ELSEVIER

Coordination Chemistry Reviews
200–202 (2000) 187–205

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Syntheses and solid-state structural chemistry of polytelluride anions

Donna M. Smith, James A. Ibers *

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Received 21 July 1999; accepted 7 January 2000

Contents

Abbreviations: 12-C-4, 1,4,7,10-tetraoxacyclododecane; 15-C-5, 1,4,7,10,13-pentaoxacyclopentadecane; 18-C-6, 1,4,7,10,13,16-hexaoxacyclooctadecane; 2.2.2-cryptand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; A, alkali metal; AE, alkaline earth metal; DMF, dimethylformamide; en, ethylenediamine; HMTN, 2,2,5,5,8,8-hexamethyl-2,5,8-triazonianonane; ICSD, Inorganic Crystal Structure Database; OC, organic cation; TMDH, 2,2,5,5-tetramethyl-2,5-diazoniahexane.

* Corresponding author. Tel.: + 1-847-4915449; fax: + 1-847-4912976.
E-mail address: ibers@chem.nwu.edu (J.A. Ibers).

PII: S0010-8545(00)00256-3

Abstract

The syntheses and structures of all published binary alkali metal and alkaline-earth tellurides and all published organic-cation (OC)/telluride anions are reviewed. Structural features amongst groups of identical anions and also between groups are compared.

Keywords: Polytelluride anions; Syntheses; Structural chemistry

1. Introduction

In recent years the chemistry of tellurometalates has been widely investigated [1–4]. The syntheses of many of these species relies on telluride anions, $[Te_y]^{2-}$, as the primary tellurium source. The history of telluride anions began in 1900 when Hugot reacted sodium with tellurium in liquid ammonia [5]. In 1922, Kraus deduced the stoichiometry of the Te^{2-} and $[Te_4]^{2-}$ anions from his investigation into the solubility of tellurium in liquid ammonia solutions of metallic sodium [6]. Zintl, Goubeau, and Dullenkopf [7] confirmed these results in 1931 and also identified the Te^{2-} and $[Te_2]^{2-}$ anions. Since that time over 200 binary tellurides have been synthesized, including 30 structurally characterized alkali/alkaline-earth (A/AE) binary tellurides. However, not until 1977 was the first organic-cation (OC)/polytelluride-anion, $[K(2.2.2.\text{-cryptand})]_2[Te_3]$,[1] isolated and structurally characterized [8]. Since then 21 different OC tellurides have been reported.

An important difference between the solid-state structural chemistry of $[Te_y]^{2-}$ and that of the lighter congeners, $[Q_y]^{2-}$ ($Q = S, Se$), arises from the propensity of tellurium to form intermolecular interactions [9,10]. This secondary bonding, which is observed in elemental Te (see below) and in many of the other compounds discussed in this Review, is virtually absent in elemental Se and S and in their compounds.

Telluride anions, $[Te_y]^{2-}$, are known for $y = 1–6$ [8,11–15], 8 [16], 12 [17], and 13 [18]. But again, in distinction from almost all polysulfide and polyselenide anions, polytelluride anions can also have charges greater than 2−, as in NaTe [19] ($[Te_5]^{4-}$) and $[Cr(en)_3][Te_6]$ [20] ($[Te_6]^{3-}$).

This Review considers the various synthetic routes to A/AE and OC polytellurides and then discusses the structures of the 30 A/AE and 21 OC tellurides that have been structurally characterized.

---

[1] See abbreviations used in this Review.

2. Syntheses

Telluride anions are generally synthesized by one of the following methods: (1) high-temperature fusion of elements with Te; (2) solution reactions involving elemental Te and $A_2(CO_3)$; (3) solventothermal reactions between elements; (4) extraction of a binary or ternary A/AE tellurium alloy in basic solvent in the presence of an encapsulating agent or large OC; (5) oxidation–reduction reactions with Lewis acids, for example $MnCl_2$; (6) by-products from electrochemical reduction of reactions of telluride anions with metal complexes in the presence of an OC. Synthetic methods (1), (2), and (3) can produce A/AE tellurides that can act as starting materials for the syntheses of some of the OC tellurides prepared by the other three methods. Syntheses of 30 binary A/AE tellurides are listed in Table 1 and those of 21 OC tellurides are listed in Table 2.

Although the majority of A/AE tellurides can be synthesized by combining elements in liquid ammonia, that process often leads to a mixture of products [21]. Growing isolable single crystals requires the more rigorous synthetic methods discussed in Table 1. Ten of the A/AE tellurides were synthesized by high-temperature fusion (300–700°C), eight by solventothermal routes (four using CH_3OH and four using ammonia), eight by the low-temperature liquid-ammonia route, and four in other ways.

