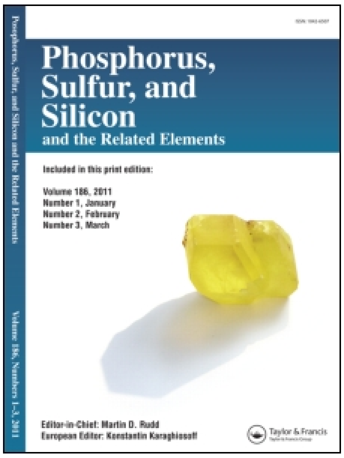

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A UNIQUE SUPRAMOLECULAR STRUCTURE OF POLY [μ-OXO -BIS(1,1,2,3,4,5-HEXAHYDRO-1-NITRATOTELLUROPHENE)] $[(C_4H_8TENO_3)_2O]_N$ WITH—0-TE-0-TE-0—CROSS LINKED CHAINS

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A UNIQUE SUPRAMOLECULAR STRUCTURE OF POLY [μ-OXO - BIS(1,1,2,3,4,5-HEXAHYDRO-1-NITRATOTELLUROPHENE)] $[(C_4H_8TENO_3)_2O]_N$ WITH ---O-TE-O-TE-O--- CROSS LINKED CHAINS

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Poly [μ-oxo bis(1,1,2,3,4,5-hexahydro-1-nitratotellurophene)] **1**, is prepared by the room temperature reaction of 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene with silver nitrate in deionised water. Crystals of **1** are monoclinic, space group C2/c with a=13.930(2) Å, b =11.665(2) Å, c=10.0682(11) Å, β=116.264(8)^0 and Z=4. The monomeric unit of the title compound is centrosymmetric, with an angular TeOTe skeleton containing bridging O atom at the centre of symmetry. These monomeric units are linked together through ---O-Te- O-Te -O --- cross linked chains and the nitrate groups are asymmetrically bidentate with a primary Te-ONO_2 and a secondary Te---O semibonding interaction. Each nitrate group further participates in another Te---O semibonding interaction forming another asymmetric $Te(NO_3)_2Te$ bridge. The structural characteristics of **1** are compared with related complexes.

Keywords: Supramolecular arrangement; tellurium; X- ray structure

INTRODUCTION

Tellurium compounds often exhibit unique structures and/or reactivities compared to their sulfur (or selenium) analogues[1] and tellurium rich metal

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compounds have attracted extensive attention since they are potential precursors for new solid state materials[2,3]. Further supramolecular association in organometallic solids is a current area of interest because of their possible use in material chemistry[4]. Supramolecular association in tellurium complexes and organotellurium compounds through Te---Te,Te---S and Te---N secondary interactions are already reported in literature[5]. We have recently synthesised and characterised tellurium compounds existing as discrete units with no molecular association[6]. Moreover we have prepared acyclic and cyclic organotellurium compounds where molecular association is restricted to two and / or three units involving Te---O secondary interactions and where the dimeric and / or trimeric molecular assemblies are not interconnected[7,8]. In this report we describe the first example of a cyclic organotellurium complex $[(C_4H_8TeNO_3)_2O]_n$ containing ---O-Te-O-Te-O--- cross linked chains. We also compare the structural characteristics of the title complex with known acyclic and cyclic organotellurium nitrates.

RESULTS AND DISCUSSION

The formation of **1** from 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene and silver nitrate in almost quantitative yield, involves metathetical reaction (eq 1) resulting in the synthesis of 1,1,2,3,4,5-hexahydro-1-nitratotellurophene and which by reaction with water gives [μ-oxo bis (1,1,2,3,4,5-hexahydro-1-nitratotellurophene)] as shown in (eq 2) which exists as poly [μ-oxo bis(1,1,2,3,4,5-hexahydro-1-nitratotellurophene)]

$$C_4H_8TeI_2 + 2AgNO_3 \longrightarrow C_4H_8Te(NO_3)_2 + 2AgI \qquad (1)$$

$$2C_4H_8Te(NO_3)_2 + H_2O \longrightarrow (C_4H_8TeNO_3)_2O + 2HNO_3 \qquad (2)$$

Such type of reactions of $R_2Te(NO_3)_2$(R = phenyl, 2-methylphenyl) with water yielding $(R_2TeNO_3)_2O$ have previously been reported by Lederer[9].

