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Secondary bonds induced supramolecular assemblies in the crystals of 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene; 1,1,2,3,4,5,6-heptahydro-1,1-diiodotellurane and 1,3-dihydro-2λ^4-benzotellurole-2,2-diyl diiodide

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Abstract

The comparative study of crystal structures of heterocyclic organotellurium diiodides viz. 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene ($C_4H_8TeI_2$) (**1**); 1,1,2,3,4,5,6-heptahydro-1,1-diiodotellurane ($C_5H_{10}TeI_2$) (**2**), and 1,3-dihydro-2λ^4-benzotellurole-2,2-diyl diiodide ($C_8H_8TeI_2$) (**3**), with respect to polymorphism, bond lengths, bond angles; (a) Te–I; (b) Te–C; (c) I–Te–I; (d) C–Te–C; (e) C–Te–I, and intermolecular secondary bonds; (f) Te···I; (g) I–Te···I; and (h) C–Te···I, are described. The structures of all heterocyclic organotellurium diiodides were established by single crystal X-ray diffraction studies. In each case a distorted octahedral (six-coordinate) geometry exists around tellurium atom with Te···I secondary bonds leading to 2-dimensional zigzag ribbons in **1**, trimeric molecular aggregates in **2** while **3** is a 3-dimensional polymer. © 2000 Published by Elsevier Science S.A.

Keywords: Heterocyclic organotellurium; Polymorphism; Intermolecular secondary bonds; Supramolecular assemblies

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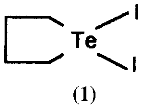
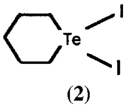
1. Introduction

Dialkyl tellurium diiodides (R_2TeI_2) were originally reported [1] to exist in α and β forms and subsequent investigations [2,3] revealed that α-Me_2TeI_2 was covalent whereas β-Me_2TeI_2 was ionic $(Me_3Te)^+(MeTeI_4)^-$. The 1-telluracycloalkane 1,1-diiodides (heterocyclic organotellurium diiodides) viz. 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene (**1**), and 1,1,2,3,4,5,6-heptahydro-1,1-diiodotellurane (**2**), have also been reported to exist in two forms, each differing in colour and crystal morphology [4,5]. Information about the constitution of these forms is currently not available. As part of our continuing study of hypervalent(+ 4) tellurium compounds [6–9], the present investigation was carried out to determine the crystal and molecular structures of **1** and **2**. Both of these structures contain two isostructural molecules in the asymmetric unit indicating absence of polymorphism in contrast to three polymorphs existing in the closely related 1,3-dihydro-2λ^4-benzotellurole-2,2-diyldiiodide (**3**) [10–12]. In these heterocyclic organotellurium systems **1**, **2**, and **3**, each has a distorted octahedral (six-coordinate) geometry around tellurium atom but differ in the size of the heterocyclic ring from a five membered to a six membered ring. The corresponding variations in; (a) Te–I; (b) Te–C; (c) ∠I–Te–I; (d) ∠C–Te–C; (e) ∠C–Te–I and secondary bonds; (f) Te···I; (g) I···I; (h) I–Te···I; and (i) ∠C–Te···I are discussed.



(1)



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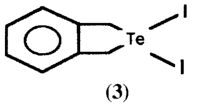

(3)

King et al. [13] have recently discussed supramolecular associations through Te···S secondary bonds in which tellurium centered coordination geometries, known in mononuclear complexes and capable of inde-

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pendent existence, associate themselves either in dimeric or polymeric structures through Te···S secondary bonds. In the present investigation, self-organisation through Te···I secondary bonds resulting in supramolecular associations is amply demonstrated in the structures of **1**–**3**.

IR spectroscopic data of anionic complexes of 1,1,2,3,4,5-hexahydro-1,1-diiodotellurophene of the type $(R_4M)_2^{+\,2}[C_4H_8TeI_2X_2X'_2]^{2-}$ (where R=CH_3, C_2H_5, C_3H_7, C_4H_9; M=N, P, As, Sb; X=Cl, Br, I and X′= NCO, NCS, N_3) have been reported [14] and Lambert et al. [15], using NMR spectral data, have proposed that 1,1,2,3,4,5,6-heptahydro 1,1-dibromotellurane has a conformation in which part of the ring is flattened and part considerably puckered. Tellurophenes and their derivatives are industrially important as their addition to hydraulic fluids increases their fire resistance [16] and supramolecular associations in organometallic compounds are a field of recent interest [17].

2. Experimental

2.1. Synthesis

1,1,2,3,4,5-Hexahydro-1,1-diiodotellurophene ($C_4H_8TeI_2$) (**1**) [4], 1,1,2,3,4,5,6-heptahydro-1,1-diiodotellurane ($C_5H_{10}TeI_2$) (**2**) [5] and 1,3-dihydro-2λ^4-benzotellurole-2,2-diyldiiodide ($C_8H_8TeI_2$) (**3**) [6] were prepared by the literature methods. **1** was recrystallised from benzene to obtain bright red prisms (m.p. 140°C) and from acetone to obtain reddish square shaped crystals (m.p. 110°C) suitable for single crystal X-ray diffraction studies. However both types of crystals have same cell constants. Morgan and Burstall [4] obtained **1** as bright red prismatic crystal (from benzene) and shiny purple plates (from acetone). Similarly, **2** was recrystallised from acetone to yield orange–brown needles (m.p. 135°C) as reported by Farrar and Gulland [18] and not two types of crystals of **2** (deep red prism and orange prism) as reported by Morgan and Burgess [5]. **3** was recrystallised from hot 2-methoxyethanol to obtain in bulk yellow orange (m.p. 225°C (d)) crystals and some orange red (m.p. 222°C (d)) crystals. They were separated, manually, from each other.

