

Isolation and X-ray structure determination of a new tellurane *Te*-oxide dimer [12-Te-6(C4O2)]₂ (λ^6 -tellane)

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Abstract

The reaction of bis(2,2'-biphenylene)tellurane (**1**) (λ^4 -tellane) with ozone at low temperature affords diastereoselectively the *O*-bridged tellurane *Te*-oxide dimer (**2**) (λ^6 -tellane) having a bis(octahedral) configuration. The compound **2** has been characterized by elemental and spectroscopic (IR and FABMS, ¹H, ¹³C, and ¹²⁵Te NMR) analyses. The crystal and molecular structure analysis of **2** identifies the product of the above reaction as the $\Lambda\Lambda$ and $\Delta\Delta$ diastereomeric isomers. © 1997 Elsevier Science S.A.

Keywords: Pertellurane; Tellurium-oxide dimer; Hexacoordinate; Crystal structure

1. Introduction

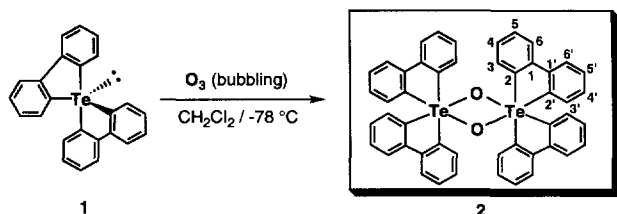
Reported studies of hexavalent organochalcogen species among perchalcogenurane [12-X-6, X = chalcogen atoms] compounds are less common than the corresponding inorganochalcogen species [1]. Only a few organoperchalcogen species have been synthesized to date. The first organoperchalcogen species [12-X-6(C2O2F2), X = S, Te] were reported by Martin and coworkers in 1984 [2], and recently, the syntheses of hexamethylpertellurane [12-Te-6(C6)] and tetramethyldifluoropertellurane [12-Te-6(C4F2)] have been reported by Morrison and coworkers [3]. The studies of inorganic hypervalent chalcogen oxides of the XOF₄ type have been reported by Seppelt and coworkers [4]. They concluded that TeOF₄ does not exist as a monomeric form in contrast to both SeOF₄ and SOF₄. The structure of the tellurium oxide dimer, TeOF₄, was characterized as having an *O*-bridged bis(octahedral) configuration [12-Te-6(F4O2)]₂ as deduced from the results of the spin-spin coupling pattern between tellurium and fluorine atoms in the ¹⁹F NMR spectra and from the molecular weight determination from its mass spectrum [5]. The tellurium atoms are sterically shielded by the six ligands and the compound exhibits a high stability as shown by its hydrophobicity and high melting point. Another, the

tellurane oxide dimer [12-Te-6(C2O4)]₂, an organopertellurane (λ^6 -tellane), has been reported by Martin and coworkers [2]. This compound had been generated by the oxidation of the tellurium(IV) using ozone in the reaction. However, the structure of this tellurane oxide dimer species has only been characterized by spectroscopic experiments and has not been determined by X-ray crystallographic analysis. We have been investigating the reactions of tetraaryltellurane [10-Te-4(C4)] using various reagents, such as OH, SH [6,7], or SO₂Cl₂ [8]. We found that the oxidation reaction of bis(2,2'-biphenylene)tellurane (**1**) [9] (λ^4 -tellane) with ozone gave a new tellurane **2** (λ^6 -tellane), as shown in Scheme 1. In this article, we describe the isolation of the organotellurane *Te*-oxide dimer [12-Te-6(C4O2)]₂ (**2**) as a bis(pertellurane) species and report its first crystal and molecular structure determination by X-ray diffraction analysis.

2. Results and discussion

Bis(2,2'-biphenylene)tellurane (**1**) reacts with ozone in CH₂Cl₂ at -78 °C to give pale yellow precipitates in 27% yield. This compound **2** has a high melting point (272–275 °C) among the known hypervalent organotellurium species and is very stable in water and halogen containing solvents. In order to confirm the structure of the pale yellow solid, ¹H, ¹³C, and ¹²⁵Te NMR spectra

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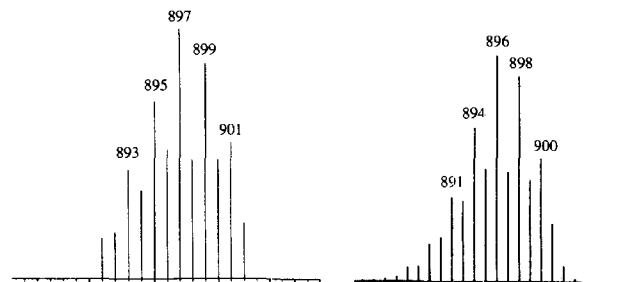


