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C(sp^3)–H···O and C(sp^2)–H···O hydrogen bonds in acyclic- and cyclic-organotellurium carboxylates

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Abstract

The reactions between R_2TeI_2 ($R_2 = (CH_3)_2$, C_4H_8, C_5H_{10}) and AgOCOR′ (R′ = C_6H_5, 4-$NO_2C_6H_4$, CH=CHC$_6$H$_5$) (molar ratio 1:2) yield diorganotellurium dicarboxylates: $(CH_3)_2Te(OCOC_6H_5)_2$ (**1**), C_5H_{10} Te(OCOC$_6$H$_5$)$_2$ (**2**), C_4H_8Te(OCO4-NO$_2$C$_6$H$_4$)$_2$ (**3**) and C_4H_8Te(OCOCH=CHC$_6$H$_5$)$_2$ (**4**). They are characterized by IR, (^{1}H, ^{13}C, ^{125}Te) solution NMR; (^{13}C, ^{125}Te) solid state NMR spectroscopy. The X-ray structures of **1**–**4** (the immediate environment about tellurium is that of distorted trigonal bipyramidal geometry with a stereochemically active electron lone pair) are described in the context of their ability to generate intermolecular C–H···O hydrogen bonds, which lead to the formation of supramolecular assemblies. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organotellurium carboxylates; Intermolecular C–H···O hydrogen bonds; Supramolecular assemblies

1. Introduction

The self assembly by means of specific intermolecular noncovalent interactions [1,2] resulting in supramolecular structures by complexation chemistry utilizing metal ions and suitable ligands is one approach to new structures with unusual, useful and interesting properties [3]. Tellurium possesses inherent tendency to form Te···X (X = F, Cl, Br, I, N, O, S) noncovalent interactions (termed as secondary bonds by Alcock [4]), which are now commonplace in organotellurium chemistry. However, the use of Te···X secondary bonds in the synthesis of supramolecular associations in organotellurium(IV) complexes is only of recent origin. King and coworkers [5] have compiled and discussed supramolecular associations in organotellurium(IV) complexes containing Te···S interactions. In the past in the X-ray structures of organotellurium(IV) carboxylates [6], Te···O interactions have been quoted but they were not interpreted in terms of supramolecular associations; may be because this concept was either not known or it was not fully developed [1,2]. We have, recently, reported ···Te–O–Te···Te–O–Te···Te–O–Te··· cross linked chains [7]; Te···O interactions containing zig-zag polymeric chains [8] based supramolecular associations, Te···I interactions induced (a) ordered oligomers (b) ribbons and (c) three dimensional supramolecular arrays [9]. Apart from specific intermolecular noncovalent interactions [1,2], the hydrogen bonds with well characterized geometry and robustness are also frequently used in designing supramolecular arrays [10,11] and amongst hydrogen bonds, C–H···O hydrogen bonds play a dominant role in the stability and possibly even in the activity of biological macromolecules [12], organometallic crystals [13] and molecular recognition processes [2]. A Cambridge Structural Data base (CSD) search reveals that there is, so far no report of C–H···O hydrogen bonds in organotellurium complexes. In the above context, we have examined acyclic- and cyclic-organotellurium carboxylates viz. bis(benzoato)dimethyl tellurium (IV) (**1**); 1,1,2,3,4,5,6-heptahydro-1,1-di(benzoato)tellurane (**2**); 1,1,2,3,4,5-hexahydro-1,1-di(4-nitrobenzoato)tellurophene (**3**) and

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Table 1
Crystal data and structure refinement parameters for complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{16}H_{16}O_4Te$	$C_{19}H_{20}O_4Te$	$C_{18}H_{16}N_2O_3Te$	$C_{22}H_{22}O_4Te$
Formula weight	399.89	439.95	515.93	478.00
Temperature (K)	293(2)	158(2)	293(2)	295(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	*Aba*2	$P2_1/c$	$P\bar{1}$	*Pcab*
Unit cell dimensions				
a (Å)	11.4337(16)	10.0876(8)	6.2813(11)	10.4865(7)
b (Å)	29.280(4)	17.0245(12)	11.534(2)	14.9597(10)
c (Å)	9.6804(11)	10.6499(8)	14.392(2)	26.2341(17)
α (°)	90	90	69.289(9)	90
β (°)	90	108.8100(10)	88.238(14)	90
γ (°)	90	90	89.792(13)	90
V (Å^3)	3240.8(8)	1731.3(2)	974.9(3)	4115.5(5)
Z	8	4	2	8
μ (mm^{-1})	1.847	1.738	1.575	1.469
Index ranges	$0\leq h\leq 17$, $-44\leq k\leq 0$, $-14\leq l\leq 0$	$-12\leq h\leq 12$, $-7\leq k\leq 21$, $-12\leq l\leq 13$	$0\leq h\leq 8$, $-14\leq k\leq 14$, $-18\leq l\leq 18$	$-13\leq h\leq 13$, $-19\leq k\leq 19$, $-34\leq l\leq 34$
Reflections collected	3017	11788	4821	43030
Independent reflections	3017 ($R_{int} = 0.0000$)	3377 ($R_{int} = 0.0297$)	4414 ($R_{int} = 0.0172$)	5063 ($R_{int} = 0.0454$)
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0444$, $wR_2 = 0.0934$	$R_1 = 0.0186$, $wR_2 = 0.0487$	$R_1 = 0.0332$, $wR_2 = 0.0777$	$R_1 = 0.0258$, $wR_2 = 0.0511$
R indices(all data)	$R_1 = 0.0809$, $wR_2 = 0.1185$	$R_1 = 0.0211$, $wR_2 = 0.0496$	$R_1 = 0.0427$, $wR_2 = 0.0831$	$R_1 = 0.0447$, $wR_2 = 0.0554$

1,1,2,3,4,5-hexahydro-1,1-di(cinnamato)tellurophene (**4**) containing acidic –CH_3, –CH_2–, >CH– groups and carboxylate groups and we have found that intermolecular C–H···O=C hydrogen bonds are responsible for the formation of supramolecular assemblies in these organotellurium (IV)carboxylates.