X-ray Single Crystal Structure

The X-ray structures of acyclic organotellurium nitrates have been reported by Alcock et al.[11], while those of cyclic organotellurium nitrates viz. phenoxatellurine dinitrate and bisphenoxatelluronium dinitrate have

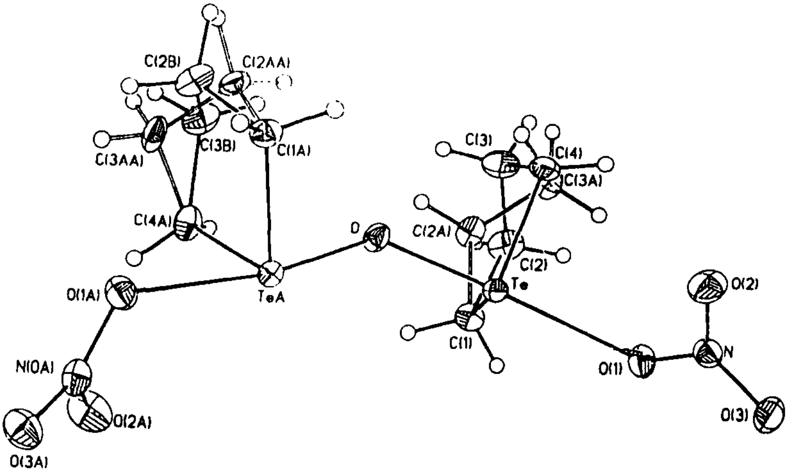

FIGURE 1 ORTEP diagram for one monomeric unit of **1**

been reported by Mangion et al.[12]. ORTEP diagram for one monomeric unit of **1** is presented in Figure 1. Important bond lengths and angles for **1** are given in Table I.

TABLE I Bond Lengths (Å) and Angles (deg) of 1

Te-O	1.955(2)	Te-C(4)	2.109(4)
Te-C(1)	2.126(4)	O-Te#1	1.955(2)
O(1)-N	1.279(5)	O(2)-N	1.236(5)
O(3)-N	1.230(5)	C(1)-C(2A)	1.52(2)
C(1)-C(2)	1.562(12)	C(2)-C(3)	1.50(2)
C(3)-C(4)	1.583(12)	C(2A)-C(3A)	1.53(2)
C(3A)-C(4)	1.48(2)		
O-Te-C(4)	89.0(2)	O-Te-C(1)	89.9(2)
C(4)-Te-C(1)	85.5(2)	Te-O-Te#1	126.4(2)
O(3)-N-O(2)	121.7(4)	O(3)-N-O(1)	119.4(4)
O(2)-N-O(1)	118.7(4)	C(2A)-C(1)-Te	101.4(6)
C(2)-C(1)-Te	107.6(5)	C(3)-C(2)-C(1)	110.0(8)
C(2)-C(3)-C(4)	109.5(8)	C(1)-C(2A)-C(3A)	108.7(10)
C(4)-C(3A)-C(2A)	106.8(8)	C(3A)-C(4)-Te	105.7(6)
C(3)-C(4)-Te	105.0(4)		

Symmetry transformations used to generate equivalent atoms: #1 -x,y, -z+1/2

The structure of **1** consists of a monomeric unit of µ-oxo bis(1,1,2,3,4,5-hexahydro-1-nitratotellurophene) which is centrosymmetric with an angular Te-O-Te 126.4(2)^0. The Te-O bond lengths within this unit are equal (1.955 Å). The 1,1,2,3,4,5-hexahydrotellurophene rings are planar. But their flipover to the chair conformation through twist boat probably relieving some strain is apparently the result of geometrical impossibility of a planar ring with ideal sp^3 bond angle of 109.5° at the carbon atoms and unstrained C-Te-C bond angles in the usual 91–100 range[13–15] (Figure 1). Each tellurium (IV) atom is bonded to two methylene carbon atoms of the C_4H_8 group and two oxygens (one bridging oxygen and the other oxygen of NO_3 group). The four closest atoms C(1A),C(4A),O(1A) and bridging O provide a distorted trigonal bipyramidal primary coordination environment at each Te atom with O(1A)(NO_2) and bridging oxygen occupying apical positions and the two methylene carbon atoms of the C_4H_8 group in the equatorial plane The fifth coordination position in the equatorial plane is apparently occupied by the sterically active electron lone pair. This is indicated by the OTe(A) O (1A) angle of 169.2°. The structure of the NO_3 group is planar [sum of the angles at nitrogen 359.8 (4)°] and the O(1)- N 1.279(5) Å, O(2)-N 1.236(5) Å, O(3)-N 1.230(5) Å bond distances and O(3)-N-O(2) 121.7(4)^0, O(3)-N-O(1) 119.4(4)^0, O(2)-N-O(1) 118.7(4)^{0}angles are comparable with the NO_3 group present in phenoxatellurine dinitrate[12a] and bisphenoxatelluronium dinitrate[12b].