Scheme 1.

were measured at room temperature. The ^1H and ^{13}C NMR spectra of each biphenylene group in the compound **2** were observed as an unequivocal state with four doublet and four triplet peaks from the ^1H NMR spectrum and 12 peaks from the ^{13}C NMR spectrum. The ^{125}Te NMR spectrum of **2** showed only one peak at 593.2 ppm. If the pale yellow solid was a pentacoordinated compound like bis(biphenylene)tellurane *Te*-oxide monomer, then each biphenylene group should have an equivalent state because the pseudo-rotation takes place more rapidly than the timescale of the NMR measurement at room temperature. In general, the hexacoordinated pertelluranes (λ^6 -tellanes) do not undergo an intramolecular ligand exchange as is generally observed for the corresponding tetra- and pentacoordinated compounds. In the case of the $[\text{12-Te-6}(\text{X4Y2})]$ type compounds where the ligands Y are more electronegative than the ligand X, it is known that the corresponding pertellurane (λ^6 -tellane) with the *cis*-configuration is more stable than that of the *trans*-configuration [2,8]. The results of various NMR spectral measurements for **2** show that the two X ligands in the Y–Te–Y plane and the other two X ligands have unequivocal states. Only the ^1H NMR chemical shift of the 3'-position of the biphenylene groups in the compound **2** appears at an unusually high field compared with those of bis(biphenylene)selenurane or -tellurane at low temperatures [10]. This result indicates that the corresponding proton at the 3'-position (shown in Scheme 1) is located in the shielding area created by the aromatic ring of the neighboring biphenylene group. Furthermore, the elemental analysis of the pale yellow solid is consistent with the molecular formula of the corresponding tellurane dimer and the FAB mass spectrum shows a molecular ion at m/e 901 ($[\text{M} + \text{H}]^+$) (2.34% relative intensity) as well as peaks due to the monomeric tellurane oxide at m/e 451 ($[\text{M}/2 + \text{H}]^+$). In Fig. 1, both the calculated and the observed FAB mass spectra of **2** are shown.

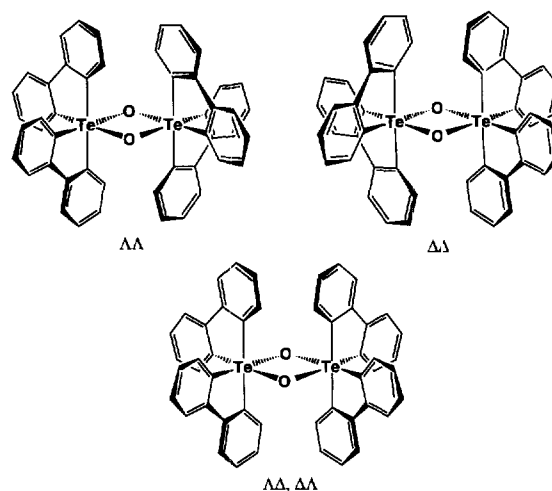
On these grounds we concluded that the compound **2** exists as the tellurane *Te*-oxide dimer having two central hexavalent tellurium atoms and that the inter- or intramolecular ligand permutation in the Te(VI) takes place at a rate slower than the NMR timescale or not at all.

Bis(2,2'-biphenylene)tellurane *Te*-oxide dimer **2**

Fig. 1. The pattern of experimental FABMS (left) and calculated MS (right) spectroscopies of **2**.

with two oxygens bridging between the central tellurium atoms can exist in the three possible diastereomeric forms $\Delta\Delta$ and/or $\Lambda\Lambda$ and/or $\Delta\Lambda$. However, the various NMR spectra of compound **2** show the presence of only one of the two environmentally different diastereomeric forms. It is possible that steric interactions between the bulky biphenylene groups in the two diastereomeric forms dictates the predominance of the less hindered chiral diastereomer, $\Delta\Delta$ and $\Lambda\Lambda$ as shown in Fig. 2. However, the NMR spectra and mass spectroscopic analysis do not give a conclusive answer about the structural aspect of **2**. Therefore, the compound was analyzed using the single crystal X-ray diffraction method. Suitable crystals were obtained by the recrystallization of **2** from a dry solution of THF/Et₂O at 0°C.