For the OC tellurides, the majority (nine) were isolated from the reaction of an A/AE telluride with the solvent or with an OC/encapsulating agent. Five reactions involved oxidation–reduction with a metal salt or borate not included in the final product. Three reactions involved a ternary telluride starting material in ethylenediamine (en), liquid ammonia, or methanol where the metals are also not found in the final product. Two products formed from electrochemical dissolution of a binary telluride and two other products formed from the reaction of the elements in en. In comparing synthetic conditions to chain length, the use of an A_2Te_3 starting material under different conditions leads to $[Te_y]^{2-}$ anions, where $y = 3$, 4, 5, and 8. This illustrates the complex nature of $[Te_y]^{2-}$ solutions and the redox chemistry that takes place.

3. Structural properties

3.1. Elemental tellurium

As a basis for comparison, consider the structure of elemental Te. Te crystallizes in space group $P3_121$. The structure consists of infinite helical chains. Each atom has, in addition to two nearest neighbors at 2.835(2) Å, four other atoms 3.495(3) Å away in neighboring chains. This distance is much closer than the sum of the van der Waals radii (ca. 4.3 Å) and illustrates the propensity of Te to form intermolecular interactions. There is a distorted octahedral coordination about each Te atom that lowers the bond order within the helical chain and results in an increased bond length. The bond angle along the chain is 103.2° [22].

Table 1
Preparative information for alkali/alkaline-earth (AE) tellurides

No.	Compound	Preparative reaction[a]	Solvent/crystallization method[a]	Yield[b] (%)	Space group (R index[c])	Ref.
1	Li_2Te	$2Li+Te$	Liq. NH_3. Removed NH_3 at elevated temps.	Not given	Cubic	[23]
2	Na_2Te	$2Na+Te$	Liq. NH_3. Removed NH_3 at elevated temps.	Not given	Cubic	[23]
3	K_2Te	$2K+Te$	Liq. NH_3. Removed NH_3 at elevated temps.	Not given	Cubic	[23]
4	Cs_2Te	$2Cs+Te$	Solid–gas reaction. Cs vapor reacted with Te at 300°C.	Not given	*Pnma* (12%)	[24]
5	K_5Te_3	K_2Te+Te	Heated to 700°C for 5 h. Slow cooled to 20°C.	Not given	*I*4/*mcm* (5.9%)	[27]
6	Rb_5Te_3	Existence is mentioned but no details are given				[24]
7	Cs_5Te_3	Cs_2Te+Te	Heated to 680°C for 10 h. Slow cooled to 20°C.	Not given	*C*2/*m* (8%)	[24]
8	NaTe	$Na+Te$	Liq. NH_3 at −70°C. Warmed to 20°C then heated at 470°C for 0.5 h. Slow cooled to 300°C. Kept there for 2 weeks. Slow cooled to 20°C.	Not given	*Pbcn* (4.2%)	[19]
9	CaTe	$Ca+Te$	500°C under H_2	Not given	$Fm\bar{3}m$ (not given)	[25]
10	BaTe	Only powder information is given in the paper; no preparatory information.				[26]
11	α-K_2Te_2	$K+Te$	Liq. NH_3 at −78°C. Warmed to 20°C.	Not given	$P\bar{6}2m$ (not given)	[30]
12	β-K_2Te_2	K_2Te+Te	Heated at 550°C for 1 h (conversion from α-K_2Te_2 phase begins at 214°C). Slow cooled to 280°C. Kept there 4 days then slow cooled to 20°C.	Not given	$P6_3/mmc$ (2.3%)	[30]
13	α-Rb_2Te_2	$Rb+Te$	Liq. NH_3 at −78°C. Warmed to 20°C.	Not given	$P\bar{6}2m$ (not given)	[30]
14	β-Rb_2Te_2	α-Rb_2Te_2	Heated to 300°C under inert gas (α to β conversion begins at 210°C).	Not given	*Pbam* (4.9%)	[31]
15	Cs_2Te_2	$Cs+Te$	Liq. NH_3, −60°C.	Not given	*Pbam* (5.6%)	[31]
16	K_2Te_3	$2K+3Te$	Heated to 600°C. Annealed at 250°C for 12 h.	Not given	*Pnma* (9.9%)	[37]
17	Rb_2Te_3	$2Rb+3Te$	Supercritical NH_3, 220°C/1000 bar. Slow cooled	Not given	*Pnma* (5.4%)	[38]
18	Cs_2Te_3	$2Cs+3Te$	Supercritical NH_3, 220°C/1000 bar. Slow cooled.	Not given	$Cmc2_1$ (3.5%)	[38]

Table 1 (*Continued*)