2.2. X-ray measurements

Red crystals (0.14 × 0.46 × 0.39 mm) of compound **1**, orange–brown crystals (0.10 × 0.64 × 0.11 mm) of compound **2**, and orange red crystals of **3** (0.36 × 0.46 × 0.42 mm) were mounted on a Bruker P4S diffractometer at 293(2) K using graphite monochromatic Mo–K_α radiation (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 solved in space group $P2_1/n$, **2** in space group *Pbcn*, and **3** in *Fdd*2. 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-86 [19] and Fourier methods and refined by full

Table 1
Crystal data and refinement details for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_4H_8TeI_2$	$C_5H_{10}TeI_2$	$C_8H_8TeI_2$
Formula weight	437.50	451.53	485.54
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	*Pbcn*	*Fdd*2
a (Å)	12.674(2)	9.684(1)	12.373(2)
b (Å)	10.363(9)	21.574(3)	14.983(2)
c (Å)	13.865(2)	19.130(2)	12.281(2)
α (°)	90	90	90
β (°)	90.84(1)	90	90
γ (°)	90	90	90
V (Å^3)	1821.0(4)	3998.5(8)	2276.7(6)
Z	8	16	8
μ (mm^{-1})	9.960	9.077	7.982
Index ranges	$0\leq h\leq 16$, $-13\leq k\leq 0$, $-18\leq l\leq 18$	$0\leq h\leq 9$, $0\leq k\leq 28$, $0\leq l\leq 24$	$-18\leq h\leq 0$, $0\leq k\leq 22$, $0<l<18$
Reflections collected	4376	4223	1066
Independent reflections	4191 ($R_{int}=0.0233$)	4223 ($R_{int}=0.0000$)	1066 ($R_{int}=0.0000$)
Final R indices, [$I>2\sigma(I)$]	$R_1=0.0475$, $wR_2=0.1282$	$R_1=0.0409$, $wR_2=0.0890$	$R_1=0.410$, $wR_2=0.1172$
R indices, (all data)	$R_1=0.0651$, $wR_2=0.1373$	$R_1=0.0846$, $wR_2=0.1086$	$R_1=0.0464$, $wR_2=0.1217$

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

Bond lengths			
Te(1)–C(14)	2.145(9)	Te(1)–C(11)	2.160(1)
Te(1)–I(11)	2.899(1)	Te(1)–I(12)	2.950(1)
Te(2)–C(21)	2.154(1)	Te(2)–C(24)	2.164(1)
Te(2)–I(21)	2.875(1)	Te(2)–I(22)	2.977(1)
C(11)–C(12)	1.51(2)	C(12)–C(13)	1.50(2)
C(13)–C(14)	1.53(2)	C(21)–C(22)	1.51(2)
C(22)–C(23)	1.50(2)	C(23)–C(24)	1.50(2)
Bond angles			
C(14)–Te(1)–C(11)	84.5(4)	C(14)–Te(1)–I(11)	91.4(3)
C(11)–Te(1)–I(11)	88.2(3)	C(14)–Te(1)–I(12)	88.0(3)
C(11)–Te(1)–I(12)	89.4(3)	I(11)–Te(1)–I(12)	177.62(3)
C(21)–Te(2)–C(24)	84.0(4)	C(21)–Te(2)–I(21)	88.1(3)
C(24)–Te(2)–I(21)	92.0(3)	C(21)–Te(2)–I(22)	88.4(3)
C(24)–Te(2)–I(22)	88.1(3)	I(21)–Te(2)–I(22)	176.48(3)
C(12)–C(11)–Te(1)	105.5(8)	C(13)–C(12)–C(11)	110.8(1)
C(12)–C(13)–C(14)	110.4(1)	C(13)–C(14)–Te(1)	105.2(7)
C(22)–C(21)–Te(2)	106.0(7)	C(23)–C(22)–C(21)	109.9(1)
C(22)–C(23)–C(24)	111.4(1)	C(23)–C(24)–Te(2)	105.1(7)

Table 4
Bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
Te(1)–C(11)	2.130(9)	Te(1)–C(15)	2.132(1)
Te(1)–I(11)	2.863(1)	Te(1)–I(12)	2.976(1)
Te(2)–C(21)	2.148(1)	Te(2)–C(25)	2.157(9)
Te(2)–I(21)	2.852(9)	Te(2)–I(22)	3.019(9)
C(11)–C(12)	1.47(2)	C(12)–C(13)	1.38(2)
C(13)–C(14)	1.43(2)	C(14)–C(15)	1.43(2)
C(21)–C(22)	1.49(2)	C(22)–C(23)	1.48(2)
C (23)–C(24)	1.50(2)	C(24)–C(25)	1.49(2)
Bond angles			
C(11)–Te(1)–C(15)	98.1(5)	C(11)–Te(1)–I(11)	91.2(3)
C(15)–Te(1)–I(11)	89.5(4)	C(11)–Te(1)–I(12)	88.9(3)
C(15)–Te(1)–I(12)	87.3(4)	I(11)–Te(1)–I(12)	176.79(3)
C(21)–Te(2)–C(25)	95.3(4)	C(21)–Te(2)–I(21)	90.3(3)
C(25)–Te(2)–I(21)	91.6(3)	C(21)–Te(2)–I(22)	87.4(3)
C(25)–Te(2)–I(22)	89.2(3)	I(21)–Te(2)–I(22)	177.66(4)
C(12)–C(11)–Te(1)	116.7(9)	C(13)–C(12)–C(11)	126.8(2)
C(12)–C(13)–C(14)	129.3(5)	C(15)–C(14)–C(13)	126.0(1)
C(14)–C(15)–Te(1)	117.3(1)	C(22)–C(21)–Te(2)	116.9(9)
C(23)–C(22)–C(21)	116.9(1)	C(22)–C(23)–C(24)	117.0(1)
C(25)–C(24)–C(23)	117.5(1)	C(24)–C(25)–Te(2)	114.5(8)

matrix least squares using the SHELXL-93 program [20] with the non-hydrogen atoms anisotropic and hydrogen atoms having fixed isotropic thermal parameters of 0.08 Å^2 (Table 1).

Selected bond lengths and bond angles for **1** and **2** are listed in Tables 2–5, and for **3** in Table 6. The crystal structures of **1** and **2** are shown in Figs. 1 and 4, respectively. The supramolecular assembly of **1** is shown in Fig. 2 and those of **2** are shown in Fig. 5. The unit cells of **1**, **2** and **3** are shown in Figs. 3, 6 and 7, respectively.