The nitrate ions are asymmetrically bidentate with a primary Te-O(NO_2) distance (2.536 Å) and a secondary interaction (Te---O 3.061 Å). Each nitrate ion further participates into another Te---O semibonding interaction (3.177 Å). The Te---O distances are longer than the covalent Te-O bond distance (2.03 Å)[16] but shorter than the sum of van der Waals radii (3.06 Å)[17] and thus correspond to semibonding interactions[18]. [O(0A)-Te(A)---O(3CA) 78.9^0,O(1A)-Te(A)---O(3CA) 111.4^0,C(1A)-Te(A)---O(3CA) 161.2^0,C(4A)-Te(A)---O(3CA) 79.5^0] These semibonding interactions are comparable with those present in organotellurium carboxylates[7,8,17,19]. If these weak Te---O semibonding interactions are considered, the tellurium atom can be regarded as hepta coordinated [O(0A)-Te(A)-O(1BA) 84.0^0,O(1A)-Te(A) ---O(1BA) 94.9^0, C(1A)-Te(A)---O(1BA) 81.9^0 C(4A)-Te(A)----O(1BA) 165.6^0].

Thus apart from symmetric Te-O-Te bridges (as described above) there are asymmetric Te-$(NO_3)_2$-Te bridges through which the monomeric units of μ-oxo bis (1,1,2,3,4,5- hexahydro-1 -nitratotellurophene) are self assembled resulting into supramolecular associations through zig-zag chains leading to a two dimensional polymer.

The Te-O-Te angle of **1** is comparable with those found in acyclic organotellurium nitrates[11] and cyclic organotellurium nitrates[12].

The molecular structure of the title complex is strikingly different from the closely related molecule bisphenoxatelluronium dinitrate[12b] where no supramolecular associations are reported. In summary, we have demonstrated that the $(C_4H_8TeNO_3)_2O$ molecule in the solid state forms a supramolecular arrangement through secondary Te---O interactions. This is a promising approach presenting new supramolecular arrays.

EXPERIMENTAL SECTION

1,1,2,3,4,5-Hexahydro-1,1-diiodotellurophene was prepared by the reported method[10]. Commercially available silver nitrate was used as received. The distilled water was carefully deionised before use. The IR spectrum of **1** was recorded using 8210 PCFTIR spectrometer in the range 4000–550 cm^{-1} with the sample as KBr disc. The ^1H NMR spectrum of **1** was obtained on a Varian VXR300S spectrometer in acetone in which it was only sparingly soluble.

Preparation of Compound 1

1,1,2,3,4,5-Hexahydro-1,1-diiodotellurophene 2.00g (4.50 mmol) was stirred with 1.56g (9.17 mmol) silver nitrate in 20 mL of deionised water for 1h. The reaction mixture was filtered several times to get rid of excess silver nitrate. Concentration of the filtrate under vacuum gave a solution from which crystals of **1** appeared after 24 h. Yield: 1.5g (75%). ^1H NMR (300 MHz): δ2.45(m,4H, CCH_2), 3.02 (m,4H, $TeCH_2$), IR: 571 (m), 470(m); (Te-O-Te)[11,20,21]; 1380 (vs) NO_2; 1015 (m) (NOstr); 830 (m) (NO_2); 729(m) (NO_2).Mp:130°C. Anal. calcd for $C_8H_{16}N_2O_7Te_2$: C,18.93; H,315. Found: C,18.90; H,3.14.