No.	Compound	Preparative reaction[a]	Solvent/crystallization method[a]	Yield[b] (%)	Space group (R index[c])	Ref.
19	$MgTe_2$	Mg + 2Te	Heat to 670 K for 15 h. Cooled, reground, and heated to 770 K for 15 h. Quenched to 20°C.	Not given	$Pa3$ (not given)	[32]
20	$BaTe_2$	$Na_2Te + BaTe + Ta + 6Te$	Heated to 525°C for 4 days. Slow cooled to 150°C, then quenched.	Not given	$I4/mcm$ (1.6%)	[34]
21	Rb_2Te_5	2Rb + 5Te	Supercritical NH_3, 200°C/2000 bar for 1 week.	Not given	$C2/m$ (2.9%)	[43]
22	Cs_2Te_5	2Cs + 5Te	Supercritical NH_3, 200°C/2000 bar. Slow cooled	Not given	$Cmcm$ (4.1%)	[44]
23	$LiTe_3$	$Li_2Te + 5Te$	Heated to 550°C for 1 h.	Not given	$P\bar{3}c1$	[46]
24	$NaTe_3$	Na + 3Te	Liq. NH_3 (−50°C). Crude product heated to 500°C for 1 day; 380°C for 5 days. Slow cooled.	Not given	$P\bar{3}c1$ (1.5%)	[47]
25	$BaTe_3$	Ba + 3Te	Heated to 550°C for 4 h.	Not given	$P\bar{4}2_1m$ (9.1%)	[36]
26	$CsTe_4$	Cs + 4Te	Heated to 570°C for 7 days. Slow cooled.	Not given	$P2_1/c$ (4.1%)	[49]
27	$RbTe_6$	$Rb_2CO_3 + 2Te + Ge$	Solventothermal method. CH_3OH heated to 160°C. Slow cooled. Ge is essential.	79	$C2/c$ (6.4%)	[45]
28	Cs_2Te_{13}	$Cs_2CO_3 + As_2Te_3$	Solventothermal method. CH_3OH heated to 160°C for 100 h. Slow cooled.	5	$Pbcm$ (5.2%)	[50]
29	Cs_4Te_{28}	$Cs_2CO_3 + 1.5As_2Te_3$	Solventothermal method. CH_3OH heated to 180°C for 10 h. Slow cooled.	3	$P4/ncc$ (3.3%)	[50]
30	Cs_3Te_{22}	$Cs_2CO_3 + 2As_2Te_3$	Solventothermal method. CH_3OH heated to 195°C for 2 days. Slow cooled.	70	$I4/m$ (5.1%)	[51]

[a] Here and in Table 2 the preparative reaction, solvent, and crystallization method are given for the product analyzed by diffraction methods. In some instances alternative preparative reactions may be found in the literature.

[b] Here and in Table 2 the yield is that given in the reference. Owing to differences in how yields are defined it is generally not possible to compare these yields from one compound to another.

[c] Here and in Table 2 this is the standard crystallographic R index on F. No distinction is made whether it is based on single-crystal or powder data.

Table 2
Preparative information for organic-cation (OC) tellurides

No.	Compound	Preparative reaction	Solvent/crystallization method	Yield (%)	Space group (R index)	Ref.
31	$[N(CH_3)_4]_2[Te_2]$	$[N(CH_3)_4][BH_4]+Te$	DMF/recrystallized from CH_3OH	'Excellent'	$Pa\bar{3}$ (1.8%)	[28]
32	$[Na(CH_3OH)_3]_2[Te_2]$	Na_2Te+O_2	CH_3OH	54	$P\bar{3}1c$ (1.9%)	[29]
33	$[K(2.2.2\text{-cryptand})]_2[Te_3]\cdot en$	$2(2.2.2\text{-cryptand})+K_2Te+$excess Te	en	Not given	$P3_2$ (9.4%)	[8]
34	$[Ba(en)_3][Te_3]$	$Ba+5Te$	en	Not given	$P2_1/c$ (8.4%)	[11]
35	$[Ba(en)_{4.5}][Te_3]$	$Ba+3Te$	en	Not given	Cc (8.0%)	[11]
36	$[N(CH_3)_4]_2[Te_3]$	$SbTe_{10}+0.15$ M $[N(CH_3)_4]I$	en/cathodic dissolution	'Very high'	$P2_1/c$ (not given)	[17]
37	$[PPh_4]_2[Te_4]\cdot 2CH_3OH$	$K_4SnTe_4+2PPh_4Br$	CH_3OH	Not given	C2/c (2.8%)	[14]
38	$[Na(2.2.2\text{-cryptand})]_2[Te_4]$	$NaTlTe_2+2.2.2$-cryptand	en	Not given	$P2_1/c$ (8.2%)	[13]
39	$[Ca(DMF)_6][Te_4]$	$CaTe_3$	DMF/layered Et_2O	30	$C2/c$ (5.5%)	[12]
40	$[Sr(15\text{-C-}5)_2][Te_4]\cdot H_2O$	$Li_2Te_3+SrCl_2+2(15\text{-C-}5)$	DMF/layered Et_2O	37	$C2/c$ (5.8%)	[12]
41	$[(18\text{-C-}6)(DMF)_2BaCl]_2[(18\text{-C-}6)(DMF)(H_2O)BaCl]_2[Te_4]_2$	$Li_2Te_3+BaCl_2+18\text{-C-}6$	DMF/layered Et_2O	29	$P\bar{1}$ (5.4%)	[12]
42	$[PPh_4]_2[Te_4]$	$2Na_2Te_3+MnCl_2+2PPh_4^+$	DMF	59	$P\bar{1}$ (3.0%)	[15]
43	$[TMDH][Te_4]$	$K_2Te_3+[TMDH]I_2$	H_2O	65	$P2_1/n$ (3.8%)	[18]
44	$[HMTN]_2[Te_4]_2[Te_5]$	$3K_2Te_3+2[HMTN]I_3$	H_2O	Not given	$P\bar{1}$ (6.6%)	[18]
45	$[Na(12\text{-C-}4)_2]_2[Te_4]\cdot OEt_2$	$3Na_2Te_3+Mn(OAc)_2\cdot 2.4H_2O+12(12\text{-C-}4)$	DMF	Not given	$C2/c$ (5.6%)	[39]
46	$[N(C_4H_9)_4]_2[Te_5]$	$K_2Te_3+2\ [N(C_4H_9)_4]Br$	H_2O/recrystallized from acetone	60	$C2/c$ (2.7%)	[41]
47	$[Ph_3PNPPh_3][Te_5]\cdot 2DMF$	$Na_2Te_3+2Te+2[Ph_3PNPPh_3]Cl+I_2$ (catalytic amount)	DMF/layered Et_2O	39	Pc (5.8%)	[12]
48	$[K(2.2.2\text{-cryptand})]_2[Te_5]$[a]	$SbWTe_6+2K+2(2.2.2\text{-cryptand})$	Liq. NH_3/recrystallized in CH_3CN layered Et_2O	37	$C2/c$ (3.7%)	[42]
49	$[Cr(en)_3][Te_6]$	$Cr(CO)_6+2BaTe_4$	en, 200°C, 7 days. Slow cooled	63.3	$R32$ (2.1%)	[20]
50	$[K(15\text{-C-}5)_2]_2[Te_8]$	$4K_2Te_3+5FeCl_3+6(15\text{-C-}5)$	DMF/layered Et_2O	Not given	$Pca2_1$ (4.8%)	[16]
51	$[N(C_2H_5)_4]_2[Te_{12}]$	$SbTe_{10}+0.30M\ [N(C_2H_5)_4]I$	en/cathodic dissolution	54	Pn (3.6%)	[17]