Table 3
Bond lengths (Å) and bond angles (°) for **1** in $P2_1/n$

TE1 I 11	2.899					
TE1 I12	2.950	177.6				
TE1 C11	2.160	88.2	89.4			
TE1 C14	2.145	91.4	88.0	84.5		
TE1 I12A	3.697	96.8	83.1	79.2	161.5	
TE1 I22A	3.796	77.3	104.9	159.0	80.7	117.3
		I11	I12	C11	C14	I12A
I11 TE1	2.899					
I11 TE2A	3.999	103.0				
		TE1				
I12 TE1	2.950					
I12 TE1A	3.697	96.9				
		TE1				
TE2 I 21	2.875					
TE2 I22	2.977	176.5				
TE2 C21	2.154	88.1	88.4			
TE2 C24	2.164	92.0	88.1	84.0		
TE2 I11A	3.999	110.4	73.2	161.0	90.8	
TE2 I22B	3.738	87.9	91.1	81.1	165.1	103.2
		I21	I22	C21	C24	I11A
I21 TE2	2.875					
I22 TE2	2.977					
I22 TE1A	3.796	106.3				
I22 TE2B	3.738	88.9	99.4			
		TE2	TE1A			

3. Results and discussion

3.1. Description and discussion of the structures of 1–3

3.1.1. Description of the structure of $C_4H_8TeI_2$ (1)

The structure of **1** comprises two molecules A and B, which are present as dimers (Fig. 1). Of the four methylene groups in the heterocycle of $C_4H_8TeI_2$ (**1**), the two methylene carbon atoms of the C_4H_8 group are bonded to the Te(IV) atom with bond distances and bond angles; Te(1)–C(11) = 2.160(1), Te(1)–C(14) = 2.145(9) Å; C(14)–Te(1)–C(11) = 84.5(4)° in molecule A, and Te(2)–C(21) = 2.154(1), Te(2)–C(24) = 2.164(1) Å; C(21)–Te(2)–C(24) = 84.0(4)° in molecule B. The four closest atoms C(11), C(14), I(11), I(12) in molecule A and C(21), C(24), I(21), I(22) in molecule B, provide a distorted trigonal bipyramidal geometry around Te(1) and Te(2) atoms with the iodine atoms in the apical positions (Te(1)–I(11) = 2.899(1), Te(1)–I(12) = 2.950(1) Å in molecule A and Te(2)–I(21) = 2.875(1), Te(2)–I(22) = 2.977(1) Å in molecule B). A stereochemically active electron lone pair apparently occupies the fifth coordination position in the equatorial plane. The I(11)–Te(1)–I(12) angle of 177.62(3)° in molecule A and I(21)–Te(2)–I(22) angle of 176.48(3)° in molecule B deviate from linearity with the iodine atoms pushed away from the equatorial electron lone pair. This type of geometry has been observed previously in a variety of acyclic and cyclic organotellurium compounds [8,9,21–23].

Table 5
Bond lengths (Å) and bond angles (°) for **2** in *Pbcn*

TE1 I11	2.864					
TE1 I12	2.975	176.8				
TE1 C11	2.149	91.1	89.1			
TE1 C15	2.147	89.5	87.3	97.4		
TE1 I21	4.065	86.8	95.4	133.3	129.1	
TE1 I22A	3.870	85.1	98.1	77.5	172.5	55.9
		I11	I12	C11	C15	I21
I21 TE2	2.852					
I21 TE1	4.065	115.8				
I21 I22A	3.722	174.3	59.4			
		TE2	TE1			
I12 TE1	2.975					
I12 TE2	3.900	123.5				
I12 I11A	3.870	173.8	61.3			
		TE1	TE2			
TE2 I21	2.852					
TE2 I22	3.019	177.7				
TE2 C21	2.145	90.1	87.7			
TE2 C25	2.152	91.5	89.3	95.1		
TE2 I12	3.900	82.5	96.4	75.6	168.8	
TE2 I11A	3.963	85.8	95.3	134.5	130.2	59.0
		I21	I22	C21	C25	I12

Table 6
Bond lengths (Å) and bond angles (°) for **3**[a]

Bond lengths			
Te–C(1)	2.165(1)	Te–C(1) # 1	2.165(1)
Te–I	2.902(7)	Te–I # 1	2.902(7)
C(2)–C(3)	1.39(1)	C(2)–C(2) # 1	1.42(2)
C(2)–C(1)	1.47(2)	C(3)–C(4)	1.37(2)
C(4)–C(4) # 1	1.53(5)		
Bond angles			
C(1)–Te–C(1) # 1	84.7(6)	C(1)–Te–I	90.5(3)
C(1) # 1–Te–I	89.1(3)	C(1)–Te–I # 1	89.1(3)
C(1) # 1–Te–I # 1	90.5(3)	I–Te–I # 1	179.49(5)
C(3)–C(2)–C(2) # 1	119.4(7)	C(3)–C(2)–C(1)	120.0(9)
C(2) # 1–C(2)–C(1)	120.7(5)	C(2)–C(1)–Te	107.0(7)
C(4)–C(3)–C(2)	123.4(1)	C(3)–C(4)–C(4) # 1	117.1(9)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x$, $-y$, z.

Molecule A is symmetrically connected to its neighbouring molecule through Te···I (3.697 Å) secondary bonds and similarly molecule B is symmetrically connected to its neighbouring molecule through Te···I (3.738 Å) secondary bonds to form the dimers. These dimers are asymmetrically connected through Te···I (3.796, 3.999 Å) secondary bonds to form a zigzag ribbon in the *a* direction (Fig. 2). With the Te···I secondary bonds, the coordination of each Te atom is octahedral with an unshared electron pair at the vertex situated *trans* to one of the $-CH_2$ groups attached to tellurium (the secondary bond itself is in the *trans* position to the other $-CH_2$ group attached to tellurium). The angles I(12A)···Te(1)–C(14) and I(12A)···Te(1)–C(11) are161.5 and 79.2°, respectively in molecule A and the angles I(22B)···Te(2)–C(24) and I(22B)···Te(2)–C(21) are 165.1 and 81.0°, respectively in molecule B.