2. Experimental

2.1. Physical measurements

Elemental analyses for C, H and N were carried out on an Elemental Analyser Heraeus Carlo Erba 1108. IR spectra were recorded using a Shimadzu 8210 PC FTIR spectrometer in the frequency range 4000–350 cm^{-1} with the samples in KBr discs. The (^{1}H, ^{13}C, ^{125}Te) solution NMR spectra were recorded in a Varian VXR-3005 spectrometer in $CDCl_3$. The operating frequency for ^{125}Te solution NMR was 94.752 MHz with a pulse width of 9.5 μs and a delay of 1 s. The ^{13}C/^{125}Te CP/MAS solid state NMR spectral studies were carried out at Institut für Anorganische Chemie Universität des Saarlandes, Saarbrücken, Germany. ^{125}Te-NMR (solution and solid) spectra were referenced to Me_2Te ($\delta = 0$ ppm). The single crystal X-ray diffraction studies were carried out at the Chemistry Department, Howard University, Washington, DC.

2.2. Synthesis

Acetone was purified by standard procedure and freshly distilled prior to use. Te was used as received. Organotellurium diiodides viz. $(CH_3)_2TeI_2$ [14], $C_4H_8TeI_2$ [15] and $C_5H_{10}TeI_2$ [16] were prepared by literature methods.

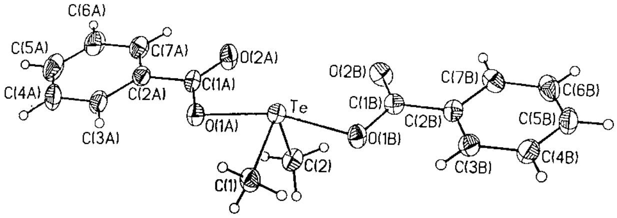

Fig. 1. Crystal structure of **1**.

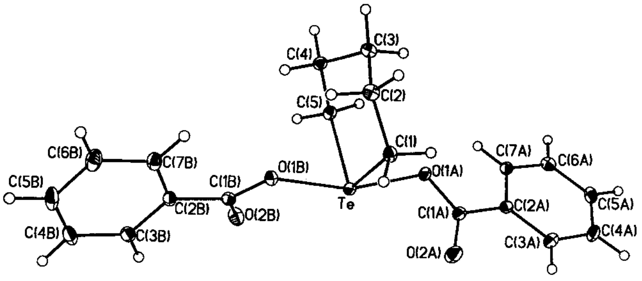

Fig. 2. Crystal structure of **2**.

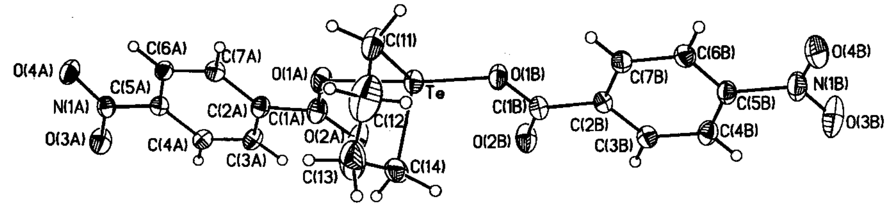

Fig. 3. Crystal structure of **3**.

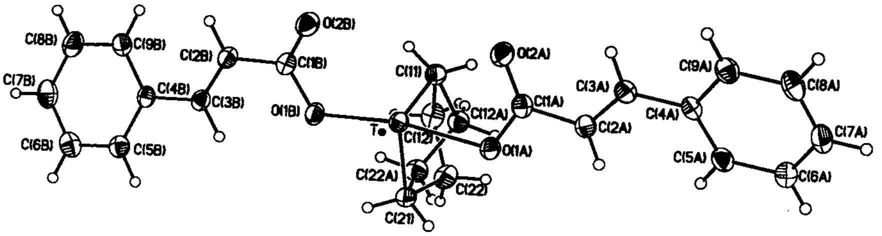

Fig. 4. Crystal structure of **4**.

2.2.1. *Bis(benzoato)dimethyltellurium(IV) (**1**)*

To an acetone solution (30 ml) of $(CH_3)_2TeI_2$ (4.116 g, 10 mmol) was added freshly prepared $AgOCOC_6H_5$ (4.580 g, 20 mmol). The mixture was stirred at room temperature for 4 h and filtered. The solid mass left after filtration was extracted twice with acetone. The acetone extract, after 24 h, yielded white needle shaped crystals of $(CH_3)_2Te(OCOC_6H_5)_2$ (**1**). Complex **1** yield: 3.40 g (85%), m.p.130 °C. Anal. Calc. for $C_{16}H_{16}O_4Te$: C, 48.04; H, 4.00; Te, 31.93. Found: C, 48.00; H, 3.98; Te, 31.82%. ^1H-NMR δ: 2.71 (s, 6H, CH_3), 7.41–8.01 (m, 10H, C_6H_5). $^{13}C\{^1H\}$-NMR δ: 17.34 (CH_3), 128.20, 129.84, 131.60, 132.39 (C_6H_5), 172.0 (>C=O). ^{125}Te-NMR δ: 943.7 (septet, $^2J_{TeH} = 24$ Hz); ^{13}C CP/MAS-NMR isotropic shift δ: 12, 22 (CH_3); 171, 173 (>C=O); ^{125}Te-CP/MAS NMR isotropic shift δ: 998.4. FT-IR (KBr, cm^{-1}): 1590 s (ν_{as} CO), 1560 s (ν_s CO).

2.2.2. *1,1,2,3,4,5,6-heptahydro-1,1-di(benzoato)tellurane (**2**)*

To an acetone solution (30 ml) of $C_5H_{10}TeI_2$ (2 g, 4.428 mmol) was added freshly prepared $AgOCOC_6H_5$ (2.028 g, 8.856 mmol). The mixture was stirred at room temperature for 2 h and filtered to get rid of AgI and excess silver benzoate. The filtrate, so obtained, on concentration under vaccum, yielded after 24 h, white needle shaped crystals of $C_5H_{10}Te(OCOC_6H_5)_2$ (**2**). Complex **2** yield: 1.56 g (80%), m.p.138–140° C. Anal. Calc. for $C_{19}H_{20}O_4Te$: C, 51.86; H, 4.54; Te, 29.02. Found: C, 51.72; H, 4.45; Te, 29.00%. ^1H-NMR δ: 3.30 (t, 4H, CH_2Te), 1.80–2.01 (m, 6H, CH_2C), 7.40–8.05 (m, 10H, C_6H_5). $^{13}C\{^1H\}$-NMR δ: 20.40, 27.07, 29.82 (CH_2), 128.19, 129.83, 131.97 (C_6H_5), 171.84 (>C=O). ^{125}Te-NMR δ: 917.8 (q, $^2J_{TeH} = 46$ Hz, $^3J_{TeH} = 12$ Hz); ^{125}Te CP/MAS NMR isotropic shift δ: 902. FT-IR (KBr, cm^{-1}): 1614 s (ν_{as} CO), 1600 s (ν_s CO).

