

Synthesis, spectral and structural characterisation of ditelluroxanes: μ -oxo-bis[nitrato-; 2,4,6-trinitrophenolato-dialkyl tellurium (IV)]

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Received 15 November 2006; received in revised form 18 February 2007; accepted 20 February 2007

Available online 24 February 2007

Abstract

The synthesis of ditelluroxanes: μ -oxo-bis[nitrato dimethyl tellurium (IV)] [(CH₃)₂TeNO₃]₂O (**1**), μ -oxo-bis[(2,4,6-trinitro)phenolato dimethyl tellurium (IV)] [(CH₃)₂TeOC₆H₂(NO₂)₃]₂O (**2**) and μ -oxo-bis[1-(2,4,6-trinitro)phenolato-1,1,2,3,4,5-hexahydro-tellurophene] [C₄H₈TeOC₆H₂(NO₂)₃]₂O (**3**) was achieved. **1** was synthesised by the reaction of (CH₃)₂TeI₂ with fuming HNO₃ while **2** and **3** were synthesised by the reactions of R₂Te(OH)₂ [R₂ = (CH₃)₂, (C₄H₈)] (*in situ*) with 2,4,6-trinitrophenol [2,4,6-(NO₂)₃C₆H₂OH] (picric acid). **1–3** have been investigated through UV/Vis; FT-IR, (¹H, ¹³C) NMR spectroscopy and single crystal X-ray diffraction studies. In **1–3** the immediate coordination geometry about the central tellurium atom can be described as pseudo trigonal bipyramidal and the stereochemically active electron lone pair occupying equatorial position. The supramolecular self-organisations of these tetraorgano ditelluroxanes (**1–3**) are explained through cooperative participation of Te···O secondary bonds, C–H···O hydrogen bonds and π -stacking of the organic substituents.

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Keywords: Ditelluroxanes; Te···O secondary bonds; C–H···O hydrogen bonds; Supramolecular associations

1. Introduction

In recent years considerable efforts have been directed to gaining an understanding of the fundamental aspects of tellurite glass chemistry because of its potential applications in non-linear optics and as ionic conductive materials [1]. Their remarkable properties arise from the free electron pair in their motif built of TeO₃ or TeO₄ units. The development of telluroxane chemistry of tellurium (IV) as model compounds might be a fruitful approach by analogy to the well-developed chemistry of oligomeric siloxanes whose importance as molecular precursors and model compounds for zeolitic material is well known [2]. Main group metalloxanes have found their applications as catalysts

and oligomeric stannoxanes are reported to be efficient homogeneous catalysts in acylation of alcohols [3]. Oligomeric titanoxanes have attracted considerable attention with regard to material science [4]. Thus in recent years efforts have been directed to develop easier and new synthetic routes to oligomeric telluroxanes [5,6]. Furukawa et al. [5] synthesized and characterized oligotelluroxanes ($n = 1–4$) from the ditelluroxane and telluroxides. They [6] also synthesized oligotelluroxanes by the oxidation of diaryltelluride with NOBF₄ or (CF₃SO₂)₂O/O₂. Ditelluroxanes have also been synthesized by the thermal dehydration of diaryl tellurium hydroxide halides and related compounds Ar₂Te(OH)X (X = Cl, Br, NO₃, SCN etc.) [7]. Domasevitch et al. [8] reported the synthesis of telluroxanes ($n = 1$) (X = nitrosocarbonyl cyanomethanide) by the dehydration procedure. The condensation product of organotellurium trihydroxides leads to the formation of

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'telluroxane' containing $\text{Te}_{12}\text{O}_{16}$ ring [9]. We reported polymeric telluroxane $[(\text{C}_4\text{H}_8\text{TeNO}_3)_2\text{O}]_n$ containing $-\text{Te}-\text{O}-\text{Te}-$ bonds [10]. In this paper we describe the easy synthesis and structures of ditelluroxanes and their supramolecular associations containing picrate groups. It might be worthwhile to mention that metal picrates possess a number of applications as (i) antioxidants (ii) surfactants, catalysts in industry (iii) reagents in organic synthesis and precursors for super conducting ceramic films [11].

2. Experimental

α - $(\text{CH}_3)_2\text{TeI}_2$ [12], $\text{C}_4\text{H}_8\text{TeI}_2$ [13] were prepared by the literature methods and $(\text{CH}_3)_2\text{Te}(\text{OH})_2$ and $\text{C}_4\text{H}_8\text{Te}(\text{OH})_2$ were generated (*in situ*) by the reactions of $(\text{CH}_3)_2\text{TeI}_2$ and $\text{C}_4\text{H}_8\text{TeI}_2$ with freshly prepared AgOH in deionised water. Te metal, iodomethane, 1,4-diiodobutane and 2,4,6-trinitrophenol (Aldrich) were commercially obtained and used as received. The organic solvents were dried by usual methods and distilled water was carefully deionised before use. Elemental analysis for C and H were carried on an Elemental Analyser Heraeus Carlo Erba 1108, Tellurium content was determined in the laboratory. UV/Vis spectra of 10^{-4} M solutions of **1–3** in methanol were recorded in the range 190–500 nm on UV-1700 (E 23) OCE spectrophotometer. Solid state IR spectra were recorded with the sample in KBr disc and solution IR spectra were recorded with the samples in CHCl_3 using a Shimadzu 8210 PCFTIR spectrophotometer in the frequency range 4000–400 cm^{-1} . Solution ^1H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded in CDCl_3 on Varian DRX 300 NMR spectrometer.

2.1. Preparation of the compounds

2.1.1. $(\text{CH}_3)_2\text{Te}(\text{OH})_2$ and $\text{C}_4\text{H}_8\text{Te}(\text{OH})_2$

To $(\text{CH}_3)_2\text{TeI}_2$ (2.0 g, 4.859 mmol) was added freshly prepared silver hydroxide (1.215 g, 9.720 mmol) in a mortar and ground with a little amount of deionised water to make a thin paste. It was ground for 45 min more after which the red crystals of dimethyl tellurium diiodide disappeared. The paste was filtered with hot water and the filtrate was taken as $(\text{CH}_3)_2\text{Te}(\text{OH})_2$ (*in situ*). Similarly $\text{C}_4\text{H}_8\text{Te}(\text{OH})_2$ (*in situ*) was obtained by the reaction of $\text{C}_4\text{H}_8\text{TeI}_2$ (2.0 g, 4.570 mmol) and freshly prepared silver hydroxide (1.143 g, 9.144 mmol) in deionised water.