Similar coordination environments for tellurium are found in di(trifluoroacetato) diphenyltellurium [23] and in *cis*-2-ethoxycycloheptyl tribromotellurium [24] in which the unshared electron pair is *trans* to the organic group. The Te···I distances (3.697, 3.738, 3.796, 3.999 Å) are shorter than the sum of van der Walls radii (4.35 Å) [25] and longer than the sum of covalent radii (2.70 Å) [26] and therefore definitely correspond to secondary bonds [27]. The values are comparable with the Te···I secondary bonds present in other R_2TeI_2 ($R_2 = C_4H_8S$, C_4H_8O, $C_{12}H_8O$ and $C_{12}H_8$)[12]. Apart from these Te···I secondary bonds, I···I interactions are also observed in the unit cell of **1** (Fig. 3).

3.1.2. Description of the structure of $C_5H_{10}TeI_2$ (2)

The structure of $C_5H_{10}TeI_2$ contains two independent A and B molecules (Fig. 4). In each molecule the tellurium atom completes a cyclohexane ring with other five carbon atoms. The ring has the expected chair conformation in both molecules due to the staggered

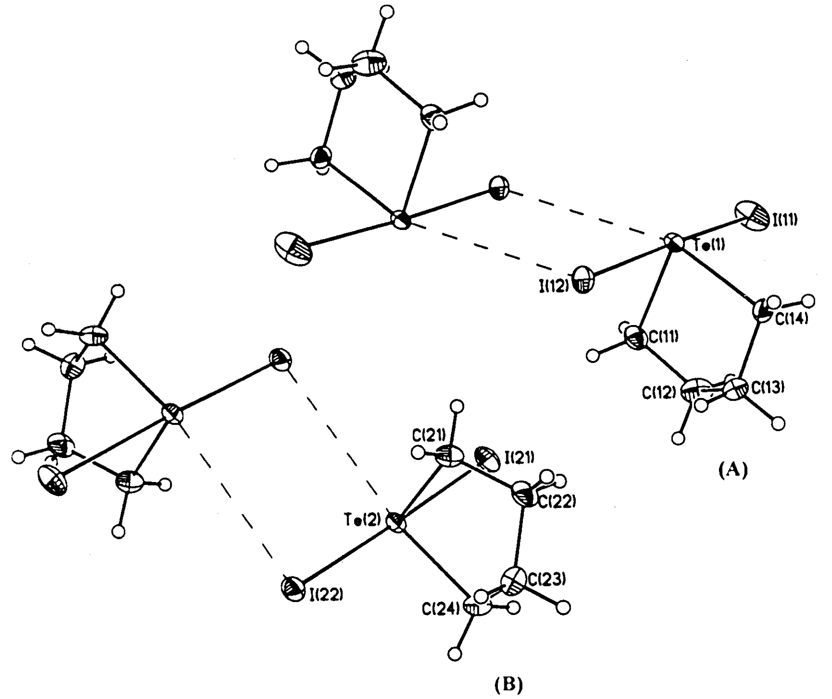

Fig. 1. Crystal structure of **1**.

situation of C–H bonds on neighbouring carbon atoms. In both molecules tellurium forms two normal bonds with the two neighbouring carbon atoms (Te(1)–C(11) 2.130(9), Te(1)–C(15) = 2.132(1) Å, C(11)–Te(1)–C(15) = 98.1(5)° in molecule A and Te(2)–C(21) = 2.148(1), Te(2)–C(25) = 2.157(9) Å, C(21)–Te(2)–C(25) = 95.3(4)° in molecule B). Two axial bonds (approximately perpendicular to the C–Te–C plane) are formed with iodine atoms with bond distances Te(1)–I(11) = 2.863(1), Te(1)–I(12) = 2.976(1) Å forming bond angle I(11)–Te(1)–I(12) = 176.79(3)° in molecule A and Te(2)–I(21) = 2.852(9), Te(2)–I(22) = 3.019 (9) Å forming bond angle I(21)–Te(2)–I(22) = 177.66(4)° in molecule B. The configuration around tellurium atom in both molecule A and molecule B approximates a distorted trigonal bipyramid with C(11), C(14) and an unshared lone pair of electrons in equatorial position and I(11) and I(12) in axial position in molecule A and C(21), C(22) and an unshared lone pair of electrons in equatorial positions and I(21), I(22) in axial positions in molecule B. The conformations adopted by the cyclohexane rings in the two molecules are significantly different. The average C–C–C angles are 127.4(1) and 117.1(3)°, respectively, in molecules A and B. The three carbon atoms at the other end of $C_5H_{10}TeI_2$ cyclohexane ring make an angle C(12)–C(13)–C(14) = 129.3(5)° in molecule A and angle C(22)–C(23)–C(24) = 117.0(1)° in molecule B. The $C_5H_{10}TeI_2$ has chair conformation in which part of the ring is flattened and a part is considerably puckered. A similar conformation has previously been qualitatively predicted for 1,2,3,4,5,6-heptahydro-1,1-dibromotellurane by Lambert et al. [15] through $R = J_{trans}/J_{cis}$ values (1.5, 3.6) in NMR spectrum of its solution.

The intermolecular interactions are presented in Figs. 5 and 6. Te(1) of molecule A forms secondary bonds

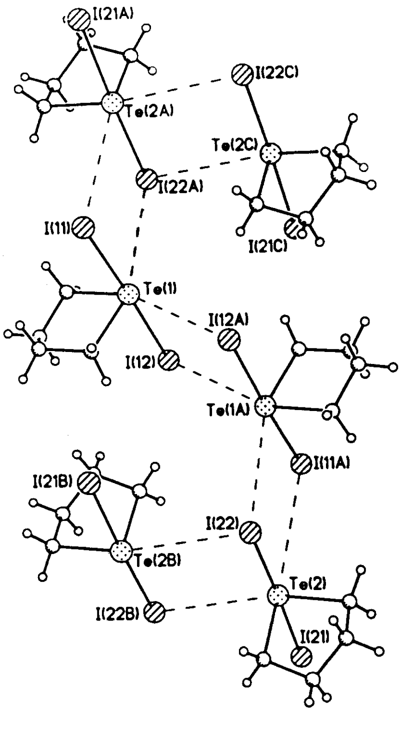

Fig. 2. Zigzag 2-dimensional ribbon for **1** in the *a* direction linked by Te···I secondary bonds.