[a] $[K(2.2.2\text{-cryptand})]_2[Te_5]$: space group $C2/c$, $a=20.717(12)$ Å, $b=12.077(3)$ Å, $c=22.220(7)$ Å, $\beta=99.38(4)°$, $V=5485(4)$ Å^3, $t=-160$°C, $Z=4$, 8443 reflections, 3770 unique, 3306 observed, 283 parameters, $R=3.67\%$ [42].

3.2. Te^{2-} anions

The primary examples of this anion are Li_2Te (**1**) [23], Na_2Te (**2**) [23], K_2Te (**3**) [23], Cs_2Te (**4**) [24], CaTe (**9**) [25], and BaTe (**10**) [26]. All these materials have been isolated as powders and structural information was obtained at room temperature by means of powder X-ray diffraction measurements. The first three compounds have the CaF_2 structure and the closest cation–anion distances are 2.75(1), 3.06(1), and 3.41(1) Å for Li_2Te, Na_2Te, and K_2Te, respectively. Cs_2Te crystallizes in the (anti)-$PbCl_2$ crystal type whereas CaTe and BaTe crystallize in the NaCl crystal type. In Cs_2Te the closest cation–anion distance is 3.705(1) Å as expected for the larger Cs^+ cations. Closest cation–anion interactions for CaTe and BaTe are 3.172 and 3.410 Å, respectively. Isolated Te^{2-} ions are also found in NaTe (**8**) [19], K_5Te_3 (**5**) [27], and Cs_5Te_3 (**7**) [24]. The structures of these three compound will be discussed below.

3.3. $[Te_2]^{2-}$ anions

Although [A/AE][Te_2] compounds are common, only two structures have been reported for [OC][Te_2] compounds, namely $[N(CH_3)_4]_2[Te_2]$ (**31**) [28] and $[Na(CH_3OH)_3]_2[Te_2]$ (**32**) [29]. These structures consist of dumbbell-shaped $[Te_2]^{2-}$ anions separated by OCs. The anions in **31** are stacked diagonally relative to each other whereas the anions in **32** are stacked linearly above each other. The Te–Te bond lengths are 2.737(1) and 2.744(1) Å for **31** and **32,** respectively (Table 3). The Te–Te bond distance in **32** is thought to be slightly longer than that in **31** because of hydrogen bonding between the Te atoms and the CH_3OH molecules (the closest interaction for **32** is 3.487 Å for Te–O1) [29]. However, this difference in bond lengths, if significant, could readily be attributed to the difference in data collection temperatures (25°C (**31**) vs. -60°C (**32**)). In both complexes the $[Te_2]^{2-}$ chains are well separated and do not interact.