2.1.2. $[(\text{CH}_3)_2\text{Te}(\text{NO}_3)]_2\text{O}$ (**1**)

$(\text{CH}_3)_2\text{TeI}_2$ (3 g, 7.29 mmol) was taken in a two neck flask fitted with a condenser and a dropping funnel. To this was added fuming nitric acid ($d = 1.574$ g/ml) (0.6 ml, 14.58 mmol) drop wise through dropping funnel. After complete addition, the reaction mixture was refluxed for 2 h. The white solid mass, deposited at the bottom of the flask, was cooled and dissolved in minimum quantity of distilled water. It was filtered and the filtrate was reduced under vacuum and poured in a petri dish. White crystals

of $[(\text{CH}_3)_2\text{Te}(\text{NO}_3)]_2\text{O}$ (**1**) suitable for X-ray diffraction were obtained after five days. Complex **1** yield: 0.6 g, (18%), m.p. 132 °C. Anal. Calc. for $\text{C}_4\text{H}_{12}\text{N}_2\text{O}_7\text{Te}_2$: C, 10.54; H, 2.63; Te, 56.06. Found: C, 10.52; H, 2.62; Te, 56.03%. ^1H NMR δ : 2.38 (s, 12H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR δ : 29.21 (CH_3). UV/Vis: 225 nm ($\epsilon = 3612$ $\text{M}^{-1}\text{cm}^{-1}$). FT-IR (KBr, cm^{-1}): 1384 s ($\nu_{\text{as}} \text{NO}_2$), 1240 m ($\nu_{\text{s}} \text{NO}_2$), 1026 s (NO str.) 819 m (NO_2), 543 m, 445 m ($\text{Te}-\text{O}-\text{Te}$); solution IR (CHCl_3) 1367 s ($\nu_{\text{as}} \text{NO}_2$), 1218 m ($\nu_{\text{s}} \text{NO}_2$), 1026 m (NO str.), 549 m, 463 m ($\text{Te}-\text{O}-\text{Te}$) [7c].

2.1.3. $[(\text{CH}_3)_2\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**2**)

To $(\text{CH}_3)_2\text{Te}(\text{OH})_2$ (0.9310 g, 4.86 mmol) (*in situ*), was added hot solution of 2,4,6-trinitrophenol (picric acid) (1.113 g, 4.86 mmol) dissolved in distilled water. The resultant reaction mixture was transparent yellow. It was reduced and kept for 24 h, when yellow needle shaped crystals of $[(\text{CH}_3)_2\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**2**) suitable for X-ray diffraction appeared. Complex **2** yield: 0.40 g, (10.5%), m.p. 190 °C. Anal. Calc. for $\text{C}_{16}\text{H}_{16}\text{N}_6\text{O}_{15}\text{Te}_2$: C, 24.39; H, 2.03; Te, 32.41. Found: C, 24.38; H, 2.00; Te, 32.39%. ^1H NMR δ : 2.35 (s, 12H, CH_3), 8.57 (s, 4H, C_6H_2). ^{13}C $\{^1\text{H}\}$ NMR δ : 39.2 (CH_3); 125.3, 141.7, 160.8 (C_6H_2). UV/Vis: 350 nm ($\epsilon = 24284$ $\text{M}^{-1}\text{cm}^{-1}$), 207 nm ($\epsilon = 40868$ $\text{M}^{-1}\text{cm}^{-1}$). FT-IR (KBr, cm^{-1}): 1487 vs ($\nu_{\text{as}} \text{NO}_2$), 1338 s ($\nu_{\text{s}} \text{NO}_2$), 1077 s (NO str.), 780 m (NO_2), 538 m ($\text{Te}-\text{O}-\text{Te}$); solution IR (CHCl_3) 1509 vs ($\nu_{\text{as}} \text{NO}_2$), 1334 m ($\nu_{\text{s}} \text{NO}_2$), 1091 m (NO str.), 773 (NO_2), 508 m ($\text{Te}-\text{O}-\text{Te}$) [7c].

2.1.4. $[\text{C}_4\text{H}_8\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**3**)

It was prepared in similar manner as described above from $\text{C}_4\text{H}_8\text{Te}(\text{OH})_2$ (0.995 g, 4.57 mmol) (*in situ*) and 2,4,6-tri nitrophenol (picric acid) (1.047 g, 4.57 mmol). Yellow needle shaped crystals of $[\text{C}_4\text{H}_8\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**3**) were obtained after 24 h. Complex **3** yield 1.10 g, (28.7%), m.p. 215 °C. Anal. Calc. for $\text{C}_{20}\text{H}_{20}\text{N}_6\text{O}_{15}\text{Te}_2$: C, 28.59; H, 2.38; Te, 30.41. Found: C, 28.56; H, 2.34; Te, 30.39%. ^1H NMR δ : 2.5 (t, 8H, CCH_2), 2.94 (s, 8H, TeCH_2), 8.78 (s, 4H, C_6H_2). ^{13}C $\{^1\text{H}\}$ NMR δ : 31.1, 39.6 (CCH_2), 45.8 (TeCH_2), 125.5, 141.0, 158.7 (C_6H_2): UV/Vis: 351 nm ($\epsilon = 27928$ $\text{M}^{-1}\text{cm}^{-1}$), 208 nm ($\epsilon = 51744$ $\text{M}^{-1}\text{cm}^{-1}$). FT-IR (KBr, cm^{-1}): 1486 vs ($\nu_{\text{as}} \text{NO}_2$), 1332 s ($\nu_{\text{s}} \text{NO}_2$), 1077 s (NO str.), 790 m (NO_2), 541 m ($\text{Te}-\text{O}-\text{Te}$); solution IR (CHCl_3) 1462 vs ($\nu_{\text{as}} \text{NO}_2$), 1363 s ($\nu_{\text{s}} \text{NO}_2$), 1073 m (NO str.), 794 w (NO_2), 545 m ($\text{Te}-\text{O}-\text{Te}$) [7c].