Preparation and characterization of 1,1,2,3,4,5-hexahydro-1,1-di(4-nitrobenzoato)tellurophene (**3**) crystals has been previously reported by us [11]. ^1H-NMR δ: 2.67 (s, 4H, CH_2C), 3.44 (s, 4H, CH_2Te), 8.12–8.25 (m, 8H, C_6H_4). $^{13}C\{^1H\}$-NMR δ: 34.75 (CCH_2), 47.66 ($TeCH_2$), 123.41, 130.92, 137.20 (C_6H_4), 169.95(>C=O). FT-IR (KBr, cm^{-1}): 1657 s (ν_{as} CO), 1650 s (ν_s CO).

Table 2
Bond lengths (Å) and bond angles (°) for **1** [a]

Bond lengths			
Te–C(1)	2.095(9)	Te–C(2)	2.101(9)
Te–O(1B)	2.143(5)	Te–O(1A)	2.185(5)
O(1A)–C(1A)	1.303(11)	O(2A)–C(1A)	1.220(12)
O(1B)–C(1B)	1.342(10)	O(2B)–C(1B)	1.206(14)
C(1A)–C(2A)	1.521(11)	C(2A)–C(7A)	1.371(15)
C(2A)–C(3A)	1.383(13)	C(3A)–C(4A)	1.416(15)
C(4A)–C(5A)	1.37(2)	C(5A)–C(6A)	1.36(2)
C(6A)–C(7A)	1.386(14)	C(1B)–C(2B)	1.504(12)
C(2B)–C(3B)	1.390(13)	C(2B)–C(7B)	1.406(13)
C(3B)–C(4B)	1.382(13)	C(4B)–C(5B)	1.397(18)
C(5B)–C(6B)	1.352(18)	C(6B)–C(7B)	1.370(16)
Bond angles			
C(1)–Te–C(2)	97.0(5)	C(1)–Te–O(1B)	83.0(3)
C(2)–Te–O(1B)	87.1(3)	C(1)–Te–O(1A)	84.8(3)
C(2)–Te–O(1A)	86.5(3)	O(1B)–Te–O(1A)	165.4(2)
C(1A)–O(1A)–Te	109.7(5)	C(1B)–O(1B)–Te	109.3(6)
O(2A)–C(1A)–O(1A)	123.0(7)	O(2A)–C(1A)–C(2A)	120.3(8)
O(1A)–C(1A)–C(2A)	116.7(7)	C(7A)–C(2A)–C(3A)	121.8(9)
C(7A)–C(2A)–C(1A)	118.2(9)	C(3A)–C(2A)–C(1A)	119.9(9)
C(2A)–C(3A)–C(4A)	117.7(12)	C(5A)–C(4A)–C(3A)	119.7(12)
C(6A)–C(5A)–C(4A)	121.4(11)	C(5A)–C(6A)–C(7A)	120.1(14)
C(2A)–C(7A)–C(6A)	119.2(12)	O(2B)–C(1B)–O(1B)	122.4(8)
O(2B)–C(1B)–C(2B)	124.4(8)	O(1B)–C(1B)–C(2B)	113.1(10)
C(3B)–C(2B)–C(7B)	120.1(10)	C(3B)–C(2B)–C(1B)	122.7(8)
C(7B)–C(2B)–C(1B)	117.1(11)	C(4B)–C(3B)–C(2B)	119.5(11)
C(3B)–C(4B)–C(5B)	119.9(14)	C(6B)–C(5B)–C(4B)	119.8(11)
C(5B)–C(6B)–C(7B)	122.1(12)	C(6B)–C(7B)–C(2B)	118.4(15)

[a] Symmetry transformations used to generate equivalent atoms.

Table 3
Bond lengths (Å) and bond angles (°) for **2** [a]

Bond lengths			
Te–C(1)	2.127(2)	Te–C(5)	2.1317(18)
Te–O(1B)	2.1568(13)	Te–O(1A)	2.1671(13)
O(1A)–C(1A)	1.306(2)	O(2A)–C(1A)	1.224(2)
O(1B)–C(1B)	1.312(2)	O(2B)–C(1B)	1.222(3)
C(1)–C(2)	1.520(3)	C(2)–C(3)	1.531(3)
C(3)–C(4)	1.526(3)	C(4)–C(5)	1.525(3)
C(1A)–C(2A)	1.501(3)	C(2A)–C(3A)	1.390(3)
C(2A)–C(7A)	1.398(3)	C(3A)–C(4A)	1.380(3)
C(4A)–C(5A)	1.383(3)	C(5A)–C(6A)	1.388(3)
C(6A)–C(7A)	1.390(3)	C(1B)–C(2B)	1.498(3)
C(2B)–C(7B)	1.390(3)	C(2B)–C(3B)	1.395(3)
C(3B)–C(4B)	1.388(3)	C(4B)–C(5B)	1.377(4)
C(5B)–C(6B)	1.385(4)	C(6B)–C(7B)	1.389(3)
Bond angles			
C(1)–Te–C(5)	97.89(7)	C(1)–Te–O(1B)	83.80(7)
C(5)–Te–O(1B)	85.97(6)	C(1)–Te–O(1A)	86.27(7)
C(5)–Te–O(1A)	82.51(6)	O(1B)–Te–O(1A)	163.60(5)
C(1A)–O(1A)–Te	113.71(12)	C(1B)–O(1B)–Te	109.89(12)
C(2)–C(1)–Te	115.52(13)	C(1)–C(2)–C(3)	115.45(17)
C(4)–C(3)–C(2)	112.96(16)	C(5)–C(4)–C(3)	114.27(16)
C(4)–C(5)–Te	113.64(12)	O(2A)–C(1A)–O(1A)	123.1(2)
O(2A)–C(1A)–C(2A)	122.11(19)	O(1A)–C(1A)–C(2A)	114.81(16)
C(3A)–C(2A)–C(7A)	119.67(19)	C(3A)–C(2A)–C(1A)	119.19(18)
C(7A)–C(2A)–C(1A)	121.12(17)	C(4A)–C(3A)–C(2A)	120.4(2)
C(3A)–C(4A)–C(5A)	120.1(2)	C(4A)–C(5A)–C(6A)	120.1(2)
C(5A)–C(6A)–C(7A)	120.1(2)	C(6A)–C(7A)–C(2A)	119.55(18)
O(2B)–C(1B)–O(1B)	123.19(18)	O(2B)–C(1B)–C(2B)	121.46(18)
O(1B)–C(1B)–C(2B)	115.34(17)	C(7B)–C(2B)–C(3B)	120.24(19)
C(7B)–C(2B)–C(1B)	121.51(18)	C(3B)–C(2B)–C(1B)	118.22(19)
C(4B)–C(3B)–C(2B)	119.7(2)	C(5B)–C(4B)–C(3B)	119.7(2)
C(4B)–C(5B)–C(6B)	121.0(2)	C(5B)–C(6B)–C(7B)	119.7(2)
C(6B)–C(7B)–C(2B)	119.6(2)		