The dumbbell-shaped $[Te_2]^{2-}$ anion is seen in the following [A/AE][Te_2] compounds: K_5Te_3 (**5**) [27], Cs_5Te_3 (**7**) [24], α- and β-K_2Te_2 (**11** and **12**) [30], α- and β-Rb_2Te_2 (**13** [30] and **14** [31]), Cs_2Te_2 (**15**) [31], $MgTe_2$ (**19**) [32], and $BaTe_2$ (**20**) [33,34]. The A_5Te_3 (A = K, Cs) compounds are more properly represented as $A_{10}Te_6$ and comprise 10 A^+ cations, four Te^{2-} anions, and one $[Te_2]^{2-}$ anion. These $[Te_2]^{2-}$ dumbbells stack end to end in K_5Te_3 (**5**) to form a linear chain with intra-chain Te–Te distances of 2.839(2) Å and inter-chain Te–Te distances of 3.525(2) Å. The remaining Te atoms build up strings of tetrahedra $^{1}_{\infty}[KTe_{4/2}]$ with common edges. Cs_5Te_3 (**7**) has the same structure as low-temperature K_5Se_3 [24], which is similar to, although not identical with, that of K_5Te_3. Again, the $[Te_2]^{2-}$ dumbbells stack end to end to form linear chains with a Te–Te bond distance of 2.808 Å. The existence of Rb_5Te_3 (**6**) has been alluded to but no information is available (see [24]).

Powder X-ray diffraction data show that α-K_2Te_2 (**11**) and α-Rb_2Te_2 (**13**) are isostructural with K_2S_2 [30] and K_2Se_2 [30], crystallizing in the Na_2O_2 structure type. $[Te_2]^{2-}$ dumbbells are stacked end to end to form linear channels that are separated by K^+ or Rb^+ cations. The Te–Te bond distances are 2.86(1) and 2.78(1) Å and the A–Te distances range from 3.39(1) to 3.67(1) and 3.47(1) to 3.86(1) Å for α-K_2Te_2 and α-Rb_2Te_2, respectively. β-K_2Te_2 (**12**) crystallizes in the Li_2O_2 structure type and consequently the Te–Te dumbbells no longer stack linearly in chains but rather each individual $[Te_2]^{2-}$ anion is separated from the next by a cation. The Te–Te bond distance (2.790(1) Å) is similar to the distances observed for α-K_2Te_2 and α-Rb_2Te_2. The closest cation–anion interaction is 3.515(1) Å. α-K_2Te_2 undergoes a phase transition at elevated temperatures to form β-K_2Te_2. As determined from Rietveld analysis of powder diffraction data [31], β-Rb_2Te_2 (**14**) and Cs_2Te_2 (**15**) crystallize in a new structure type, designated the

Table 3
Bond distances (Å) and angles (°) for compounds containing $[Te_2]^{2-}$ and $[Te_3]^{2-}$ anions[a]

No.	Compound	Te1–Te2	Temp. of data collection (°C)	Ref.
31	$[N(CH_3)_4]_2[Te_2]$	2.737(1)	25	[28]
32	$[Na(CH_3OH)_3]_2$-$[Te_2]$	2.744(1)	−60	[29]
5	K_5Te_3	2.839(2)	25	[27]
7	Cs_5Te_3	2.808[b]	25	[24]
11	α-K_2Te_2	2.86(1)	25	[30]
12	β-K_2Te_2	2.790(1)	25	[30]
13	α-Rb_2Te_2	2.78(1)	25	[30]
14	β-Rb_2Te_2	2.814	25	[31]
15	Cs_2Te_2	2.781	25	[31]
19	$MgTe_2$	2.70(1)	25	[32]
20	$BaTe_2$	2.772	25	[34]

No.	Compound	Te1–Te2	Te2–Te3	Te1–Te2–Te3	Temp. (°C)	Ref.
33	$[K(2.2.2\text{-cryptand})]_2[Te_3]\cdot en$	2.692(5)	2.720(4)	113.1(2)	25	[8]
34	$[Ba(en)_3][Te_3]$[c]	2.785(2)	2.739(2)	105.7(2)	Not given	[11]
35	$[Ba(en)_{4.5}][Te_3]$ (a)	2.724(6)	2.721(6)	110.9(2)	Not given	[11]
35	$[Ba(en)_{4.5}][Te_3]$ (b)	2.705(6)	2.731(6)	112.2(2)	Not given	[11]
36	$[N(CH_3)_4]_2[Te_3]$	No bond angles reported; only cell information given.			Not given	[17]
16	K_2Te_3	2.802	2.805	104.38	Not given	[37]
17	Rb_2Te_3	2.796(6)	2.803(6)	104.2(2)	Not given	[38]
18	Cs_2Te_3	2.770(1)	2.770(1)	100.06(5)	Not given	[38]
23	$BaTe_3$	2.775(4)	2.775(4)	109.4(2)	Not given	[36]

[a] Here and in all subsequent tables we have tried to make the table as useful as possible by changing the atom designations in some of the published reports to a standard labeling scheme.

[b] Bond distance not given in published account, comes from ICSD.

[c] This cation also shows some Ba–Te interactions: Ba–Te1, 3.605(2) Å; next anion: Ba–Te1a, 3.916(2) Å; Ba–Te2a, 3.805(2) Å; Ba–Te3a, 3.760(2) Å.