Crystal Structure of Compound 1

A colourless crystal (0.60 × 0.86 × 0.80 mm) of 1 was mounted on a Siemens R 3m/v diffractometer. The unit cell was determined from 25 randomly selected reflections using the automatic search index and least square approach. The data collected in the θ range (2.39 to 34.99°) correspond to the monoclinic cell. The data were corrected for Lorentz polarization and absorption effects. The maximum and minimum transmission values of the correction factor are 0.5123 and 0.3208. The data were monitored by measuring two standard reflections every 60 min of X-ray exposure time. The structure was solved by heavy atom using SHELXS86[22] and Fourier methods and refined by full matrix least squares with the non hydrogen atoms anisotropic at hydrogens having fixed isotropic thermal parameters of 0.07 $Å^2$ using the SHELXL-93 program[23]. Crystal data: $C_8H_{16}N_2O_7Te_2$, monoclinic, *C2/c*, a =13.930(2) Å, b =11.665(2) Å, c =10.0682 Å, $\beta = 116.264$ $(8)^0$, V=1467.1(3) $Å^3$, M=507.43, Dc=2.297mgm^{-3}, Z=4, λ(MoKα) 0.71073 Å, Final R indices [$I > 2\sigma(I)$] $R1$=0.0362, $wR2$=0.0983, R indices (all data) $R1$=0.0393, $wR2$=0.1013, GOF on F^2 1.180. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 134838. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code +(44)-1223336–033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] T. Chivers, *J. Chem. Soc. Dalton Trans.* 1185 (1996).
[2] M.A. Ansari, J. Ibers, *Coord. Chem. Rev.* **100**, 223 (1990).
[3] D.A. Lesch, T.B. Rauchfuss, *Inorg. Chem.* 20, 3583 (1981).
[4] D. Braga, F. Grepioni, *Chem. Commun.* 571 (1996) and references therein.
[5] (a) M.G. Newton, R.B. King, I. Haiduc, A. Silvestru, *Inorg. Chem.* **32**, 3795 (1993).
(b) A. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, *Inorg. Chem.* **33**, 1253 (1994).
(c) J.-S. Lee, D.D. Titus, R.F. Ziolo, *J. Chem. Soc. Chem. Commun.* 501 (1976).
(d) I. Haiduc, R.B. King, M.G. Newton, *Chem. Rev.* **94**, 301 (1994).
[6] P.C. Srivastava, H.G. Schmidt, H.W. Roesky, *Z. Naturforsch.* **50b**, 695 (1995).
[7] P.C. Srivastava, A. Sinha, S. Bajpai, H.G. Schmidt, M. Noltemeyer, *J. Organometal. Chem.* **575**, 261 (1999).
[8] P.C. Srivastava, S. Bajpai, R.J. Butcher, *J. Organometal. Chem.* **586**, 119 (1999).

[9] K. Lederer, *Ber.* **49**, 1071 (1916).
[10] G.T. Morgan, F.H. Burstall, *J. Chem. Soc.* 180 (1931).
[11] N.W. Alcock, W.D. Harrison, *J. Chem. Soc. Dalton Trans.* 1421 (1982).
[12] (a) M.M. Mangion, M.R. Smith, E.A. Meyers, *J. Heterocycl. Chem.* **10**, 533 (1973).
(b) M.M. Mangion, M.R. Smith, E.A. Meyers, *J. Heterocycl. Chem.* **10**, 543 (1973).
[13] J.D. McCullough, *Inorg. Chem.* **12**, 2669 (1973).
[14] H. Hope, C. Knobler, J.D. McCullough, *Inorg. Chem.* **12**, 2665 (1973).
[15] C. Knobler, J.D. McCullough, H. Hope, *Inorg. Chem.* **9**, 797 (1970).
[16] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, pp. 93 (1964).
[17] S.B. Bulgarevich, B.B. Rivkin, N.G. Furmanova, O.O. Exner, D. Ya. Movshovich, T.A. Yusman, I.D. Sadekov, V.I. Minkin, *Zh. Strukt. Khim.* **25**, 97 (1984).
[18] N.W. Alcock, *Adv. Inorg. Chem. Radiochem.* **15**, 1 (1972).
[19] N.W. Alcock, W.D. Harrison, C. Howes, *J. Chem. Soc. Dalton Trans.* 1709 (1984).
[20] W.E. Dasent, T.C. Waddington, *J. Chem. Soc.* 3350 (1960).
[21] W.E. Dasent, T.C. Waddington, *Proc. Chem. Soc.* 71 (1960).
[22] G.M. Sheldrick, Crystallographic computing 3; Oxford University Press U.K. 175 (1986).
[23] G.M. Sheldrick, SHELXL – 93, Program for Crystal Structure Refinement. University of Göttingen, 1993.