[a] Symmetry transformations used to generate equivalent atoms.

2.2.3. 1,1,2,3,4,5-hexahydro-1,1-di(cinnamato)-tellurophene (4)

Complex (**4**) was prepared in the same way as (**2**) from $C_4H_8TeI_2$ (2 g, 4.570 mmol) and freshly prepared $AgOCOCH{=}CHC_6H_5$ (2.33 g, 9.140 mmol). White hexagonal single crystals of $C_4H_8Te(OCOCH{=}CHC_6H_5)_2$ (**4**) grew by slow diffusion method in the filtrate after 24 h. Complex **4** yield: 1.66 g (76%), m.p.160 °C. Anal. Calc. for $C_{22}H_{22}O_4Te$: C, 55.27; H, 4.60; Te, 26.71. Found: C, 55.16; H, 4.52; Te, 26.68%. FT-IR (KBr, cm^{-1}): 1645 s (ν_{as} CO), 1608 s (ν_s CO).

2.3. X-ray measurements

X-ray measurements were performed in a Bruker P4S diffractometer using graphite monochromated Mo–K_α radiation. The unit cells were determined from 25 randomly selected reflections using the automatic search index and least square refinement. The structure of **1** was solved in space group *Aba*2, **2** in space group $P2_1/c$, **3** in space group *P*1 and **4** in space group *Pcab*. The data were corrected for Lorentz, polarization and absorption effects. The data were monitered by measuring three standard reflections at every 97 reflections. The structures were solved by the routine heavy atom method using SHELXS-86 [17] and Fourier methods and refined by full matrix least squares using the SHELXL-93 program [18] with the nonhydrogen atoms anisotropic and hydrogen atoms having fixed isotropic thermal parameters of 0.08 Å^2. Relevent crystallographic parameters are given in Table 1.

3. Results and discussion

The X-ray structures of bis(benzoato)dimethyltellurium(IV) (**1**); 1,1,2,3,4,5,6-heptahydro-1,1-di(benzoato)tellurane (**2**); 1,1,2,3,4,5-hexahydro-1,1-di(4-nitrobenzoato) tellurophene (**3**) and 1,1,2,3,4,5-hexa-

Table 4
Bond lengths (Å) and bond angles (°) for **3** [a]

Bond lengths			
Te–C(11)	2.085(4)	Te–C(14)	2.109(4)
Te–O(1B)	2.167(2)	Te–O(1A)	2.178(2)
O(1A)–C(1A)	1.297(4)	O(2A)–C(1A)	1.220(4)
O(3A)–N(1A)	1.213(4)	O(4A)–N(1A)	1.219(4)
O(1B)–C(1B)	1.306(4)	O(2B)–C(1B)	1.223(4)
O(3B)–N(1B)	1.213(5)	O(4B)–N(1B)	1.215(5)
N(1A)–C(5A)	1.473(4)	N(1B)–C(5B)	1.482(4)
C(11)–C(12)	1.472(9)	C(12)–C(13)	1.466(10)
C(13)–C(14)	1.519(8)	C(1A)–C(2A)	1.494(4)
C(2A)–C(3A)	1.392(4)	C(2A)–C(7A)	1.400(4)
C(3A)–C(4A)	1.377(4)	C(4A)–C(5A)	1.383(4)
C(5A)–C(6A)	1.382(4)	C(6A)–C(7A)	1.369(4)
C(1B)–C(2B)	1.498(4)	C(2B)–C(7B)	1.388(4)
C(2B)–C(3B)	1.396(4)	C(3B)–C(4B)	1.374(5)
C(4B)–C(5B)	1.380(5)	C(5B)–C(6B)	1.376(5)
C(6B)–C(7B)	1.375(4)		
Bond angles			
C(11)–Te–C(14)	86.6(2)	C(11)–Te–O(1B)	83.69(13)
C(14)–Te–O(1B)	88.10(12)	C(11)–Te–O(1A)	83.04(13)
C(14)–Te–O(1A)	88.90(12)	O(1B)–Te–O(1A)	166.54(8)
C(1A)–O(1A)–Te	111.7(2)	C(1B)–O(1B)–Te	109.0(2)
O(3A)–N(1A)–O(4A)	123.1(3)	O(3A)–N(1A)–C(5A)	118.7(3)
O(4A)–N(1A)–C(5A)	118.1(3)	O(3B)–N(1B)–O(4B)	123.8(3)
O(3B)–N(1B)–C(5B)	117.5(4)	O(4B)–N(1B)–C(5B)	118.7(3)
C(12)–C(11)–Te	105.7(3)	C(13)–C(12)–C(11)	114.6(5)
C(12)–C(13)–C(14)	112.4(5)	C(13)–C(14)–Te	104.6(3)
O(2A)–C(1A)–O(1A)	122.5(3)	O(2A)–C(1A)–C(2A)	122.0(3)
O(1A)–C(1A)–C(2A)	115.6(3)	C(3A)–C(2A)–C(7A)	119.3(3)
C(3A)–C(2A)–C(1A)	119.4(3)	C(7A)–C(2A)–C(1A)	121.3(3)
C(4A)–C(3A)–C(2A)	120.8(3)	C(3A)–C(4A)–C(5A)	118.3(3)
C(6A)–C(5A)–C(4A)	122.2(3)	C(6A)–C(5A)–N(1A)	119.1(3)
C(4A)–C(5A)–N(1A)	118.7(3)	C(7A)–C(6A)–C(5A)	119.0(3)
C(6A)–C(7A)–C(2A)	120.3(3)	O(2B)–C(1B)–O(1B)	123.2(3)
O(2B)–C(1B)–C(2B)	121.5(3)	O(1B)–C(1B)–C(2B)	115.3(3)
C(7B)–C(2B)–C(3B)	119.5(3)	C(7B)–C(2B)–C(1B)	122.2(3)
C(3B)–C(2B)–C(1B)	118.3(3)	C(4B)–C(3B)–C(2B)	120.2(3)
C(3B)–C(4B)–C(5B)	118.6(3)	C(6B)–C(5B)–C(4B)	122.8(3)
C(6B)–C(5B)–N(1B)	118.4(3)	C(4B)–C(5B)–N(1B)	118.8(3)
C(7B)–C(6B)–C(5B)	118.0(3)	C(6B)–C(7B)–C(2B)	120.9(3)

[a] Symmetry transformations used to generate equivalent atoms.