2.2. X-ray measurements

A summary of the crystal data and refinement parameters for $[(\text{CH}_3)_2\text{TeNO}_3]_2\text{O}$ (**1**), $[(\text{CH}_3)_2\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**2**) and $[\text{C}_4\text{H}_8\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**3**) is given in Table 1. The crystals were mounted on a Bruker SMART CCD diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cells were determined from 25 randomly selected reflections using the automatic search index and least-squares refinement. The structure of **1** was

Table 1
Crystal data and refinement details for complexes 1–3

	1	2	3
Empirical formula	C ₄ H ₁₂ N ₂ O ₇ Te ₂	C ₁₆ H ₁₆ N ₆ O ₁₅ Te ₂	C ₂₀ H ₂₀ N ₆ O ₁₅ Te ₂
Formula weight	455.36	787.55	839.62
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	C2/c	P2(1)/c	P4c2
Temperature (K)	295(2)	293(2)	93(2)
a (Å)	12.9322 (13)	7.7840(7)	14.5837(4)
b (Å)	10.4524(10)	43.781(3)	14.5837(4)
c (Å)	10.5185(10)	8.0936(8)	16.6575(7)
α (°)	90	90	90
β (°)	108.259(2)	117.061(7)	90
γ (°)	90	90	90
V (Å ³)	1350.2(2)	2456.3(4)	3542.8(2)
Z	4	4	4
Radiation λ (Å)	0.71073	0.71073	0.71073
ρ (calcd.) (g cm ⁻³)	2.240	2.130	1.574
μ (Mo Kα) (mm ⁻¹)	4.337	2.462	1.713
θ _{max} (°)	28.3	27.5	29.18
Number of data	1592	5408	4462
Number of parameters	72	363	225
Final R indices [I > 2σ(I)]	R ₁ = 0.0229, wR ₂ = 0.0537	R ₁ = 0.0327, wR ₂ = 0.0708	R ₁ = 0.0429, wR ₂ = 0.1183
R indices (all data)	R ₁ = 0.0272, wR ₂ = 0.0555	R ₁ = 0.0448, wR ₂ = 0.0762	R ₁ = 0.0515, wR ₂ = 0.1233

solved in space group C2/c, **2** in space group P2(1)/c, and **3** in space group P4c2. The data were corrected for Lorentz, polarization and absorption effects. The data were monitored by measuring three standard reflections at every 97 reflections. The structures were solved by the routine heavy atom method SHELXS-97 [14] and Fourier methods and refined by full-matrix least-squares using the SHELXL-97 program [14] with the non-hydrogen atoms anisotropic and hydrogen atoms having fixed isotropic thermal parameters of 0.08 Å². Figure related to π–π interaction was created using DIAMOND [15].

3. Results and discussion

3.1. Synthetic and spectroscopic aspects

The reaction of dimethyl tellurium diiodide with fuming nitric acid resulting in the formation of [(CH₃)₂TeNO₃]₂O (**1**) indicates high stability of Te–C bond in acidic medium. The reactions of (CH₃)₂Te(OH)₂ and C₄H₈Te(OH)₂ (*in situ*) with 2,4,6-trinitrophenol yield [(CH₃)₂TeOC₆H₂(NO₂)₃]₂O (**2**) and [C₄H₈TeOC₆H₂(NO₂)₃]₂O (**3**). The ditelluroxanes (**1–3**) are thermally stable and unaffected by atmospheric moisture and oxygen. Spectroscopic data of **1–3** are given in experimental section. In UV/Vis spectra of **1–3**, the high ε values of **2** (ε = 40 868 M⁻¹ cm⁻¹) and **3** (ε = 51 744 M⁻¹ cm⁻¹) are attributed to strong (π, π*) benzoid transitions in accordance with the earlier observations [16,17]. In **2** the absorptions at λ_{max} 350 nm; ε = 24 284 M⁻¹ cm⁻¹ and in **3** the absorptions at λ_{max} 351 nm; ε = 27 928 M⁻¹ cm⁻¹ are apparently because of the transfer of electron density from O(NO₂) of 2,4,6-trinitrophenolate group into the d-orbitals of Te termed as charge transfer transitions [18–20]. When IR (solid & solu-

tion) data is clubbed with X-ray structures of **1–3** in term of supramolecular associations, the shift of 20 ± 4 cm⁻¹ in ν_{as} NO₂ stretching in **1–3** may be probably due to the loss of some Te···O secondary bonds in solution. The solution (¹H, ¹³C) NMR data exhibit the characteristic signals at their expected positions with expected multiplicity.

3.1.1. Description of the structure of [(CH₃)₂TeNO₃]₂O (**1**)

The structure of **1** contains a monomeric unit of μ-oxo-bis[nitrato dimethyl tellurium (IV)] (Fig. 1). The monomeric unit is centrosymmetric with angular Te–O–Te [124.44(2)°]. The Te–O bond lengths within this unit are equal [1.9624(1) Å] (Table 2). The Te (IV) atoms of the monomeric unit are bonded to two –CH₃ groups and two oxygen atoms (one bridging oxygen and the other oxygen of NO₃ group). The coordination geometry formed by the four closest atoms C(1), C(2), O(1) and bridging oxygen(O) is distorted trigonal bipyramidal with the oxygen atom O(1) (NO₃) and bridging oxygen (O) in the apical positions [Te–O(1) = 2.464(2) Å, Te–O = 1.9624(1) Å] and the two –CH₃ groups in the equatorial plane. The fifth coordination position in the equatorial plane is apparently

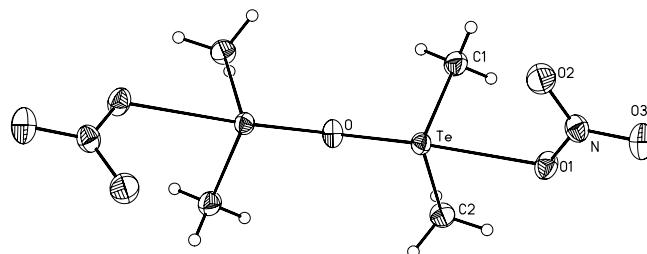


Fig. 1. Crystal structure of [(CH₃)₂TeNO₃]₂O (**1**).