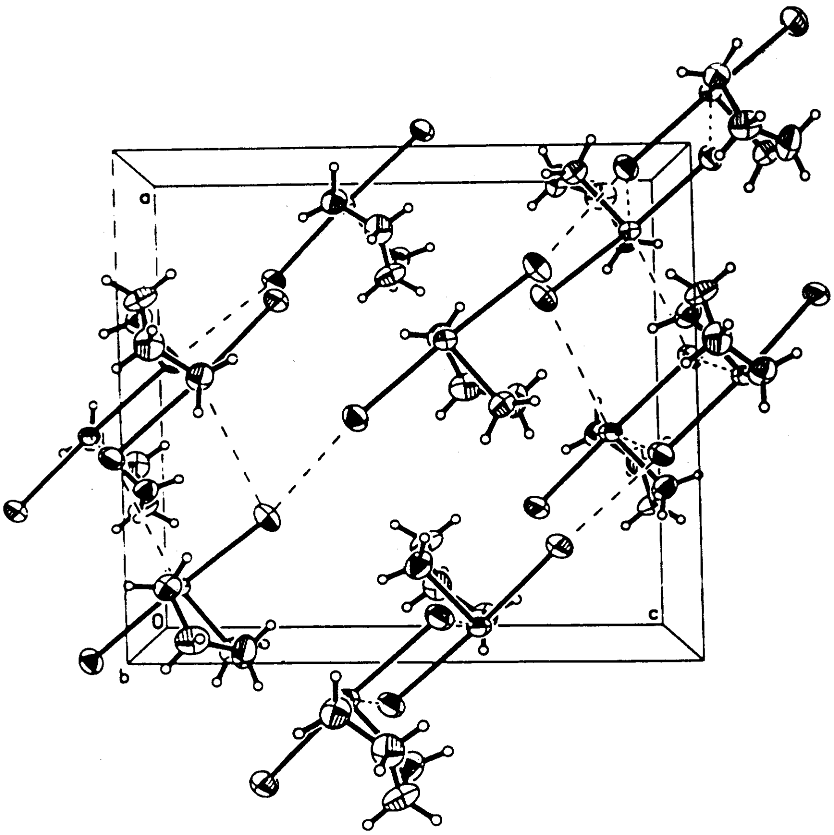

Fig. 3. The unit cell of **1** projected down *b*, showing the intermolecular Te···I and I···I secondary bonds (broken).

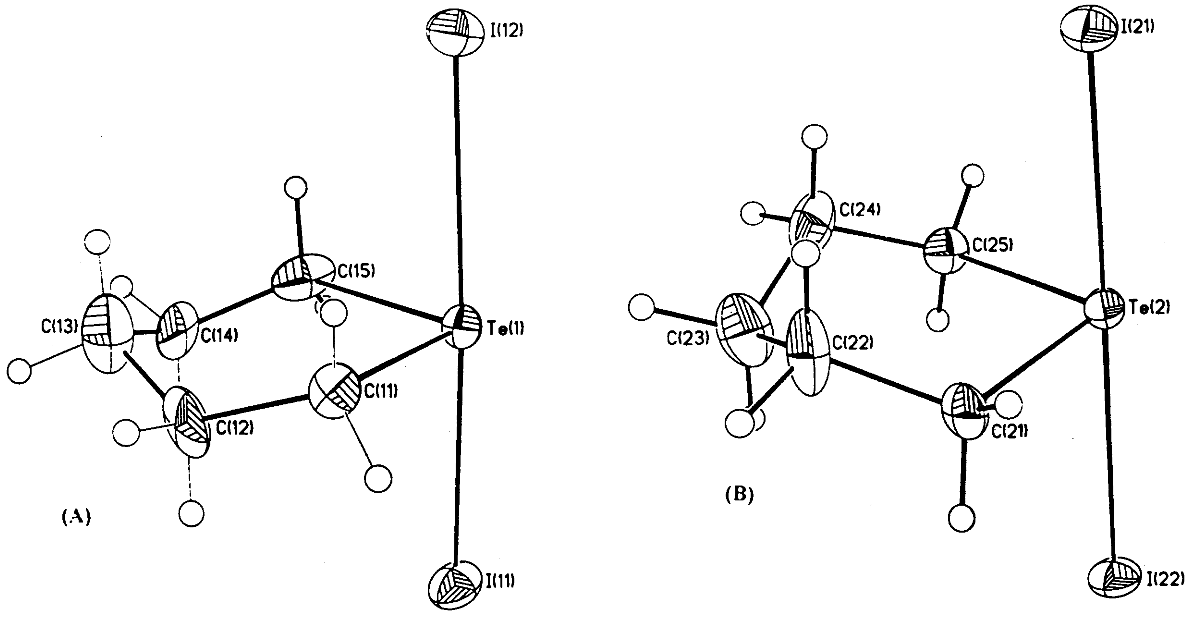

Fig. 4. Crystal structure of **2**.

with the I(21) of molecule B and I(22A) of other adjacent molecule of $C_5H_{10}TeI_2$, with bond distances Te(1)···I(21) = 4.065 and Te(1)···I(22A) = 3.870 Å. These Te···I secondary bonds form an angle I(22A)···Te(1)···I(21) = 55.9°. The secondary bond Te(1)···I(22A) is *trans* to one of the $-CH_2$ groups, having C(15) attached to Te(1) forming an angle C(15)–Te(1)···I(22A) = 172.5°. Similarly, the other secondary bond, Te(1)···I(21), is in slightly deviated *trans*-position to the $-CH_2$ group having C(11) attached to

Te(1) forming an angle C(11)–Te(1)···I(21) = 133.3°. The iodine atoms forming secondary bonds with Te(1) are also linked together by a weak I(22A)···I(21) secondary bond having bond distance 3.722 Å (Fig. 5, Table 5) which is shorter than combined van der Waals radii 4.30 Å [28a,b] and longer than the sum of covalent radii (2.66 Å) [29]. In this way Te···I and I···I secondary bonds form a trimeric aggregate, in which B type molecules are *trans* to each other with respect to Te(2)···I(21)···I(22A)···Te(2A) axis. Molecule B also