Table 5
Bond lengths (Å) and bond angles (°) for **4** [a]

Bond lengths			
Te–C(21)	2.115(2)	Te–C(11)	2.122(2)
Te–O(1B)	2.1505(15)	Te–O(1A)	2.1527(15)
O(1A)–C(1A)	1.306(3)	O(2A)–C(1A)	1.223(3)
O(1B)–C(1B)	1.316(3)	O(2B)–C(1B)	1.218(3)
C(11)–C(12A)	1.519(5)	C(11)–C(12)	1.522(4)
C(21)–C(22A)	1.521(6)	C(21)–C(22)	1.533(4)
C(12)–C(22)	1.510(5)	C(12A)–C(22A)	1.507(7)
C(1A)–C(2A)	1.477(3)	C(2A)–C(3A)	1.318(3)
C(3A)–C(4A)	1.471(3)	C(4A)–C(9A)	1.389(3)
C(4A)–C(5A)	1.390(3)	C(5A)–C(6A)	1.373(3)
C(6A)–C(7A)	1.377(3)	C(7A)–C(8A)	1.361(4)
C(8A)–C(9A)	1.382(3)	C(1B)–C(2B)	1.474(3)
C(2B)–C(3B)	1.317(3)	C(3B)–C(4B)	1.464(3)
C(4B)–C(5B)	1.382(3)	C(4B)–C(9B)	1.398(3)
C(5B)–C(6B)	1.377(3)	C(6B)–C(7B)	1.365(4)
C(7B)–C(8B)	1.383(4)	C(8B)–C(9B)	1.385(3)
Bond angles			
C(21)–Te–C(11)	85.96(10)	C(21)–Te–O(1B)	82.06(8)
C(11)–Te–O(1B)	86.53(9)	C(21)–Te–O(1A)	81.31(8)
C(11)–Te–O(1A)	87.44(9)	O(1B)–Te–O(1A)	162.66(6)
C(1A)–O(1A)–Te	114.11(14)	C(1B)–O(1B)–Te	112.40(14)
C(12A)–C(11)–C(12)	25.9(3)	C(12A)–C(11)–Te	103.6(4)
C(12)–C(11)–Te	105.7(2)	C(22A)–C(21)–C(22)	27.9(4)
C(22A)–C(21)–Te	104.8(4)	C(22)–C(21)–Te	105.40(19)
C(22)–C(12)–C(11)	110.9(3)	C(12)–C(22)–C(21)	110.4(3)
C(22A)–C(12A)–C(11)	110.2(6)	C(12A)–C(22A)–C(21)	108.5(6)
O(2A)–C(1A)–O(1A)	122.9(2)	O(2A)–C(1A)–C(2A)	123.3(2)
O(1A)–C(1A)–C(2A)	113.8(2)	C(3A)–C(2A)–C(1A)	123.0(2)
C(2A)–C(3A)–C(4A)	127.1(2)	C(9A)–C(4A)–C(5A)	117.6(2)
C(9A)–C(4A)–C(3A)	119.8(2)	C(5A)–C(4A)–C(3A)	122.60(19)
C(6A)–C(5A)–C(4A)	121.1(2)	C(5A)–C(6A)–C(7A)	120.1(3)
C(8A)–C(7A)–C(6A)	120.0(2)	C(7A)–C(8A)–C(9A)	120.1(2)
C(8A)–C(9A)–C(4A)	121.1(2)	O(2B)–C(1B)–O(1B)	122.4(2)
O(2B)–C(1B)–C(2B)	121.9(2)	O(1B)–C(1B)–C(2B)	115.7(2)
C(3B)–C(2B)–C(1B)	124.0(2)	C(2B)–C(3B)–C(4B)	127.2(2)
C(5B)–C(4B)–C(9B)	118.2(2)	C(5B)–C(4B)–C(3B)	119.7(2)
C(9B)–C(4B)–C(3B)	122.1(2)	C(6B)–C(5B)–C(4B)	121.5(2)
C(7B)–C(6B)–C(5B)	119.9(3)	C(6B)–C(7B)–C(8B)	120.2(2)
C(7B)–C(8B)–C(9B)	120.1(3)	C(8B)–C(9B)–C(4B)	120.1(2)

[a] Symmetry transformations used to generate equivalent atoms.

hydro-1,1-di(cinnamato)tellurophene (**4**) show them to possess distorted trigonal bipyramidal geometry around Te with two $-CH_3$ groups in **1** or two $-CH_2-$ groups in **2**–**4** and stereochemically active electron lone pair occupying equatorial positions while unidentate carboxylates ($OCOC_6H_5$, $OCO_4-NO_2C_6H_4$, $OCOCH{=}CHC_6H_5$) groups are at axial positions as per Valence Shell Electron Pair Repulsion (VSEPR) model [19,20] (Figs. 1–4) (Tables 2–5).