The structure determination of **2** establishes that the compound exists as both the $\Lambda\Lambda$ and $\Delta\Delta$ diastereomeric isomers. The crystal lattice consists of tellurane *Te*-oxide dimers and disordered water molecules. The latter was identified by infrared spectroscopy ($\nu(\text{O-H}) = 3402 \text{ cm}^{-1}$) and modeled as water molecules. These solvent molecules are located in the lattice spaces between the tellurium dimers. The shortest intermolecular contacts with these molecules are to the oxygen atom

Fig. 2. The three possible isomers for **2**.

O(2) of the dimer and range from 3.66(3) to 5.33(4) Å longer than the sum of the van der Waals radii O–O (2.80 Å) [1].

An ORTEP diagram of **2** showing the numbering scheme is displayed in Fig. 3. The Te-dimer exhibits three mutually perpendicular non-crystallographic two-fold rotation axes of symmetry passing through the atoms Te1 and Te2, O1 and O2, and passing through the mid-point of the line joining the atoms Te1 and Te2 respectively. With the two *cis*-bridging atoms O1 and O2, the two tellurium atoms have a distorted octahedral coordination geometry resulting from the three restricted bidentate bite angles ranging from 79.7(4) to 80.7(4)°, as shown in Table 3. The Te(VI)–C bonds are in the range from 2.122(9) to 2.159(9) Å and are thus similar to the Te–C single bond distance of 2.123 Å [11]. In contrast, the Te(VI)–O bond lengths (1.997(6)–2.019(6) Å) are significantly shorter than the Te–O single bond distance of 2.101 Å [11]. As listed in Table 3, the respective complementary angles C–Te(VI)–C and O–Te(VI)–C range from 93.7(4) to 172.9(4)° and from 90.3(3) to 165.1(3)°. The two tellurium and two oxygen atoms in the dimer form a four-membered ring. Within experimental error, the sum of the bond angles O–Te(VI)–O and Te(VI)–O–Te(VI) is equal to 360°. Therefore, the tellurium and oxygen atoms of the four-membered ring are in the same plane.

Furthermore, the bond angles between equatorial carbons and tellurium atom VI, C(1)–Te(1)–C(24) and C(25)–Te(2)–C(48), are equal to 101.3(3)° and 102.9(4)° and are significantly smaller than the reported angle between tellurium and equatorial carbon atoms in the tellurane **1**, 108.2(2)° [6]. Fig. 4 shows a space-filling view of **2** illustrating that the 3'-position hydrogens of the tellurane Te-oxide dimer **2** are located at positions closer to the aromatic rings of the neighboring

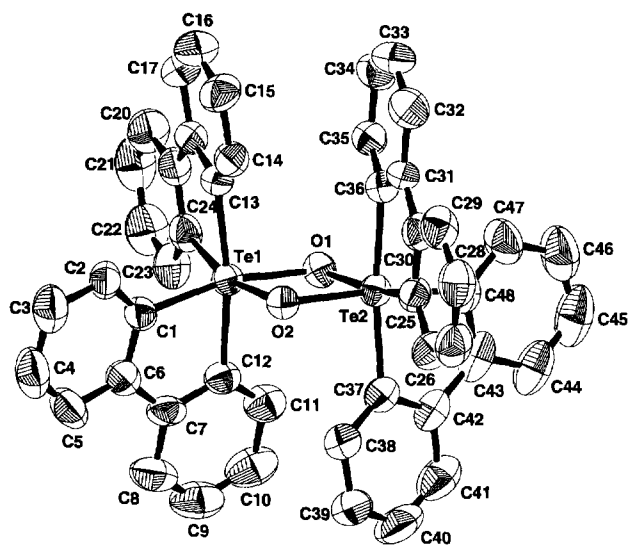


Fig. 3. ORTEP view of **2**. The water molecules are omitted.