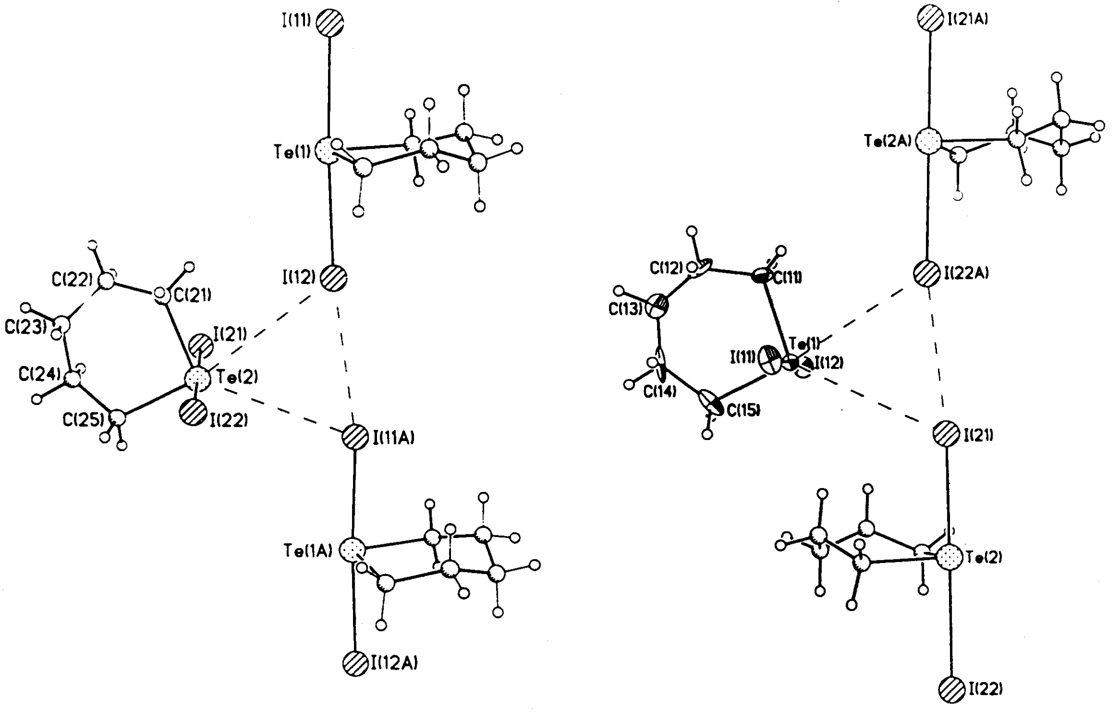

Fig. 5. Trimers of **2**.

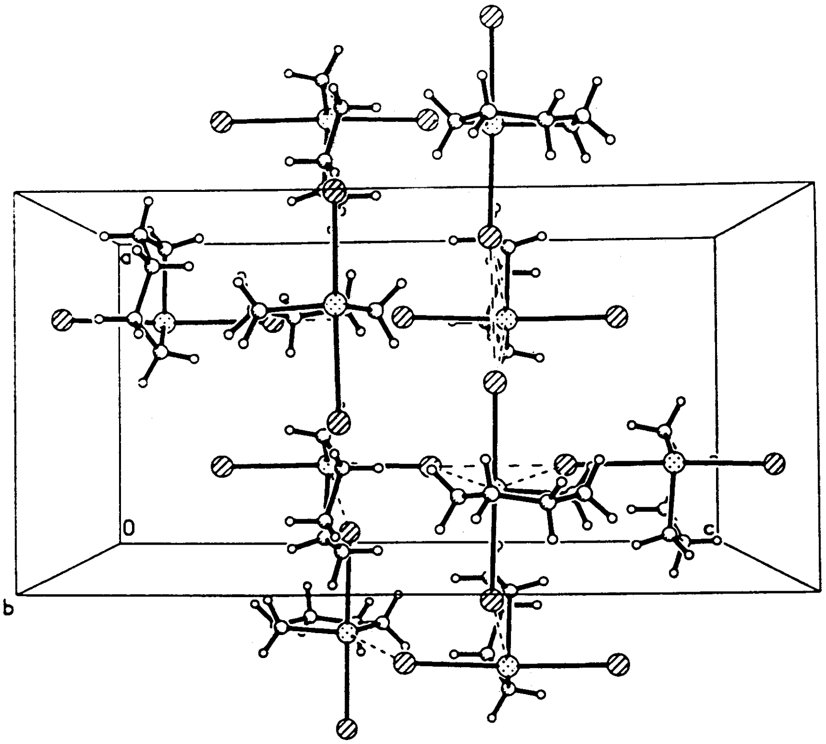

Fig. 6. The unit cell of **2** projected down *b*, showing the intermolecular Te···I and I···I secondary bonds (broken).

forms another trimeric aggregate with molecule A. Te(2) of molecule B forms secondary bonds with I(12) of molecule A and with I(11A) of the other adjacent molecule, with bond distances Te(2)···I(12) = 3.90, Te(2)···I(11A) = 3.963 Å. These secondary bonds form an angle I(11A)···Te(2)···I(12) = 59.0°. The secondary bond Te(2)···I(12) is in the *trans*-position to one of the $-CH_2$ group having C(25) attached to Te(2) forming an angle C(25)–Te(2)···I(12) = 168.8° and I(11A)···Te(2) bond is slightly deviated from a *trans*-position to other $-CH_2$ group having C(21) attached to the Te(2) forming an angle I(11A)···Te(2)–C(21) = 134.5°. The iodine atoms are linked by a weak secondary bond I(12)···I(11A) = 3.870 Å. The Te···I and I···I bond distances fall in the range of secondary bonds (as discussed above). In these trimeric aggregates, the A type molecules are in a *cis* position with respect to Te(1)–I(12)···I(11A)···Te(1A) axis. In the unit cell these molecular aggregates are interlinked through Te···I and I···I secondary bonds (Fig. 6).

In the present study, we did not find two types of crystals of **2** by using two different solvents (acetone, benzene) but in the case of $C_5H_{10}Te(OCOC_6H_5)_2$ we did find two crystal types; light brown prisms and white needle shaped crystals. When single crystal X-ray diffraction studies were carried out on these crystals, it was found that they were not polymorphs. Hence at the moment, on the basis of available data, we rule out the possibility of the presence of polymorphism in $C_5H_{10}TeI_2$ [30].