C–H···O hydrogen bond, in organic compounds, is assumed to exist in those cases where the C···O distance (D), H···O distance (d) and the C–H···O angle (θ) are such that $2.8 < D < 4.0$ Å, $2.0 < d < 3.0$ Å and $110 < \theta < 180°$ [21]. A retrieval from the Cambridge Structural Data base of organometallic crystal structures of the first row transition elements containing CO ligands has been reported by Braga et al. [13a] and geometrical calculations are performed by using QUEST 3D-GSTAT, an automatic graphics nonbonded search program of the CSD. A bonafide C–H···O hydrogen bond is considered to be one where the C···O distance, H···O distance and C–H···O angle are in the ranges 3.10–3.50 Å, 2.00–2.80 Å, 150–180°, respectively. These C–H···O hydrogen bonds are primarily electrostatic, falling off much more slowly with distance [13a] and in the context of supramolecular associations, it is their directionality which makes them important as crystal structure directors [13f]. In the present report, the parameters related to C–H···O interactions viz. C···O distance, H···O distance and C–H···O angle lie in the ranges 3.16–3.53 Å, 2.44–2.63 Å, 150.4–175.6°, respectively (Table 6). They are in close agreement with the above quoted reports of organic and organometallic compounds and hence it is concluded that the complexes **1**–**4** contain C–H···O hydrogen bonds which lead to the formation of supramolecular assemblies. ^{125}Te CP-MAS solid state NMR of **1** shows isotropic shift at 998.4 ppm, which is comparable to the shift in solution ^{125}Te NMR (943.7 ppm) of **1**. The ^{13}C CP-MAS NMR of **1** indicates two methyl resonances (12, 22 ppm) and two C=O resonances (171, 173 ppm). The aryl resonances are overlapping. These results are in sharp contrast to solution ^{13}C NMR of **1** (δCH_3 17.34 ppm, δ_{CO} 172.0 ppm) and indicate that there are two types of symmetrically equivalent $-CH_3$ and –C=O groups in solid state of **1** because of selective participation of one $-CH_3$ and one –C=O in intermolecular C–H···O hydrogen bond formation (Fig. 5). The ^{125}Te CP-MAS solid state NMR of **2** shows isotropic shift at 902.0 ppm, which is also comparable to that of solution ^{125}Te NMR (917.83 ppm). In FT-IR spectra of **1**–**4**, the

Table 6
C–H···O hydrogen bond related parameters of **1**–**3**

Complex	C···O (D) (Å)	H···O (d) (Å)	C–H···O (θ) (°)
$(CH_3)_2Te(OCOC_6H_5)_2$ (**1**)	3.169 [C1C···O2A]	2.510 [H1C···O2A)	175.6 [C1C–H1C···O2A]
$C_5H_{10}Te(OCOC_6H_5)_2$ (**2**)	3.318 [C1C···O2A]	2.618 [H1A···O2A]	152.9 [C1C–H1A···O2A]
$C_6H_8Te(OCO4\text{-}NO_2C_6H_4)_2$ (**3**)	3.297 [C4A···O2B]	2.449 [H4A···O2B]	161.7 [C4A–H4A···O2B]
	3.532 [C3A···O2A]	2.638 [H3A···O2A]	166.3 [C3A–H3A···O2A]
	3.432 [C3B···O3A]	2.602 [H3B···O3A]	150.4 [C3B–H3B···O3A]

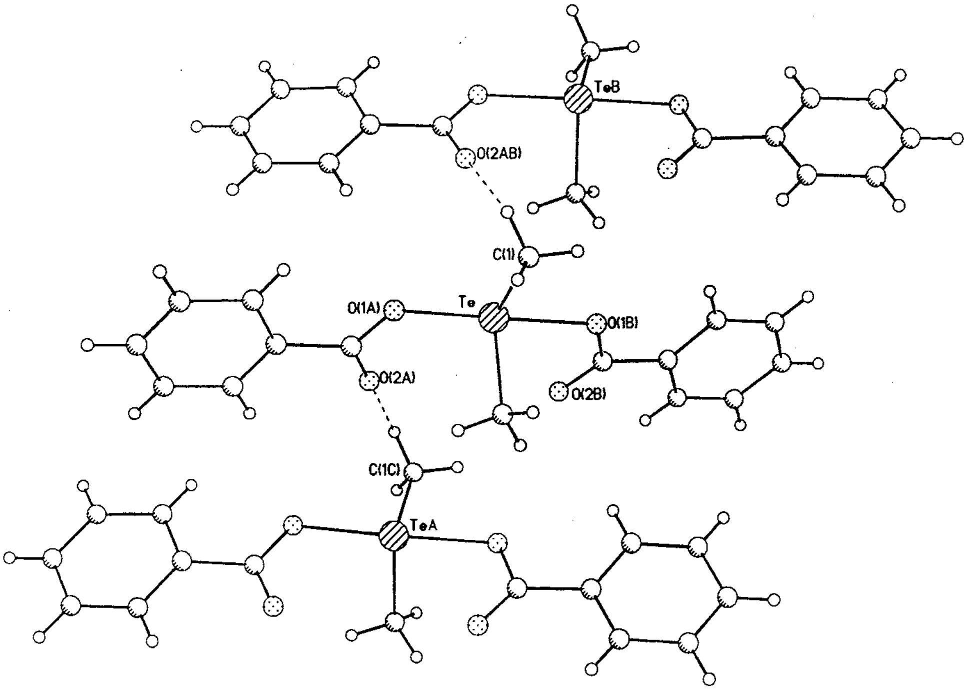

Fig. 5. Molecules of **1** connected through C(sp^3)–H···O hydrogen bonds.

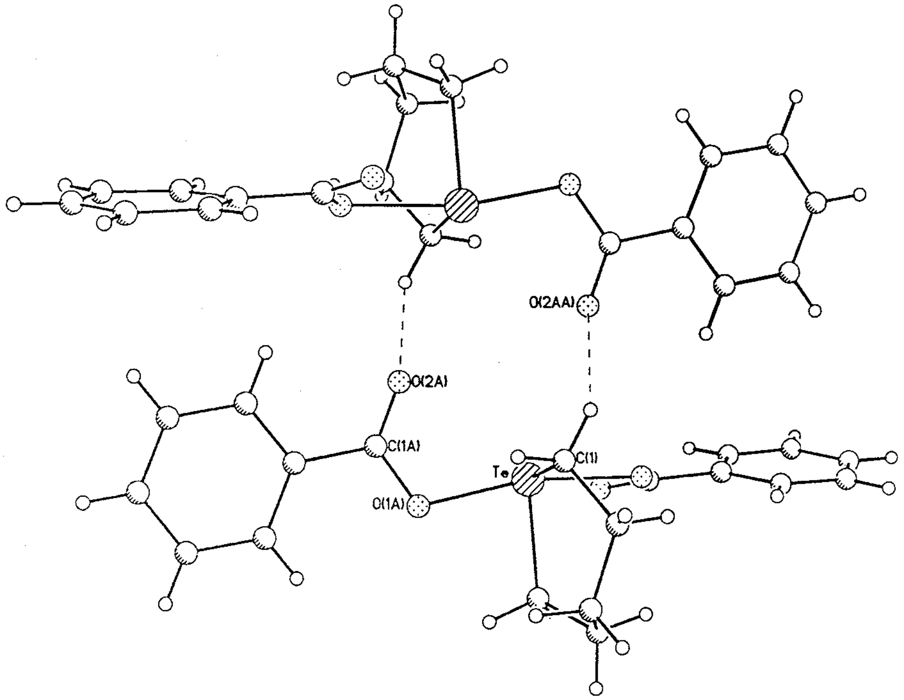

Fig. 6. Molecules of **2** connected through C(sp^3)–H···O hydrogen bonds.