Table 2
Bond lengths (Å) and angles (°) for **1**

Bond lengths	
Te–O	1.9624(1)
Te–C(1)	2.090(3)
Te–C(2)	2.093(3)
O(1)–N	1.269(3)
O(2)–N	1.227(3)
O(3)–N	1.216(3)
Te–O(1)	2.464(2)
Te–O(2)#1	3.044(2)
Te–O(2)#2	3.224(3)
Te–O(3)#2	3.397(3)
Bond angles	
O–Te–O(1)	165.90(9)
Te–O–Te#3	124.44(2)
O(3)–N–O(2)	121.9(3)
O(3)–N–O(1)	119.8(3)
O(2)–N–O(1)	118.3(3)

occupied by a stereochemically active electron lone pair in accordance with the valence shell electron pair repulsion (VSEPR) model. This is also indicated by the O–Te–O(1) angle of 165.9(9)° which deviates considerably from linearity with both oxygen atom atoms pushed away from the equatorial tellurium lone pair. The structure of –NO₃ group is planar [sum of the angles at nitrogen is 360.0(3)°] and the O(1)–N = 1.269(3) Å, O(2)–N = 1.227(3) Å, O(3)–N = 1.216(3) Å bond distances and O(3)–N–O(2) = 121.9(3)°, O(3)–N–O(1) = 119.8(3)°, O(2)–N–O(1) = 118.3(3)° angles are comparable with the NO₃ group present in μ -oxo-bis(1-nitrato-1,1,2,3,4,5-hexahydro-tellurophene) [10], phenoxo tellurine dinitrate [21] and bis phenoxo telluronium dinitrate [22]. The nitrate groups are asymmetrically tridentate with primary Te–O(1) (NO₂) distance (2.464(2) Å) and two secondary interactions Te–O(2)#2 = 3.224(3) Å, Te–O(3)#2 = 3.397(3) Å. Both the free oxygen atoms of the nitrate groups of a molecule form Te···O secondary bonds with both Te atoms of another molecule [Te···O(2)#2 = 3.224(3) Å, Te···O(3)#2 = 3.397(3) Å]. Second nitrate group of this molecule is connected in the same fashion to the another molecule. The Te···O distances are longer than the sum of covalent (Te–O) radii (2.03 Å) [23] and

shorter than the sum of van der Waals radii (3.60 Å) [24]. The intermolecular Te···O secondary bonds join the molecules to form a trimer (Fig. 2).

Apart from Te···O secondary bonds, C(sp³)–H···O hydrogen bonds are present where CH is from one of the methyl groups attached to Te and that of O from the O(NO₂) group of another molecule. C–H···O hydrogen bonds [C(1)–O(1)#4 = 3.508(4) Å, H(1B)···O(1)#4 = 2.56 Å and \angle C(1)–H(1B)···O(1)#4 = 168.8°] parameters are in close agreement with the values of C–H···O hydrogen bonds in organotellurium complexes (Table 5) [25–27].

In the unit cell, the molecules of [(CH₃)₂TeNO₃]₂O are interlinked through Te···O [Te···O(2)#1 = 3.044(2) Å] secondary bonds and C–H···O hydrogen bonds leading to the formation of hexameric supramolecular association (Fig. 3) in which hepta- and hexa coordinated tellurium are present. The cooperative participation of Te···O secondary bonds and C–H···O hydrogen bonds has been discussed by us [25–27] recently and we believe C–H···O hydrogen bonds give strength to the supramolecular assembly.

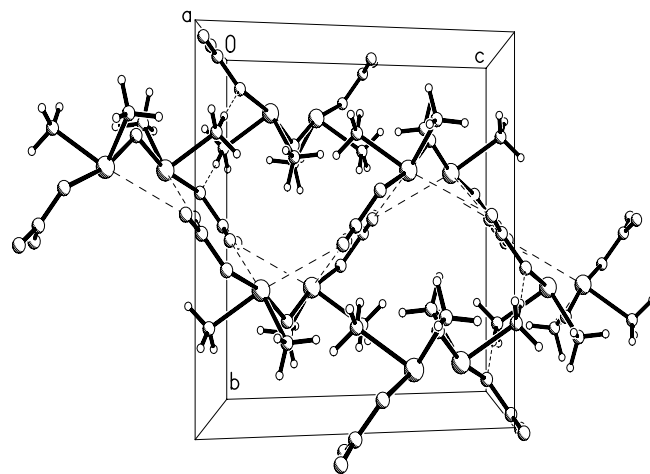


Fig. 3. Hexameric supramolecular assembly of **1** built up by connecting the molecules through Te···O secondary bonds and C(sp³)–H···O hydrogen bonds.

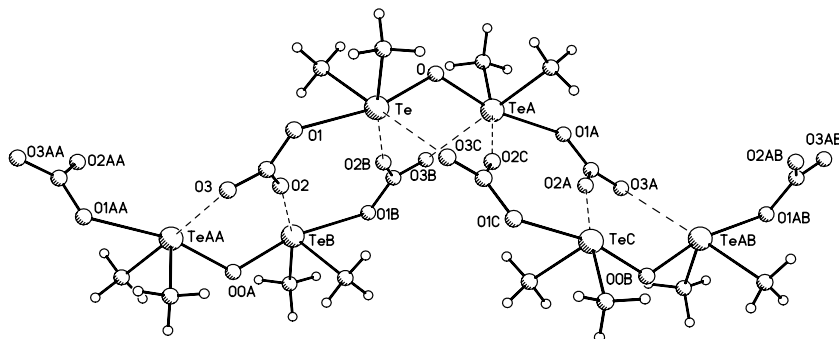


Fig. 2. Trimeric supramolecular assembly of **1** built up through Intermolecular Te···O secondary bonds.