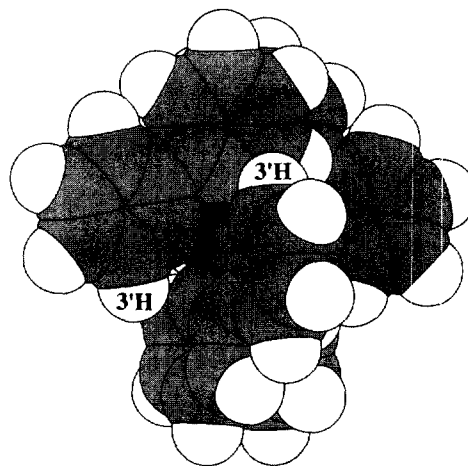


Fig. 4. A space-filling illustration of **2** showing the close proximity of the 3' hydrogen atom to neighboring rings.

biphenylene group than in the bis(2,2'-biphenylene)tellurane compound **1**. This result explains the magnetic behavior of the 3'-positional hydrogens of **2** as described above.

Interestingly, the distance between the two tellurium atoms in **2** is 3.1243(8) Å which is about 41% smaller than the sum of the van der Waals radii (4.40 Å) and is about 15% greater than a Te–Te single bond distance (2.712 Å) [11]. However, due to a lack of available electrons the two tellurium atoms cannot be involved in a bonding interaction.

The present results provide the synthesis and structure of the *O*-bridged tellurane Te-oxide dimer (λ^6 -tellurane), and further work in this area is currently underway in our laboratory.

3. Experimental details

3.1. General remarks

All NMR spectra were obtained with a Bruker ARX-400 spectrometer. Mass spectra were taken with a JEOL JMX SX102 mass spectrometer. IR spectra were taken with a JASCO FT/IR-300F spectrometer. The X-ray crystallographic analysis was performed on a four-circle Enraf–Nonius CAD4-FR automatic diffractometer. Elemental analyses were carried out by the Chemical Analytical Center at the University of Tsukuba. All melting points are uncorrected. Each chemical shift was determined by two-dimensional shift correlation (^1H – ^1H - and ^{13}C – ^1H -COSY) spectra.

All solvents and reagents were dried and purified according to standard methods. Bis(2,2'-biphenylene)tellurane **1** was prepared according to Ref. [10].

3.2. Bis(2,2'-biphenylene)tellurane Te-oxide dimer (2)

Ozone was bubbled through a solution of **1** (950 mg, 2.2 mmol) in CH_2Cl_2 (60 ml) at -78°C until the solution became blue. It was then warmed to room temperature. After removal of the solvent, the residue was recrystallized from 2:1 dry THF:Et₂O under argon at 0°C to give pale yellow crystals **2** (266 mg, 27%). M.p. $272\text{--}275^\circ\text{C}$ (decomp.). ¹H NMR (400 MHz, CDCl_3 , room temperature): δ 6.58 (d, $J = 7.5$ Hz, 2H, 3'-ArH), 6.73 (t, $J = 7.5$ Hz, 2H, 4-ArH), 6.83 (t, $J = 7.5$ Hz, 2H, 4'-ArH), 7.18 (t, $J = 7.5$ Hz, 2H, 5'-ArH), 7.28 (t, $J = 7.5$ Hz, 2H, 5-ArH), 7.45 (d, $J = 7.5$ Hz, 2H, 6'-ArH), 7.82 (d, $J = 7.5$ Hz, 2H, 6-ArH), 7.92 (d, $J = 7.5$ Hz, 2H, 3'-ArH). ¹³C NMR (100 MHz, CDCl_3 , room temperature): δ 121.9, 122.1, 127.2, 128.6, 128.8, 130.0, 130.9, 133.5, 134.5, 135.8, 140.0, 140.1. ¹²⁵Te NMR (126 MHz, CDCl_3 , room temperature): δ 593.2. IR (KBr, cm^{-1}): $\nu(\text{O-H})$ 3402 b. FABMS (m/z) 901 ($[\text{M} + \text{H}]^+$), 451 ($[\text{M}/2 + \text{H}]^+$) (matrix 2-nitrophenyl *n*-octyl ether). Anal. Found: C, 64.21; H, 4.14. $\text{C}_{48}\text{H}_{32}\text{O}_2\text{Te}_2$. Calc.: C, 64.35; H, 3.60%.