3.1.3. Description of the structure of $C_8H_8TeI_2$ (3)

There are three reports on the structure of **3**. Ziolo and Gunther [10] in their preliminary reports (as compared to none of the structure of **1** and **2**) described a yellow–orange or α-form of **3** as monoclinic, space group $P2_1/c$; $a = 12\ 573(5)$; $b = 9.881(2)$; $c = 9.271(7)$ Å, $\beta = 104.96(4)°$ and a orange–red, β-form as monoclinic space group $I2/c$, $a = 8.703(3)$; $b = 14.965(5)$; $c = 8.703(3)$ Å, $\beta = 90.23(3)°$. Knobler and Ziolo [11] described in detail the molecular structure of the α-modification of **3** and confirmed their earlier findings [10] with regards to yellow–orange α-modification. Later, McCullough, Knobler, and Ziolo [12] described the molecular structure of the orange–red β-modification of **3** which crystallised in the orthorhombic space group $Fdd2$ with unit cell parameters; $a = 12.328(3)$; $b = 14.974(2)$ and $c = 12.291(4)$ Å, with $Z = 8$. In our course of studies on **3**, when the yellow–orange form of **3** was reacted with $AgNO_3$ or $Ag(OCOC_6H_5)$ in acetone, we obtained some solid with orange–red crystals. The single crystal X-ray diffraction study of these orange–red crystals indicated that the compound crystallized in the orthorhombic space group $Fdd2$; $a = 12.373(2)$; $b = 14.983(2)$; $c = 12.281(2)$ Å, $Z = 8$. The Te–C and Te–I distances are 2.165(1), 2.902(7) Å, respectively. In the unit cell of **3**, Te···I and I···I secondary bonds are present. The crystal data suggest that these orange–red crystals, obtained in the present investigation, correspond to orange–red β-modification of **3** as described by McCullough, Knobler and Ziolo [12]. In order to confirm that the yellow–orange or α-modification of **3** changes to the orange–red or β-modification only in the presence of acetone and $AgNO_3$ and $Ag(OCOC_6H_5)$ do not play any role in the transformation of α-modification into β-modification, the yellow–orange, α-modification was stirred with acetone only for 2 h and the orange–red crystals obtained had the same cell constants. When the yellow–orange crystals α-modification of **3** were stirred with CH_2Cl_2 or benzene, the α-modification was not converted into β-modification.

From the above discussion it is evident that we did not find the β-modification of **3** (monoclinic, space group $I2/c$) but we did observe β-modification of **3** (orthorhombic, space group $Fdd2$) in at least the above three sets of reactions. Although not conclusive, on the base of available observations, it might be reasonable to predict that the orange–red β-modification (orthorhombic, space group $Fdd2$) is more stable than the yellow–orange α-modification of **3**. In **3** the Te···I and I···I secondary bonds led to the formation of 3-dimensional polymers (Fig. 7).

It is worth comparing the salient structural features of **1**–**3** (Table 7).

1. In **1** and **2** because of stronger Te···I interactions TBP geometry is destroyed whereas it is retained in **3** because of lesser Te···I interactions. Similar predictions have been made in dimethyltellurium dihalides.
2. The elongation in Te–I bond lengths is of the order **2** > **1** > **3**.
3. The deviation in I–Te–I angles from 180° are of the order **2** > **1** > **3**.
4. The length of Te···I secondary bonds increases in the order **2** > **1** > **3**.
5. The elongation in Te–C bond lengths is of the order **3** > **1** > **2**.
6. The angle C–Te–C changes in the order **2** > **3** > **1**.
7. The angle C–Te–I varies in the order **2** > **1** > **3**.
8. The angle I–Te···I increases in the order **1** > **2** > **3**.
9. The angle C–Te···I increases in the order **1** > **2** > **3**.
10. Polymorphism exists in **3** but it is absent in **1** and **2**.
11. 2-Dimensional zigzag ribbons in the *a* direction are present in **1**, trimeric molecular aggregates are present in **2**, and a 3-dimensional polymer is present in **3**.

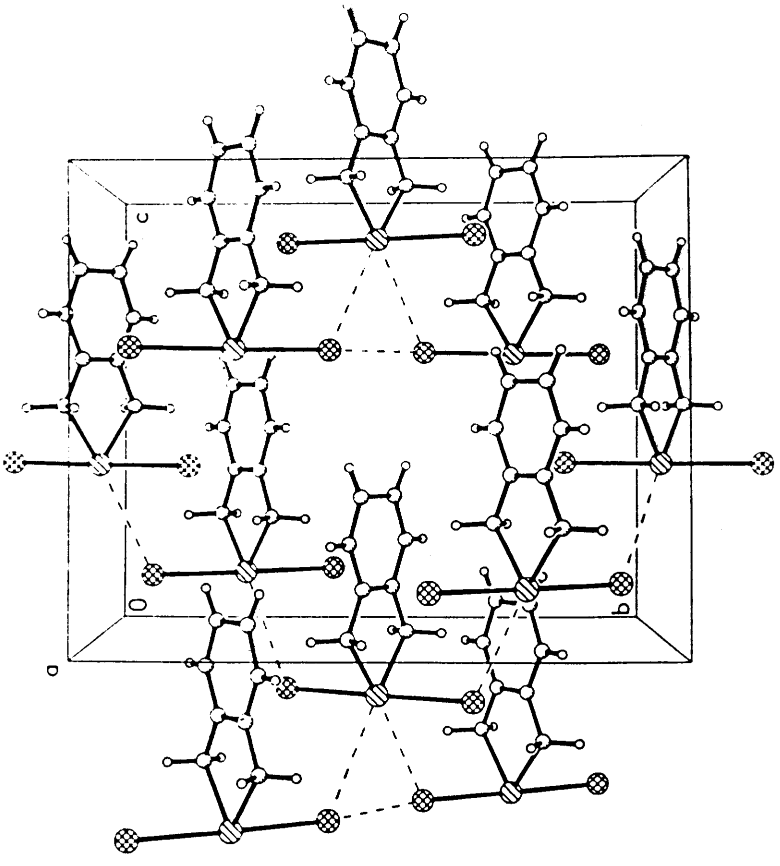

Fig. 7. The unit cell of **3** projected down *a*, showing the intermolecular Te···I and I···I secondary bonds (broken).