3.1.2. Description of the structure of $[(\text{CH}_3)_2\text{TeO}-\text{C}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**2**)

The structure of **2** contains two asymmetric units of μ -oxo-bis[(2,4,6-trinitro)phenolato(picrato) dimethyl tellurium (IV)] which is centrosymmetric with an angular $[\text{Te}(1)-\text{O}(1)-\text{Te}(2) = \text{Te}(1)-\text{O}(1')-\text{Te}(2) = 134.0(3)^\circ]$ (Fig. 4). The Te–O bond lengths within a unit are $[\text{Te}(1)-\text{O}(1) = \text{Te}(1)-\text{O}(1') = 1.968(4) \text{ \AA}]$ and $[\text{Te}(2)-\text{O}(1) = \text{Te}(2)-\text{O}(1') = 1.970(4) \text{ \AA}]$ respectively (Table 3). The four closest atoms C(11), C(12), O(1A) and bridging oxygen O(1) or O(1') provide a distorted trigonal bipyramidal primary coordination environment at Te(1) atom with O(1A) (phenolic group of 2,4,6-trinitrophenol) and bridging oxygen O(1) or O(1') occupying apical positions and the two methyl carbon atoms in the equatorial plane. The fifth coordination position in the equatorial plane is apparently occupied by stereochemically active electron lone pair.

The O(1)–Te(1)–O(1A) angle of $177.2(2)^\circ$ or O(1')–Te(1)–O(1A) angle of $165.8(8)^\circ$ deviates considerably from linearity with both oxygen atoms pushed away from the

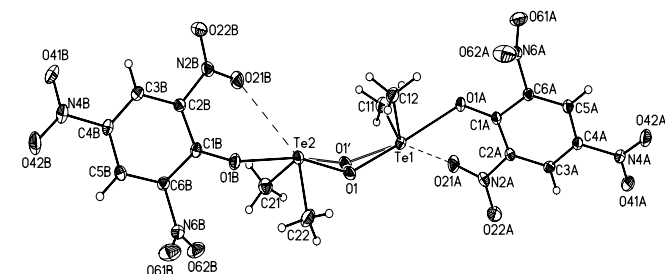


Fig. 4. Crystal structure of $[(\text{CH}_3)_2\text{TeOC}_6\text{H}_2(\text{NO}_2)_3]_2\text{O}$ (**2**).

equatorial electron lone pair. The pseudotrigonal bipyramidal arrangement around tellurium and fairly large deviation of $\angle\text{O}-\text{Te}-\text{O}$ from linearity is in agreement with the earlier reports [7d,28,29] and may be attributed to the presence of intermolecular – [10,20,25,28,30–34] and intramolecular – [35,36] $\text{Te}\cdots\text{O}$ secondary bonds. One of the free oxygen atoms of the *p*- NO_2 groups of 2,4,6-trinitrophenol of a molecule forms $\text{Te}\cdots\text{O}$ secondary bonds with the Te atom of another molecule $[\text{Te}(1)\cdots\text{O}(42A)\#1 = 3.352(3) \text{ \AA}, \text{Te}(2)\cdots\text{O}(41B)\#2 = 3.356(4) \text{ \AA}]$ (Table 3). As discussed above these $\text{Te}\cdots\text{O}$ distances correspond to $\text{Te}\cdots\text{O}$ secondary bonds [23,24]. These intermolecular $\text{Te}\cdots\text{O}$ secondary bonds join the molecules to form trimer (Fig. 5). Apart from these intermolecular $\text{Te}\cdots\text{O}$ secondary bonds, intramolecular $\text{Te}\cdots\text{O}$ secondary bonds $[\text{Te}(1)-\text{O}(21A) = \text{Te}(2)-\text{O}(21B) = 3.078(4) \text{ \AA}]$ are also present. Considering the lone pair of electrons, intermolecular and intramolecular $\text{Te}\cdots\text{O}$ secondary bonds, tellurium atoms of **2** are hexa- and hepta-coordinated.

Apart from $\text{Te}\cdots\text{O}$ secondary bonds, $\text{C}(\text{sp}^3)-\text{H}\cdots\text{O}$ and $\text{C}(\text{sp}^2)-\text{H}\cdots\text{O}$ hydrogen bonds are present where hydrogen atom of one of the methyl group attached to Te and O

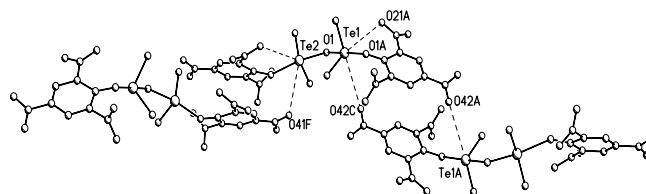


Fig. 5. Trimeric supramolecular assembly of **2** built up through Intra- and Intermolecular $\text{Te}\cdots\text{O}$ secondary bonds.

Table 3
Bond lengths (Å) and angles (°) for **2**

Bond lengths			
Te(1)–O(1)	1.968(4)	C(1B)–C(2B)	1.427(5)
Te(1)–O(1')	1.968(4)	C(1B)–C(6B)	1.436(5)
Te(1)–O(1A)	2.377(3)	C(1A)–O(1A)	1.283(4)
Te(2)–O(1B)	2.354(3)	C(1B)–O(1B)	1.261(5)
Te(1)–C(11)	2.083(5)	N(2A)–O(21A)	1.221(5)
Te(1)–C(12)	2.110(4)	N(2A)–O(22A)	1.222(5)
Te(2)–O(1)	1.970(4)	N(2B)–O(21B)	1.227(5)
Te(2)–O(1')	1.970(4)	N(2B)–O(22B)	1.225(5)
Te(2)–C(21)	2.096(5)	N(6A)–O(61A)	1.218(5)
Te(2)–C(22)	2.093(5)	N(6A)–O(62A)	1.197(5)
Te(1)–O(42A)#1	3.352(3)	N(6B)–O(61B)	1.204(5)
Te(2)–O(41B)#2	3.356(4)	N(6B)–O(62B)	1.213(5)
Te(1)–O(21A)	3.078(4)	N(4A)–O(41A)	1.214(4)
Te(2)–O(21B)	3.078(4)	N(4A)–O(42A)	1.216(5)
C(1A)–C(2A)	1.419(5)	N(4B)–O(41B)	1.230(5)
C(1A)–C(6A)	1.432(5)	N(4B)–O(42B)	1.222(5)
Bond angles			
Te(1)–O(1)–Te(2)	134.0(3)	O(21B)–N(2B)–O(22B)	123.9(4)
Te(1)–O(1')–Te(2)	134.0(3)	O(62A)–N(6A)–O(61A)	123.4(4)
O(1)–Te(1)–O(1A)	177.2(2)	O(61B)–N(6B)–O(62B)	123.4(4)
O(1')–Te(1)–O(1A)	165.8(8)	O(41A)–N(4A)–O(42A)	124.1(4)
O(21A)–N(2A)–O(22A)	123.3(4)	O(41B)–N(4B)–O(42B)	123.1(4)