3.3. X-ray crystallographic analysis

Diffraction data were measured with an ω - 2θ scan technique at 296 K on an Enraf-Nonius CAD4-FR diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). The cell constants were determined and refined using 25 reflections ($10.00^\circ < 2\theta < 21.00^\circ$) obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data

Table 1
Crystallographic data and refinement details for compound **2**

Formula	$\text{C}_{48}\text{H}_{32}\text{O}_2\text{Te}_2 \cdot 2.33(\text{H}_2\text{O})$
Formula wt.	937.95
Crystal size (mm^3)	$0.20 \times 0.30 \times 0.70$
Crystal system	monoclinic
Space group	$P2_1/n$
a (\AA)	11.454(1)
b (\AA)	15.032(1)
c (\AA)	24.152(1)
β (deg)	96.87(1)
V (\AA^3)	4128.6(4)
D_{calc} (g cm^{-3})	1.509
$F(000)$	1853.20
Z	4
μ (cm^{-1})	14.57
Transmission coefficients	0.820–1.000
Data collected	$+h, -k, \pm l$
No. of data	7963
$2\theta_{\text{max}}$ (deg)	50.0
No. of unique data ($I > 3.0\sigma(I)$)	3962
R	0.037
R_w	0.045
Residual density (e \AA^{-3})	0.76 (1.12 \AA from Te(2))

Table 2

Fractional atomic coordinates with e.s.d.s for the non-hydrogen atoms of **2**

Atom	x	y	z
Te(1)	0.45143(5)	0.21052(5)	0.64321(2)
Te(2)	0.19985(5)	0.28951(5)	0.64579(2)
O(1)	0.2954(5)	0.1794(4)	0.6678(2)
O(2)	0.3569(5)	0.3207(4)	0.6233(3)
C(1)	0.5905(8)	0.2544(6)	0.5975(4)
C(2)	0.6785(9)	0.3124(8)	0.6168(5)
C(3)	0.762(1)	0.3379(9)	0.5818(7)
C(4)	0.755(1)	0.304(1)	0.5293(7)
C(5)	0.665(1)	0.2468(9)	0.5097(5)
C(6)	0.5804(8)	0.2215(7)	0.5443(4)
C(7)	0.4805(9)	0.1595(7)	0.5270(4)
C(8)	0.458(1)	0.1175(9)	0.4741(4)
C(9)	0.366(1)	0.0604(9)	0.4631(5)
C(10)	0.292(1)	0.0419(7)	0.5038(5)
C(11)	0.3111(9)	0.0825(6)	0.5555(4)
C(12)	0.4052(8)	0.1422(6)	0.5668(4)
C(13)	0.5267(7)	0.2707(7)	0.7194(4)
C(14)	0.5231(9)	0.3600(8)	0.7319(5)
C(15)	0.585(1)	0.3904(9)	0.7816(6)
C(16)	0.648(1)	0.331(1)	0.8158(6)
C(17)	0.653(1)	0.242(1)	0.8042(5)
C(18)	0.5917(7)	0.2108(8)	0.7549(4)
C(19)	0.5897(8)	0.1158(8)	0.7376(4)
C(20)	0.640(1)	0.048(1)	0.7701(5)
C(21)	0.634(1)	-0.038(1)	0.7518(6)
C(22)	0.573(1)	-0.0592(8)	0.7000(6)
C(23)	0.5205(8)	0.0102(7)	0.6653(4)
C(24)	0.5302(8)	0.0965(6)	0.6857(4)
C(25)	0.1400(9)	0.4252(6)	0.6341(5)
C(26)	0.084(1)	0.4591(8)	0.5846(5)
C(27)	0.051(1)	0.551(1)	0.5852(7)
C(28)	0.071(1)	0.5990(9)	0.6344(8)
C(29)	0.125(1)	0.5618(8)	0.6806(6)
C(30)	0.1607(9)	0.4745(7)	0.6818(5)
C(31)	0.2152(8)	0.4295(7)	0.7326(5)
C(32)	0.245(1)	0.4699(9)	0.7853(7)
C(33)	0.283(1)	0.419(1)	0.8308(6)
C(34)	0.297(1)	0.330(1)	0.8271(5)
C(35)	0.2752(9)	0.2905(8)	0.7752(4)
C(36)	0.2364(8)	0.3385(6)	0.7288(4)
C(37)	0.1439(8)	0.2501(6)	0.5623(4)
C(38)	0.1936(8)	0.2731(7)	0.5158(4)
C(39)	0.149(1)	0.2449(9)	0.4635(4)
C(40)	0.051(1)	0.1907(1)	0.4595(5)
C(41)	-0.003(1)	0.1661(9)	0.5054(6)
C(42)	0.0425(8)	0.1961(7)	0.5582(4)
C(43)	-0.0107(8)	0.1796(7)	0.5102(4)
C(44)	-0.1094(8)	0.1270(8)	0.5135(5)
C(45)	-0.1562(9)	0.1188(8)	0.5622(6)
C(46)	-0.106(1)	0.1613(8)	0.7093(5)
C(47)	-0.0047(8)	0.2109(7)	0.7077(4)
C(48)	0.0412(7)	0.2191(7)	0.6589(4)

are listed in Table 1. The data were corrected for absorption, a linear decomposition (5.8%), Lorentz and polarization effects. The structure was solved by direct methods and refined by a full-matrix least-squares method based on F [12]. The crystal lattice consists of

