_2Te$, Mr = 598.2, monoclinic, space group $P2_1/c$, $a = 9.982(4)$, $b = 20.409(6)$, $c = 13.397(6)$ Å, $\beta = 98.84(5)$°, $U = 2697$ Å^3, $Z = 4$, $D_c = 1.473$ g cm^{-3}, $F(000) = 1200$, m(Mo K$\alpha) = 1.17$ mm^{-1}.

For both compounds cell dimensions and intensity data were measured on an Enraf-Nonius CAD-4 diffractometer operating in the ω-2θ scan mode, using Mo Kα radiation, $\lambda = 0.71069$ Å. 4398 unique reflections (II) and 4729 (III) were measured within the θ range 2–25° and of these 3460 (II) and 2951 (III) were considered observed $[F > 5\sigma(F)]$ and were used in the analyses. Three standard reflections re-measured every 2 h showed no significant variation in intensity.

The structures were determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions [d(C–H) 1.08 Å] riding on their respective bonded atoms. Methyl substituents were treated as rotating rigid groups. Weights of the form $w = 1/[\sigma^2(F) + gF^2]$ were used in the refinements with $g = 0.0002$ (II) and 0.00008 (III). The calculations were terminated when all shift/e.s.d. ratios were < 0.1 and R, R' were 0.0297, 0.0372 (II) and 0.0424, 0.0481 (III). For both structures the residual electron density in the final difference map was within the range ± 0.6 e Å^{-3}.

Computations were carried out on the University of Birmingham IBM 3090 computer with the SHELXS 86 [13] and SHELX 76 [14] programs. Molecular diagrams were drawn using PLUTO [15]. Atomic coordinates and selected bond lengths and angles are given in Tables 3 and 4, respectively. Tables of H-atom coordinates, thermal parameters and full lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Discussion

The molecular structures of compounds (II) and (III) are shown in Figs. 1 and 2, respectively. The geometry at tellurium is quite similar in the two structures (Table 4), and can be described as approximating to trigonal, bipyramidal, with the oxygen atoms axial (O–Te–O angles 162.1(1) and 167.8(2)°) and the bonded carbon atoms and the Te 5s lone-pair electrons equatorial. The C–Te–C angles, 95.1(2) and 95.8(3)° are less than the 120° predicted by VSEPR theory.

The Te–O and Te–C bond lengths are normal and are similar to those found [1,11,16–18] in analogous Te(IV)O$_2$R$_2$ structures, in which Te–O and Te–C bond lengths are in the ranges 2.100–2.180 and 2.092–

2.151 Å, respectively. There appears to be some in-verse relationship between the lengths of the Te-O bonds and the length of the bond between these oxygen atoms and their bonded carbon atoms. Taking the sum of Te-O and O-C the range of values is 3.425–3.473 Å, significantly less than the range of Te-O lengths. The bonding geometry at tellurium in II and III is also closely paralleled in these structures; thus the O-Te-O, O-Te-C and C-Te-C angles are in the ranges 162–168°, 81–91° and 97–101°, respectively.

The Te $\cdots$ N distances in I and II are in the range 2.840(6) to 2.899(4) Å typical [1] of such coordinate interactions when there is a carbon atom bonded to tellurium *trans* (or within about 35° of *trans*) to the Te $\cdots$ N vector. In the crystal structure of the quite analogous dimethyl-bis(2-(4-nitrobenzylideneimino) phenoxy)-tellurium(IV), the Te $\cdots$ N distances are 2.922 and 2.962 Å, with C-Te $\cdots$ N angles 146.6 and 141.3° [11], similar to the corresponding values in II and III. In contrast, when in geometrically similar situations the atom bonded to tellurium *trans* to nitrogen is halogen, sulfur or oxygen, Te $\cdots$ N distances are typically 2.2–2.4 Å [1]. These longer distances are, nevertheless, well within the sum of the van der Waals radii of tellurium and nitrogen (3.61 Å) [19], and prob-ably represent a weak but significant interaction.

3.1. Spectroscopic data

IR spectra of the new compounds were scanned to 150 cm^{-1}. As would be expected for such low symmetry species containing complex organic groups, the spectra are extremely complex. It was possible to assign ν(Me-Te) to two m-w vibrations at 584 and 572 cm^{-1} for I. For II, ν(Me-Te) was located at 580 cm^{-1}, which may imply an accidental degeneracy of ν_s and ν_{as} or, more probably, the obscuring of ν_{as} below a strong absorption at 597 cm^{-1} [20]. The increased energy of the vibrations for I and II is consistent with the in-crease in oxidation state for tellurium. It was certainly not possible to assign with confidence any vibration associated with the long Te $\cdots$ N contacts observed in the structural studies of II and III.

The coordination environment for tellurium in solu-tions of the new compounds is a matter of interest since two forms can be envisaged: the 14-Te-6 pertellu-rane structure seen in the crystallographic studies of II and III or a 10-Te-4 tellurane structure in which the weak Te $\cdots$ N interactions are no longer present. Al-ternatively an equilibrium such as that shown in (1) may exist:

$$14\text{-Te-}6 \rightleftharpoons 10\text{-Te-}4 \qquad (1)$$

Minkin *et al.* [11] in their study of analogous com-pounds such as bis-(2-(4-nitrobenzylideneimino)phe-

noxy)dimethyltellurium(IV) noted no evidence from ^{1}H NMR spectra for the presence of more than one species in solution, but in many cases study of the ^{125}Te NMR spectra revealed two resonances ($\delta \sim 1055$, 1100 ppm *vs.* Me$_2$Te) that were suggested to involve equilibria such as (1) (fast on the ^{1}H, but slow on the ^{125}Te time scales).

The ^{1}H NMR and ^{13}C spectra at room temperature for CDCl$_3$ solutions of I, II and III show a single environment for the R and OR^1 groups in R$_2$Te(OR^1)$_2$. On heating of a DMF(d$_7$) solution of II to 70°C the single environment of both R and (OR^1) is preserved, though there is a significant solvent shift. Use of a coordinating solvent such as DMF, together with higher temperatures, might be expected to favour the 10-Te-4 form, but the ^{1}H NMR study is inconclusive since it fails to differentiate between the existence of single species (14-Te-6 or 10-Te-4) and that of a fast dynamic equilibrium such as (1). Unfortunately the ^{125}Te spec-tra did not clarify matters greatly. In CDCl$_3$ solutions of I, II and III a single resonance showing the expected temperature dependence (see Table 2) was seen. Low temperatures and weakly coordinating solvents may be expected to favour the 14-Te-6 form of the compounds, but the same species is present at 70°C in DMF (d$_7$). Simplistic arguments suggest that the tellurium atom may be less shielded in the 10-Te-4 than in the 14-Te-6 structure, and so the resonance observed at ~ 1100 ppm by Minkin *et al.* [11] may arise from the presence of the 14-Te-6 pertellurane. The tellurium resonance observed for I, II and III is even more shielded, and crystallography of II and III has revealed slightly shorter Te $\cdots$ N contacts in these compounds than those observed by Minkin *et al.* [11], thus there is circumstantial evidence that the 14-Te-6 pertellurane structure is retained in solution over the temperature range 343–216 K. This conclusion is not unambiguous; the failure of our attempt to obtain further support for the hypothesis from solid state NMR spectroscopy is explained in the Experimental section.

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