from the O of (*p*-NO₂) group of another molecule forms C(sp³)-H···O hydrogen bonds [C(11)-O(41B)#3 = 3.298(5) Å, H(11A)···O(41B)#3 = 2.65 Å, ∠C(11)-H(11A)···O(41B)#3 = 125.1°] whereas the hydrogen atom of C-H of phenyl group is attached to O from the (*o*-NO₂) group forming C(sp²)-H···O hydrogen bonds [C(5B)-O(21B)#4 = 3.205(5) Å, H(4BA)···O(21B)#4 = 2.76 Å, and ∠C(5B)-H(4BA)···O(21B)#4 = 110.5°] (Table 5). These parameters of C-H···O hydrogen bonds are in close agreement with the values of C-H···O hydrogen bonds in organotellurium complexes [25–27].

In the unit cell, the molecules of [(CH₃)₂TeOC₆H₂(NO₂)₃]₂O are interlinked through Te···O[3.352(3) Å, 3.356(4) Å] secondary bonds and C-H···O hydrogen bonds and leads to the formation of tetrameric supramolecular association (Fig. 6) in which hexa- and hepta-coordinated tellurium are present [25–27].

The O of *o*-NO₂ groups of picrate form intramolecular Te···O secondary bonds whereas O of the para NO₂ groups of picrate forms intermolecular Te···O secondary bonds. The bond lengths and angles of 2,4,6-trinitrophenolate (picrate) group show characteristic values [C(1A)-C(2A) = 1.419(5) Å, C(1A)-C(6A) = 1.432(5) Å; C(1B)-C(2B) = 1.427(5) Å, C(1B)-C(6B) = 1.436(5) Å] which are longer and deviate from the regular aromatic values; the C(1A)-O(1A) value is 1.283(4) Å and C(1B)-O(1B) = 1.261(5) Å which are intermediate between the single and double bonds. These effects are due to the loss of hydroxyl proton at O(1A) or O(1A') [37]. The bond distances and bond angles of the *o*-NO₂ groups of 2,4,6-trinitrophenolate group are [N(2A)-O(21A) = 1.221(5) Å, N(2A)-O(22A) = 1.222(5) Å, ∠O(21A)-N(2A)-O(22A) = 123.3(4)°, N(2B)-O(21B) = 1.227(5) Å, N(2B)-O(22B) = 1.225(5) Å, ∠O(21B)-N(2B)-O(22B) = 123.9(4)°; N(6A)-O(61A) = 1.218(5) Å, N(6A)-O(62A) = 1.197(5) Å, ∠O(62A)-N(6A)-O(61A) = 123.4(4)°, N(6B)-O(61B) = 1.204(5) Å, N(6B)-O(62B) = 1.213(5) Å, ∠O(61B)-N(6B)-O(62B) = 123.4(4)° and bond distances and angles for *p*-NO₂ group are N(4A)-O(41A) = 1.214(4) Å, N(4A)-O(42A) = 1.216(5) Å, ∠O(41A)-

N(4A)-O(42A) = 124.1(4)°, N(4B)-O(41B) = 1.230(5) Å, N(4B)-O(42B) = 1.222(5) Å, ∠O(41B)-N(4B)-O(42B) = 123.1(4)° (Table 3).

3.1.3. Description of the structure of [C₄H₈TeOC₆H₂(NO₂)₃]₂O (3)

The structure of **3** is shown in Fig. 7. It consists of a monomeric unit of μ-oxo-bis[1-(2,4,6-trinitro)phenolato-1,1,2,3,4,5-hexahydro-tellurophene] which is centro symmetric with an angular Te-O-Te = 127.1(4)°. The Te-O bond lengths within this unit are [1.968(3) Å]. The expected planar 1,1,2,3,4,5-hexahydro-tellurophene rings flip over to the chair conformation through twist boat probably relieving some strain. This is apparently because of geometrical impossibility of a planar ring with ideal sp³ bond angle of 109.5° at the carbon atoms and unstrained C-Te-C bond angles in the usual 91–100° range [10,38–40] (Fig. 7) (Table 4). Each tellurium (IV) atom is bonded to two methylene carbon atoms of the C₄H₈ group and two oxygens (one bridging oxygen and the other oxygen of phenolic group of 2,4,6-trinitrophenol). The four closest atoms C(1A), C(4A), O(1P) and bridging oxygen (O) provide a distorted trigonal bipyramidal primary coordination

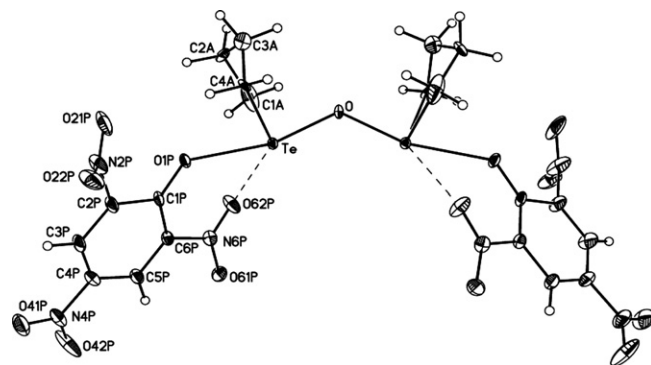


Fig. 7. Crystal structure of **3**.