splittings of >C=O stretching in each case, supports the presence of C–H···O hydrogen bond [22]. The FT-IR data (**1**–**4**) coupled with solid state NMR data of **1**, **2** are additional supportive evidences in favour of C–H···O hydrogen bond formation.

In each case (**1**–**4**) the oxygen of >C=O of carboxylate group acts as acceptor of hydrogen bond from acidic –CH_3– group (**1**); acidic –CH_2– group (**2**) attached to Te and >CH– group (of phenyl of ligand) of another molecule (**3**, **4**) resulting in intermolecular C(sp^3)–H···O and C(sp^2)–H···O hydrogen bonds respectively. Although, on the basis of the above available data, it is difficult to comment on the strength (strong or weak) of the C–H···O hydrogen bonds in **1**–**4** but it is clear that they do form supramolecular assemblies (Figs. 5–8).

In **1**, one hydrogen of the –CH_3 groups attached to Te, systematically enters into C(sp^3)–H···O bond formation whereas the other –CH_3 groups attached to Te remains inert and it results in the formation of zig-zag chain type supramolecular association (Fig. 5) (cf. corrugated sheets are present in the precursor $(CH_3)_2TeI_2$ involving linking of $(CH_3)_2TeI_2$ molecules through intermolecular Te···I secondary bonds [23]). In **2**, one hydrogen of the –CH_2 groups attached to Te and part of tellurium heterocycle (present in chair form part of which is flattened) enters into C(sp^3)–H···O hydrogen bond formation resulting in the ring formation (Fig. 6) (cf. trimeric aggregates which exist in the precursor $C_5H_{10}TeI_2$ interlinked through Te···I and I···I secondary bonds [9]). In both cases (**1**,**2**), the CO groups are in approximately trans plane to that of –CH_3– or –CH_2– group attached to Te. In **3**, **4** C(sp^2)–H of phenyl group of the carboxylate ($OCO4–NO_2C_6H_4$, $OCOCH=CHC_6H_5$) groups enters into hydrogen bond formation with $>$C=O of carboxylate group attached to other Te resulting in ten membered and eleven membered rings alternatively stacked together (Fig. 7) and ring formation (Fig. 8) (cf. two-dimensional zig-zag ribbons are present in the precursor $C_4H_8TeI_2$ interlinked through Te···I secondary bonds [9]). In **3** the C(sp^2)–H of phenyl group of $OCO4–NO_2C_6H_4$ also enters into hydrogen bond formation with $>$N=O of –NO_2 group. In **3**, **4** the CO group and CH group of the ligands are in the same plane. In the former cases (**1**, **2**) the acidic hydrogens of –CH_3– or –CH_2– group attached to Te are involved in the hydrogen bond formation whereas in the latter cases (**3**, **4**), the hydrogens of the ligand (carboxylate group) enter into hydrogen bond formation leading to supramolecular associations in **1**–**4**.

These results (a) represent the first detection of C–H···O hydrogen bonds in organotellurium(IV) carboxylates which lead to the formation of supramolecular assemblies (b) indicate that the change of iodide (anion) to carboxylate (anion) leads to supramolecular associations of relatively smaller complexity. By judicious choice of organotellurium moiety and that of the carboxylate ion, it would be possible to reliably use C–H···O hydrogen bonds in the crystal engineering and supramolecular associations [24] in organotelluriums.

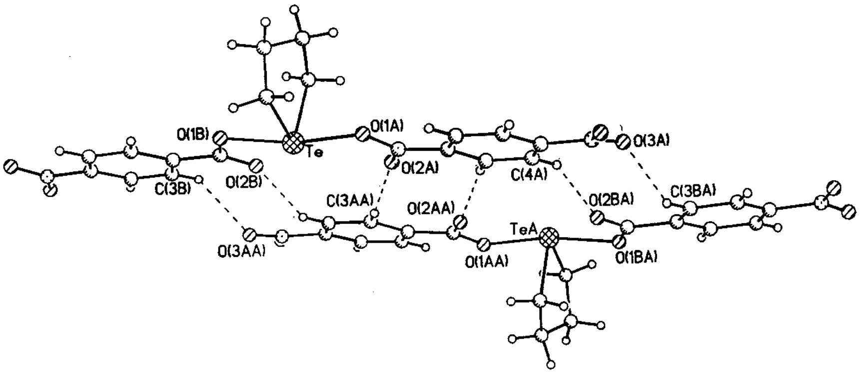

Fig. 7. Molecules of **3** connected through C(sp^2)–H···O hydrogen bonds.

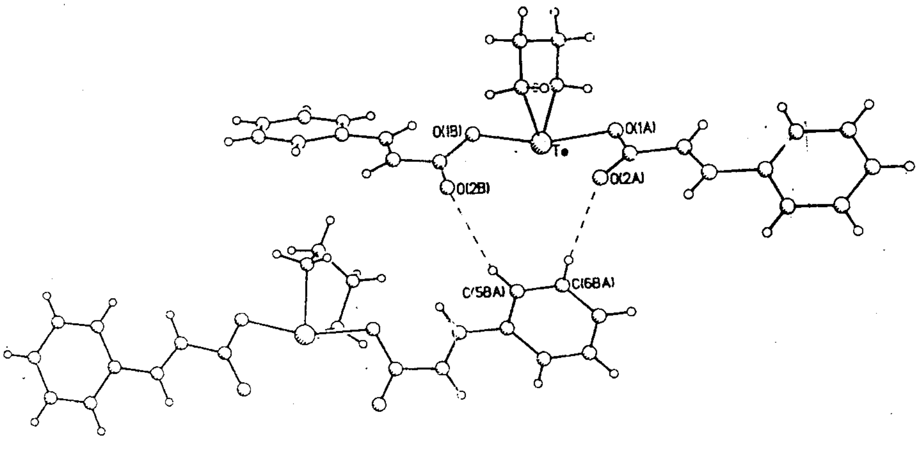

Fig. 8. Molecules of **4** connected through C(sp^2)–H···O hydrogen bonds.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 138545, 138546, 116643 and 138547 for compounds **1**–**4**, respectively. 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] (a) J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 27 (1988) 89;
(b) E. Weber, J. Mol. Graphics 7 (1989) 12;
(c) F. Vögtle, Supramolecular Chemistry, Wiley, Chichester, 1991;
(d) J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.