Cs_2Te_2 structure type. It is a distorted, lower-symmetry version of the CsCl structure type. These structures also contain $[Te_2]^{2-}$ dumbbells with Te–Te distances of 2.814 and 2.781 Å for **14** and **15**, respectively.

As determined from powder diffraction data, $MgTe_2$ (**19**) [32] crystallizes in the pyrite structure and features rows of $[Te_2]^{2-}$ dumbbells stacked in a herringbone fashion around Mg^{2+} cations. The Te–Te bond distance of 2.70(1) Å is much shorter than those in the ATe_2 (A = K, Rb, Cs) structures but is similar to those observed in the $[OC][Te_2]$ compounds **31** and **32**. The structure of $BaTe_2$ (**20**) [33–35] features the same $[Te_2]^{2-}$ dumbbell units, this time stacked in a staggered fashion above one another to form an infinite pillar. The pillars are separated by Ba^{2+} cations. The Te–Te bond distance is 2.772 Å and the closest Te–Te interaction is 3.94 Å, implying that the dumbbells are isolated from one another.

In most of the A/AE tellurides containing $[Te_2]^{2-}$ anions, the inter-dumbbell distance is shorter than the sum of the van der Waals radii, the exception being $BaTe_2$. In addition, the intra-dumbbell distance is longer than the expected single-bond distance.

3.4. $[Te_3]^{2-}$ *anions*

The bent $[Te_3]^{2-}$ anion is found in $[K(2.2.2\text{-cryptand})]_2[Te_3]$ (**33**) [8], $[N(CH_3)_4]_2[Te_3]$ (**34**) [17], $[Ba(en)_3][Te_3]$ (**35**) [11], and $[Ba(en)_{4.5}][Te_3]$ (**36**) [11], as well as in the $[A/AE][Te_3]$ compounds $BaTe_3$ (**25**) [36], K_2Te_3 (**16**) [37], Rb_2Te_3 (**17**) [38], and Cs_2Te_3 (**18**) [38].

In all of these compounds the bent $[Te_3]^{2-}$ anion has essential (or sometimes crystallographically imposed) C_{2v} symmetry with Te–Te distances of 2.69 to 2.80 Å and Te–Te–Te bond angles of 100 to 113° (Table 3). It is necessary here to offer some caveats that apply to all such comparisons among $[Te_n]^{2-}$ anions, for $n > 2$. The terminal atoms in such chains are most susceptible to interactions of varying strengths with atoms elsewhere in the crystal structure. Such interactions, whether bonding or Coulombic, will tend to lengthen the terminal Te–Te bonds Opposing this tendency is the apparent shortening in derived X-ray determinations of such bond lengths owing to the effects of thermal vibrations that are apt to be largest for terminal atoms. It is thus extremely difficult and patently unwise to read too much significance into the sometimes striking differences displayed in Table 3 and beyond, especially given the wide range of temperatures used in the collection of the X-ray data. Nevertheless, on occasion a few comments will be offered. For $[K(2.2.2\text{-cryptand})]_2[Te_3]$ (**33**), there is a weak Te3···HN1 bond (3.46(6) Å) that probably accounts for the Te2–Te3 distance (2.720(4) Å) being longer than the Te1–Te2 distance (2.692(5) Å). For the $[Ba(en)_y]^{2+}$ compounds, the Te–Te distances are shorter when the anion is more isolated as a result of the coordination sphere of the cation being larger. Similarly, the strong Coulombic interactions between cations and anions in the $[A/AE][Te_3]$ compounds probably account for their generally longer Te–Te distances. The reason for the variations in the Te–Te–Te bond angles in Table 3 is unclear.

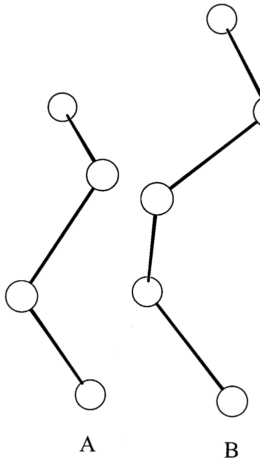

Fig. 1. Typical $[Te_4]^{2-}$ (A) and $[Te_5]^{2-}$ (B) chains.