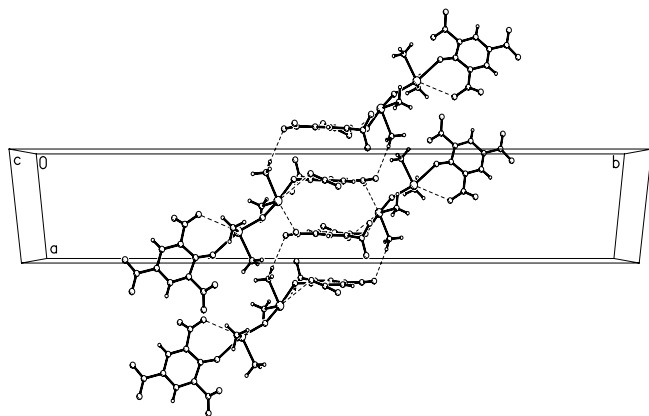


Fig. 6. Tetrameric supramolecular assembly of **2** built up by connecting the molecules through Intra- and Intermolecular Te···O secondary bonds and C-H···O hydrogen bonds.

Table 4
Bond lengths (Å) and angles (°) for **3**

Bond lengths			
Te-O	1.968(3)	Te-O(43P)#1	3.310(19)
Te-O(1P)	2.392(4)	Te-O(41P)#2	3.425(15)
Te-C(1A)	2.161(3)	C(1P)-C(6P)	1.396(9)
Te-C(4A)	2.148(15)	C(1P)-C(2P)	1.439(8)
Te-C(1B)	2.081(3)	C(1P)-O(1P)	1.269(8)
Te-C(4B)	2.041(2)	N(2P1)-O(21P)	1.246(14)
Te-O(62P)	3.059(5)	N(4P1)-O(42P)	1.247(15)
Te-O(44P)#1	3.22(2)	N(4P1)-O(41P)	1.264(17)
Te-O(42P)#1	3.229(17)	N(6P)-O(62P)	1.199(7)
Te-O(43P)#2	3.244(17)	N(6P)-O(61P)	1.244(7)
Bond angles			
O-Te-O(1P)	165.1(2)	C(1B)-C(2B)-C(3B)	107.0(2)
Te-O-Te#3	127.1(4)	C(2B)-C(3B)-C(4B)	114.2(14)
C(4A)-Te-C(1A)	82.4(5)	O(22P)-N(2P1)-O(21P)	127.2(17)
C(4B)-Te-C(1B)	87.8(7)	O(42P)-N(4P1)-O(41P)	122(2)
C(1A)-C(2A)-C(3A)	107.7(17)	O(62P)-N(6P)-O(61P)	122.6(6)
C(2A)-C(3A)-C(4A)	110.5(7)		

environment at each tellurium atom with O(1P) of 2,4,6-trinitrophenol and bridging oxygen (O) occupying apical positions and the two methylene carbon atoms of the C₄H₈ group in the equatorial plane. The fifth coordination position in the equatorial plane is apparently occupied by the stereochemically active electron lone pair.

The O–Te–O (1P) angle of 165.1(2)° deviates considerably from linearity with both oxygen atoms pushed away from the equatorial electron lone pair. The pseudotrigonal bipyramidal arrangement around tellurium and fairly large deviation of ∠O–Te–O from linearity [7d,28,29] may be attributed to the presence of intermolecular – [10,25,28,30–33] and intramolecular-[35,36] Te···O secondary bonds. The two free oxygen atoms of the nitro group of 2, 4, 6-trinitrophenols form intermolecular Te···O secondary bonds with both tellurium atoms of another molecule. One oxygen of –NO₂ group of 2,4,6-trinitrophenolate group forms intramolecular Te···O secondary bonds [Te···O (62P) = 3.059(5) Å]. The second oxygen of this group and the four oxygens of the other two nitro group of 2,4,6-trinitrophenolate group form intermolecular

Te···O secondary bonds [Te···O(42P)# 1 = 3.229(17) Å, Te···O (43P)#1 = 3.310(19) Å, Te···O(44P)#1 = 3.220(2) Å, Te···O(41P)#2 = 3.425(15) Å and Te···O(43P)#2 = 3.244(17) Å] (Table 4). Considering the lone pair of electrons, intermolecular- and intramolecular Te···O secondary bonds, tellurium atoms of **3** are hexa- and hepta coordinated.

In the unit cell, these intermolecular Te···O secondary bonds join the molecules to form a pentamer which, in turn, is connected to another pentamer through intermolecular C(sp³)–H···O hydrogen bonds leading to the formation of decameric supramolecular associations (Fig. 8). The C–H···O hydrogen bond related parameters are: C(1B)···O(61P)#4 = 3.42(6) Å, H(1BB)···O(61P)#4 = 2.54 Å, ∠C(1B)–H(1BB)···O(61P)#4 = 147.8° ; C(1B)···O(24P)#5 = 3.01(3) Å, H(1BA)···O(24P)#5 = 2.26 Å, ∠C(1B)–H(1BA)···O(24P)#5 = 131.0° (25–27) (Table 5).

The bond lengths and angles of 2,4,6-trinitrophenolate group in **3** are almost same as in **2** indicating same type of bonding to Te of C₄H₈Te through oxygen of the ligand 2,4,6-trinitrophenol due to loss of hydroxyl proton at oxygen (Table 4).

The π–π interaction data for **3** is listed in (Table 6). The distance between the centroid of each ring of picrate group is 3.6689(1) Å and the perpendicular distance is 3.5210 Å; both values below the “cut off” distance of 3.8 Å for a π–π interaction [41,42]. The angle between this perpendicular distance and the direct line is 16.29° (Fig. 9).