[2] G.R. Desiraju, Angew. Chem. Int. Ed. Engl. 34 (1995) 2311.

[3] (a) D. Philip, J.F. Stoddart, Angew. Chem. 108 (1996) 1242;
(b) D. Philip, J.F. Stoddart, Angew. Chem. Int. Ed. Engl. 35 (1996) 1155;
(c) D.S. Lawrence, T. Jiang, M. Levett, Chem. Rev. 95 (1996) 2229;
(d) P.N.W. Baxter, in: J.L. Atwood, J.E.D. Davis, D.D. MacNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, Pergamon, Oxford, 1996 (Chapter 6);
(e) M. Fujita, in: J.L. Atwood, J.E.D. Davis, D.D. MacNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, Pergamon, Oxford, 1996 (Chapter 7).

[4] N.W. Alcock, Adv. Inorg. Chem. Radiochem. 15 (1972) 1.

[5] I. Haiduc, R.B. King, M.G. Newton, Chem. Rev. 94 (1994) 301 (and references therein).

[6] (a) M.M. Mangion, E.A. Meyers, Cryst. Struct. Commun. 2 (1973) 629;
(b) N.W. Alcock, W.D. Harrison, C. Howes, J. Chem. Soc. Dalton Trans. (1984) 1709;
(c) 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;
(d) O.E. Kompan, A.A. Maksimenko, Z. Galdetskii, I.D. Sadekov, Metalloorg. Khim. (Organomet. Chem. USSR) 4 (1991) 571;
(e) J.O. Bogason, D. Dakternieks, S. Husebye, K. Maartmann-Moe, H. Zhu, Phosphorus, Sulfur Silicon 71 (1992) 13;
(f) N.W. Alcock, J. Culver, S.M. Roe, J. Chem. Soc. Dalton Trans. (1992) 1477.

[7] H.W. Roesky, R.J. Butcher, S. Bajpai, P.C. Srivastava, Phosphorus, Sulfur Silicon 161 (2000) 135.

[8] P.C. Srivastava, S. Bajpai, R.J. Butcher, J. Organomet. Chem. 586 (1999) 119.

[9] P.C. Srivastava, S. Bajpai, R. Lath, R.J. Butcher, J. Organomet. Chem. 608 (2000) 96.

[10] (a) G.M. Whitesides, E.C. Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen, D.M. Gordon, Acc. Chem. Res. 28 (1995) 37;
(b) J. Bernstein, M.C. Etter, L. Leiserowitz, in: H.B. Burgi, J.D. Dunitz (Eds.), Structure Correlation, vol. 2, VCH, Weinheim, 1994, pp. 431–507;
(c) G.R. Desiraju, in: Crystal Engineering: The Design of Organic Solids, Elsevier, New York, 1989.

[11] (a) M.C. Etter, Acc. Chem. Res. 23 (1990) 120;
(b) M.C. Etter, J. Phys. Chem. 95 (1991) 4601.

[12] (a) Z.S. Derewenda, U. Derewenda, P.M. Kobos, J. Mol. Biol. 241 (1994) 83;
(b) Z.S. Derewenda, L. Lee, V. Derewenda, J. Mol. Biol. 252 (1995) 248;
(c) M. Egli, R.V. Gessner, Proc. Natl. Acad. Sci. USA 92 (1995) 189;
(d) G.A. Leonard, K. McAuleyHecht, T. Brown, W.N. Hunter, Acta Crystallogr. D 51 (1995) 136.

[13] (a) D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi, G.R. Desiraju, J. Am. Chem. Soc. 117 (1995) 3156;
(b) V.R. Pedireddi, W. Jones, A.P. Chorlton, R. Docherty, Chem. Commun. (1996) 997;
(c) K. Biradha, G.R. Desiraju, D. Braga, F. Grepioni, Organometallics 15 (1996) 1284;
(d) D. Braga, F. Grepioni, E. Tedesco, H. Wadepohl, S. Geben, J. Chem. Soc. Dalton Trans. (1997) 1727;
(e) T. Steiner, Chem. Commun. (1997) 727;
(f) G.R. Desiraju, J. Chem. Soc. Dalton Trans. (2000) 3745.

[14] R.H. Vernon, J. Chem. Soc. (1920) 86.

[15] G.T. Morgan, F.H. Burstall, J. Chem. Soc. (1931) 180.

[16] W.V. Farrar, J.M. Gulland, J. Chem. Soc. (1945) 11.

[17] G.M. Sheldrick, Crystallographic Computing 3, Oxford University Press, London, 1986, p. 175.

[18] G.M. Sheldrick, SHELXL-93, Program for Crystal structure Refinement, University of Göttingen, Göttingen, Germany, 1993.

[19] R.J. Gillispie, J. Chem. Educ. 47 (1970) 18.

[20] R.J. Gillispie, Molecular Geometry, Van Nostrand Reinhold, New York, 1972.

[21] G.R. Desiraju, Acc. Chem. Res. 24 (1991) 290.

[22] S.N. Vinogradov, R.H. Linell, Hydrogen Bonding, Van Nostrand Reinhold, New York, 1971, pp. 75–77 (Chapter 3).

[23] L.Y.Y. Chan, F.W.B. Einstein, J. Chem. Soc. Dalton Trans. (1972) 316.

[24] (a) E.M.D. Keegstra, A.L. Spek, J.W. Zwikker, L.W. Jenneskens, J. Chem. Soc. Chem. Commun. (1994) 1633;
(b) V.R. Thalldi, K. Paneerselvam, C.J. Carrell, H.L. Carrell, G.R. Desiraju, J. Chem. Soc. Chem. Commun. (1995) 341;
(c) D. Braga, J. Chem. Soc. Dalton Trans. (2000) 3705.