Table 3
Selected bond distances (Å) and angles (deg) with e.s.d.s in parentheses for **2**

Te(1)–O(1)	2.005(6)	Te(1)–O(2)	2.006(6)	Te(1)–C(1)	2.147(9)
Te(1)–C(12)	2.122(9)	Te(1)–C(13)	2.138(9)	Te(1)–C(24)	2.141(9)
Te(2)–O(1)	2.019(5)	Te(2)–O(2)	1.997(6)	Te(2)–C(25)	2.159(10)
Te(2)–C(36)	2.130(10)	Te(2)–C(37)	2.125(10)	Te(2)–C(48)	2.159(9)
Te(1)···Te(2)	3.1243(8)				
O(1)–Te(1)–O(2)	77.8(2)	O(1)–Te(1)–C(1)	165.1(3)		
O(1)–Te(1)–C(12)	90.3(3)	O(1)–Te(1)–C(13)	97.2(3)		
O(1)–Te(1)–C(24)	90.6(3)	O(2)–Te(1)–C(1)	92.0(3)		
O(2)–Te(1)–C(12)	96.9(3)	O(2)–Te(1)–C(13)	90.4(3)		
O(2)–Te(1)–C(24)	163.9(3)	C(1)–Te(1)–C(12)	79.9(4)		
C(1)–Te(1)–C(13)	93.7(4)	C(1)–Te(1)–C(24)	101.3(3)		
C(12)–Te(1)–C(13)	170.4(3)	C(12)–Te(1)–C(24)	94.4(4)		
C(13)–Te(1)–C(24)	79.8(4)	O(1)–Te(2)–O(2)	77.7(2)		
O(1)–Te(2)–C(25)	164.1(3)	O(1)–Te(2)–C(36)	89.8(3)		
O(1)–Te(2)–C(37)	96.5(3)	O(1)–Te(2)–C(48)	89.9(3)		
O(2)–Te(2)–C(25)	91.4(3)	O(2)–Te(2)–C(36)	95.3(3)		
O(2)–Te(2)–C(37)	89.2(3)	O(2)–Te(2)–C(48)	163.1(3)		
C(25)–Te(2)–C(36)	79.7(4)	C(25)–Te(2)–C(37)	94.8(4)		
C(25)–Te(2)–C(48)	102.9(4)	C(36)–Te(2)–C(37)	172.9(4)		
C(36)–Te(2)–C(48)	96.1(4)	C(37)–Te(2)–C(48)	80.7(4)		
Te(1)–O(1)–Te(2)	101.9(2)	Te(1)–O(2)–Te(2)	102.6(3)		

the Te-oxide dimers and 2.33 water molecules (per dimer) disordered over six sites. In the final refinement all non-hydrogen and non-disordered atoms were modeled anisotropically, the rest isotropically, and all hydrogen atom attached carbons were included at calculated positions (C–H = 0.97 Å) but not refined. The refinement using 3962 unique reflections ($I > 3.0\sigma(I)$) and 493 variable parameters converged with the unweighted and weighted agreement factors equal to $R = (\sum ||F_o| - |F_c||) / (\sum |F_o|) = 0.037$; $R_w = [\sum \omega (|F_o| - |F_c|)^2] / (\sum \omega F_o^2) = 0.045$ where the weighting scheme was based on counting statistics. The non-hydrogen atom fractional coordinates of the tellurium oxide dimer **2** are given in Table 2. Selected bond lengths and angles are listed in Table 3 and the numbering scheme employed is illustrated with the ORTEP [13] plot (50% probability ellipsoids) in Fig. 3. During all calculations the neutral atom scattering factors [14] were corrected for f' and f'' [15] using the teXsan crystallographic software package from Molecular Structure Corporation [16]. Additional crystallographic details and tables of crystal data, positional parameters, thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

4. Supplementary material available

Detailed crystallographic data, positional and thermal parameters, and bond distances and angles have been

deposited (37 pages). The procedure for ordering information is given on any current masthead page.

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