3.5. $[Te_4]^{2-}$ anions

Whereas [OC]$[Te_4]$ compounds comprise the largest class of OC/tellurides, there are no characterized simple A/AE systems that contain $[Te_4]^{2-}$ anions. Structures have been reported for [OC]$[Te_4]$ for OC = $[PPh_4]_2 \cdot 2CH_3OH$ (**37**) [14], $[Na(2.2.2\text{-cryptand})]_2$ (**38**) [13], $[Ca(DMF)_6]$ (**39**) [12], $[Sr(15\text{-C-5})_2]$ (**40**) [12], $\{[(18\text{-C-6})(DMF)_2BaCl]_2[(18\text{-C-6})(DMF)(H_2O)BaCl]_2\}_{0.5}$ (**41**) [12], $[PPh_4]_2$ (**42**) [15], [TMDH] (**43**) [18], and $[Na(12\text{-C-4})_2]_2 \cdot OEt_2$ (**45**) [39], as well as for $[HMTN]_2[Te_4]_2[Te_5]$ (**44**) [18]. Bond distances, bond angles, and dihedral angles for these compounds are given in Table 4 and a typical $[Te_4]^{2-}$ anion is drawn in Fig. 1. A comparison of bond distances (Fig. 2) indicates the greatest fluctuation in distances occurs among the terminal Te–Te bonds. For the majority of these compounds, the internal Te–Te bond is about 0.04 Å longer than the terminal bonds. In general, the internal Te–Te distance is 2.75–2.77 Å, with the exception of $[(18\text{-C-6})(DMF)_2BaCl]_2[(18\text{-C-6})(DMF)(H_2O)BaCl]_2[Te_4]_2$ (**41**) where the internal bond is approximately 0.04–0.05 Å shorter than in the others. Compound **41** has the largest cations of the set and hence the most isolated $[Te_4]^{2-}$ chains, but does this affect the length of the internal Te–Te bond?

As indicated above, the lengths of external Te–Te bonds are sensitive both to intermolecular and Coulombic interactions (of unknown strength) and to apparent foreshortening as a result of the X-ray model. Given these opposing effects, the variations shown in Table 4 and Fig. 2 (bond lengths) and Fig. 3 (bond angles) are generally minor if one ignores the Te3–Te4 bond length of 2.964(3) Å in one of the $[Te_4]^{2-}$ anions (a) in $[HMTN]_2[Te_4]_2[Te_5]$ (**44**) [18]; this distance is unusual and may be a result of the close interaction (3.165(3) Å) between atom Te4 and the terminal Te atom of the next adjacent chain. The closest Te–Te interaction for the second $[Te_4]^{2-}$ anion in **44** is 3.376(3) Å. There seems to be no correlation between Te–Te bond lengths and the Te1–Te2–Te3–Te4 dihedral angles (Table 4), although such a correlation between disulfide bond lengths and dihedral angles has been noted and ascribed to the eclipsing of lone pairs on the chalcogen atoms [40].

3.6. $[Te_5]^{2-}$ anions

Four compounds containing the $[Te_5]^{2-}$ anion are known: $[HTMN]_2[Te_1]_2[Te_5]$ (**44**) [18], $[Ph_3PNPPh_3]_2[Te_5] \cdot 2DMF$ (**46**) [12], $[N(C_4H_9)_4]_2[Te_5]$ (**47**) [41], and $[K(2.2.2\text{-cryptand})]_2[Te_5]$ (**48**) [42]. Bond distances, bond angles, and dihedral angles are given in Table 5, and a typical $[Te_5]^{2-}$ anion is drawn in Fig. 1. Similar to one of the two $[Te_4]^{2-}$ chains present in **44**, the terminal Te–Te bond distances (Table 5) for the $[Te_5]^{2-}$ chain in this compound are significantly elongated. The end atoms on the $[Te_5]^{2-}$ chain interact with both of the $[Te_4]^{2-}$ chains at distances of 3.306(5) and 3.540(5) Å. Compound **46** has two highly unsymmetrical Te–Te internal bonds (including the longest reported one, probably as a result of the difficulty of modeling the disorder of atom Te3 in the structure). Disorder is potentially more of a problem as the chains get longer.

Although the compounds Rb_2Te_5 (**21**) [43] and Cs_2Te_5 (**22**) [44] are known, they do not contain isolated $[Te_5]^{2-}$ anions, but rather they contain infinite one-dimensional ${}^{1}_{\infty}[Te_4Te^{2-}_{2/2}]$ chains.