The Te–O(1)(NO₃) distance in **1** is 2.464(2) Å [N–O(1) = 1.269(3) Å is slightly longer than the other two N–O(2) = 1.227(3) Å, N–O(3) = 1.216(3) Å]. In **2** the Te(1)–O(1A) = 2.377(3) Å and in **3** Te(1)–O(1P) = 2.392(4) Å (Tables 2–4). It appears that the bonding to the nitrate must be weak and presumably partly ionic in agreement with the earlier observations [7f] whereas in **2** and **3** Te–O (picrate) possess more covalent character.

4. Conclusion

In conclusion, easy synthetic routes for ditelluroxanes (**1–3**) containing hypervalent Te–O bonds have been developed. **1** contains partly ionic nitrate groups bonded to tellurium while **2** and **3** contain 2,4,6-(trinitro) phenolate groups largely covalently bonded to tellurium. In the solid state **1** exists as hexameric-, **2** as tetrameric- and **3** as

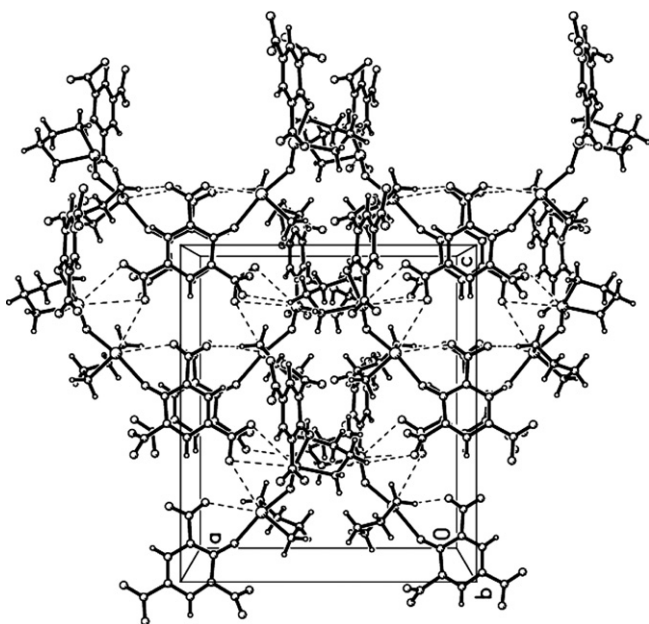


Fig. 8. Decameric supramolecular associations of **3** built up by connecting the molecules through Intra- and Intermolecular Te···O secondary bonds and C–H···O hydrogen bonds.

Table 5
C–H···O hydrogen bond related parameters of **1–3**

Complex	C···O(<i>D</i>) (Å)	H···O(<i>d</i>) (Å)	C–H···O(<i>θ</i>) (°)
[(CH ₃) ₂ TeNO ₃] ₂ O (1)	3.508(4)[C(1)–O(1)#4]	2.56 [H(1B)···O(1)#4]	168.8 [C(1)–H(1B)···O(1)#4]
[(CH ₃) ₂ TeOC ₆ H ₂ (NO ₂) ₃] ₂ O (2)	3.298(5)[C(11)···O(41B)#3]	2.65 [H(11A)···O(41B)#3]	125.1 [C(11)–H(11A)···O(41B)#3]
	3.205(5)[C(5B)···O(21B)#4]	2.76 [H(4BA)···O(21B)#4]	110.5 [C(5B)–H(4BA)···O(21B)#4]
	3.223(6)[C(21)···O(42B)#3]	2.56 [H(21B)···O(42B)#3]	126.6 [C(21)–H(21B)···O(42B)#3]
[C ₄ H ₈ TeOC ₆ H ₂ (NO ₂) ₃] ₂ O (3)	3.42(6)[C(1B)···O(61P)#4]	2.54 [H(1BB)···O(61P)#4]	147.8 [C(1B)–H(1BB)···O(61P)#4]
	3.01(3)[C(1B)···O(24P)#5]	2.26 [H(1BA)···O(24P)#5]	131.0 [C(1B)–H(1BA)···O(24P)#5]

Table 6
 π - π interaction data

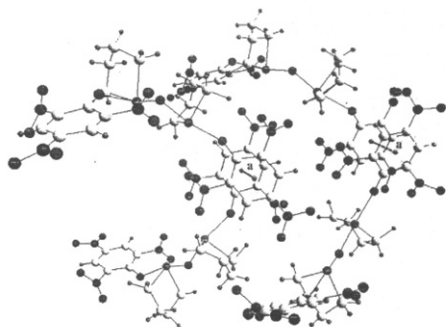
Analysis of short ring interactions with Cg-Cg distances <6.0 Angstrom and Beta <60.0°

- Cg(I) = Plane number I (= ring number in () above)
 -Alpha = Dihedral Angle between Planes I and J (Deg)
 -Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
 -Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
 -Cg-Cg = Distance between ring Centroids (Ang.)
 -CgI_perp = Perpendicular distance of Cg(I) on ring J (Ang.)
 -CgJ_perp = Perpendicular distance of Cg(J) on ring I (Ang.)
 -P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I)	Res(I)	Cg(J)	[ARU(J)]	Cg-Cg	Transformed J-Plane	P, Q, R, S	Alpha	Beta	Gamma	CgI_perp	CgJ_perp
Cg3	[1]	-> Cg3	[3565.01]	3.6688	0.3226-0.9464-0.0186	-8.6601	2.13	16.29	16.29	3.521	3.521
			Min or Max	3.669			2.13	16.29	16.29	3.521	3.521
			[3565] = -X,1-Y ,Z								

The Cg(I) refer to the Ring Center-of-Gravity numbers given in () in the Ring-Analysis above

Cg(I)	x	y	z	Xo	Yo	Zo
Cg3	0.005628	0.374343	-0.004433	0.08207	5.45931	-0.07385



a (Distance between the centroids of each ring of picrate group) = 3.6689(1) Å

Fig. 9. π - π interactions in 3.

decameric supramolecular assembly organised by Te \cdots O secondary bonds, C-H \cdots O hydrogen bonds and/or π - π interactions.

5. Supplementary material

CCDC 287042, 287043 and 287044 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

PCS is thankful to the Department of Science and Technology (DST) Government of India and Council of Scientific & Industrial Research (CSIR), New Delhi for the financial support. SB is thankful to DST for Women Scientist Programme.

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