Table 7
Comparative bond lengths (Å) and angles (°) of **1**–**3**[a]

	1	**2**			**3**
Crystal system	Monoclinic (present work)	Orthorhombic (present work)	Monoclinic (α-form)[10]	Orthorhombic (β-form)[11]	Orthorhombic (β-form) (present work)
Space group	$P2_1/n$	$Pbcn$	$P2_1/c$	$Fdd2$	$Fdd2$
Bond lengths					
Te–C	2.157(7)	2.147(1)	2.145(1)	2.136(8)	2.165(1)
Te–I	2.925(4)	2.928(7)	2.928(1)	2.905(1)	2.902(7)
Te···I	3.808(1)	3.930(1)	3.653(1)	3.668(1)	3.673
I···I	4.039(1)	3.796(8)	–	4.042(1)	4.072
Bond angles					
C–Te–C	84.4(2)	96.6(1)	86.0(5)	86.1(5)	84.7(6)
C–Te–I	89.2(1)	89.4(1)	90.2(3)	–	89.8(7)
I–Te–I	177.0(6)	177.2(4)	176.53(4)	179.53(3)	179.49(5)
I–Te···I	90.6	90.7(6)	74.68(3)	–	90.2(4)
C–Te···I	83.0(5)	76.6(9)	74.7(3)	–	104.1
	161.6(2)	131.8(2)			170.6
		170.6(2)			

[a] Estimated S.D. is derived from averaging equivalent distances or angles.

3.2. Comparative ^{1}H-NMR spectra of 1–3

The ^{1}H-NMR spectra of **1**–**3** in $CDCl_3$ at 60 MHz gives a distinct triplet for CH_2–Te protons and a multiplet for CH_2–C protons in **1** (3.60 ppm(t), 2.84 ppm(m)) and **2** (3.58 ppm(t), 2.16 ppm(m)). CH_2–Te protons appear as a singlet (5.05 ppm) and CH protons appear as a multiplet centered at 7.49 ppm in **3** indicating the presence of **1**–**3** as monomers in solution at ambient temperature. The variable temperature multinuclear (^{1}H, ^{13}C, ^{125}Te) NMR studies in the range −60 to +60°C are in progress to ascertain the presence of supramolecular assemblies in solution.

4. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136386 for 1,1,2,3,4,5-hexahydro-,1,1-diodotellurophene (**1**) and CCDC no. 136387 for 1,1,2,3,4,5,6-heptahydro-,1,1-diiodotellurane (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

[1] R.H. Vernon, J. Chem. Soc. (1920) 86.
[2] H.D.K. Drew, J. Chem. Soc. (1929) 560.
[3] F. Einstein, J. Trotter, C. Williston, J. Chem. Soc. A (1967) 2018.
[4] G.T. Morgan, F.H. Burstall, J. Chem. Soc. (1931) 180.
[5] G.T. Morgan, H. Burgess, J. Chem. Soc. (1928) 321.
[6] T.N. Srivastava, P.C. Srivastava, R. Kumar, J. Ind. Chem. Soc. 59 (1982) 186.
[7] P.C. Srivastava, H.G. Schmidt, H.W. Roesky, Z. Naturforsch. Teil B 50 (1995) 695.
[8] P.C. Srivastava, A. Sinha, S. Bajpai, H.G. Schmidt, M. Noltemeyer, J. Organomet. Chem. 575 (1999) 261.
[9] P.C. Srivastava, S. Bajpai, R.J. Butcher, J. Organomet. Chem. 586 (1999) 119.
[10] R.F. Ziolo, W.H.H. Gunther, J. Organomet. Chem. 146 (1978) 245.
[11] C. Knobler, R.F. Ziolo, J. Organomet. Chem. 178 (1979) 423.
[12] J.D. McCullough, C. Knobler, R.F. Ziolo, Inorg. Chem. 24 (1985) 1814.
[13] I. Haiduc, R.B. King, M.G. Newton, Chem. Rev. 94 (1994) 301.
[14] T.N. Srivastava, R.C. Srivastava, M. Singh, J. Organomet. Chem. 157 (1978) 405.
[15] J.B. Lambert, R.G. Keske, Tetrahedron Lett. 47 (1967) 4755.
[16] R.T. Morrison, in: R.N. Boyd (Ed.), Organic Chemistry, sixth edition, Prentice-Hall, Englewood Cliffs, NJ, 1997, p. 446.
[17] C.V.K. Sharma, G.R. Desiraju, Perspectives in supramolecular chemistry, in: G.R. Desiraju (Ed.), The Crystal as a Supramolecular Entity, Wiley, Chichester, 1996.
[18] W.V. Farrar, J.M. Gulland, J. Chem. Soc. (1945) 11.
[19] G.M. Sheldrick, Crystallographic Computing 3, Oxford University Press, London, 1986, p. 175.
[20] G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1993.
[21] N.W. Alcock, W.D. Harrison, C. Howes, J. Chem. Soc. Dalton Trans. (1984) 1709.
[22] N.W. Alcock, J. Culver, S.M. Roe, J. Chem. Soc. Dalton Trans. (1992) 1477.
[23] 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 (1984) 97.
[24] T.S. Cameron, R.B. Amero, C. Chau, R.E. Cordes, Cryst. Struct. Commun. 9 (1980) 543.
[25] J.D. McCullough, Inorg. Chem. 14 (1975) 1142.
[26] L. Pauling, The Nature of Chemical Bond, third edition, Cornell University Press, New York, 1960.
[27] N.W. Alcock, Adv. Inorg. Chem. Radiochem. 15 (1972) 1.
[28] (a) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1964, pp. 93. (b) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1964, pp. 104.
[29] C. Knobler, J.D. McCullough, H. Hope, Inorg. Chem. 9 (1970) 797.
[30] P.C. Srivastava, S. Bajpai, R. Lath, C. Ram, R.J. Butcher, M. Zimmer, M. Veith, unpublished results.