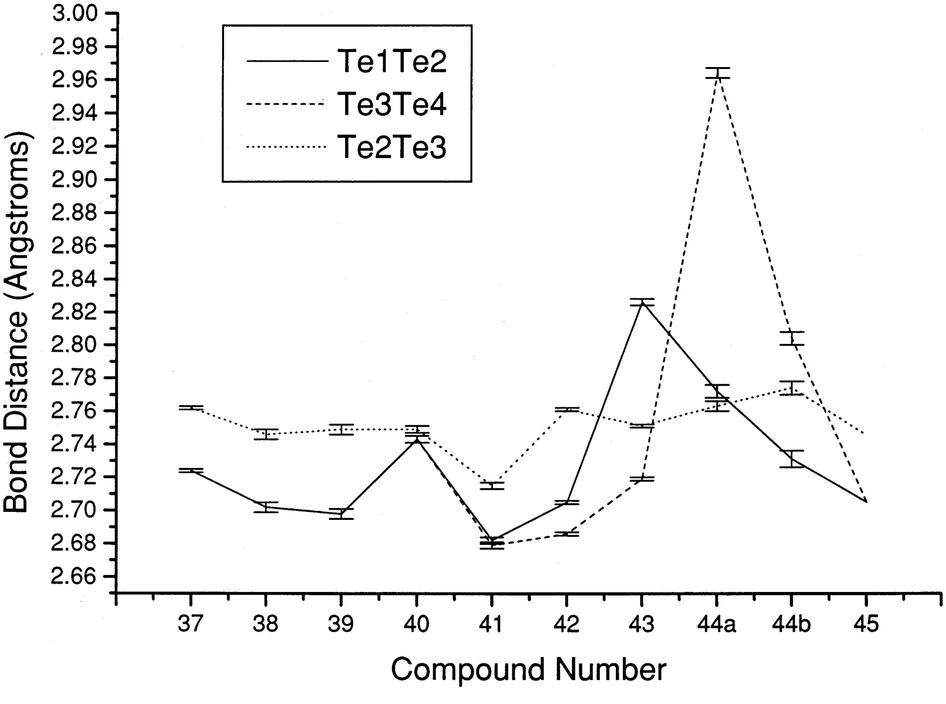

Fig. 2. Bond distances (Å) in the $[Te_4]^{2-}$ anions.

Table 4
Bond distances (Å) and angles (°) for compounds containing $[Te_4]^{2-}$ anions

No.	Cation	Te1–Te2	Te2–Te3	Te3–Te4	Te1–Te2–Te3	Te2–Te3–Te4	Te1–Te2–Te3–Te4	Temp. (°C)	Ref.
37	$[PPh_4]_2 \cdot 2CH_3OH$	2.724(1)	2.762(1)	2.724(1)	110.78(4)	110.78(4)	99.9(1)	−169	[14]
38	[Na(2.2.2-cryptand)]$_2$	2.702(3)	2.746(3)	2.702(3)	109.7(1)	110.0(1)	105.3(1)	22	[13]
39	$[Ca(DMF)_6]$	2.698(3)	2.749(3)	2.698(3)	111.66(9)	111.66(9)	−97.2(1)	−70	[12]
40	$[Sr(15\text{-}C\text{-}5)_2]$	2.743(2)	2.749(2)	2.743(2)	107.55(4)	107.55(4)	−102.5(1)	−70	[12]
41	$[(18\text{-}C\text{-}6)(DMF)_2BaCl]_2[(18\text{-}C\text{-}6)(DMF)(H_2O)BaCl]_2$	2.682(2)	2.715(2)	2.679(2)	110.77(8)	112.05(8)	95.04(9)	19	[12]
42	$[PPh_4]_2$	2.705(1)	2.761(1)	2.686(1)	110.1(1)	111.2(1)	98.6(1)	−60	[15]
43	[TMDH]	2.826(2)	2.751(1)	2.719(2)	108.0(1)	112.3(1)	±100.3(1)	20	[18]
44	$[HMTN]_2$ (a)	2.772(4)	2.763(3)	2.964(3)	114.1(1)	104.4(1)	±93.4(1)	20	[18]
44	$[HMTN]_2$ (b)	2.731(5)	2.774(4)	2.804(4)	109.7(1)	105.1(1)	±104.9(2)	20	[18]
45	$[Na(12\text{-}C\text{-}4)_2]_2 \cdot OEt_2$	2.705	2.745	2.705	109.6	109.6	−82.3	−80	[39]

Table 5
Bond distances (Å) and angles (°) for compounds containing $[Te_5]^{x-}$ anions

No.	Cation	Te1–Te2	Te2–Te3	Te3–Te4	Te4–Te5	Temp. (°C)	Ref.
44	$[HMTN]_2$	2.871(5)	2.757(4)	2.793(4)	2.742(5)	20	[18]
47	$[PPh_3PNPPh_3]_2 \cdot 2DMF$[a]	2.745(6)	2.778(6) (2.681(6))	2.647(7) (2.793(6))	2.732(4)	20	[12]
46	$[N(C_5H_9)_4]_2$	2.704(1)	2.746(1)	2.746(1)	2.704(1)	−138	[41]
48	[K(2.2.2-cryptand)]$_2$	2.729(1)	2.744(1)	2.744(1)	2.729(1)	−160	[42]
8	NaTe	2.82(1)	3.08(1)	3.08(1)	2.82(1)	25	[19]

No.	Cation (A)	Te1–Te2–Te3	Te2–Te3–Te4	Te3–Te4–Te5	Te1–Te2–Te3–Te4	Te2–Te3–Te4–Te5	Ref.
44	$[HMTN]_2$	111.6(1)	118.1(1)	111.5(1)	±86.0(2)	±99.7(2)	[18]
47	$[PPh_3PNPPh_3]_2 \cdot 2DMF$[a]	101.2(2)	111.4(2)	115.8(2)	−112.3(2) (94.0(2))	−92.6(2) (112.7(2))	[12]
46	$[N(C_5H_9)_4]_2$	105.1(1)	107.2(1)	105.1(1)	−108	−108	[41]
48	[K(2.2.2-cryptand)]$_2$	108.9(1)	111.37(4)	108.95(4)	−84.6	−84.6	[42]
8	NaTe	105.3	180.0	105.3			[19]

[a] Atom Te3 is disordered giving rise to two sets of bond angles and distances for that atom. The numbers in parentheses are those for the second Te3 atom.

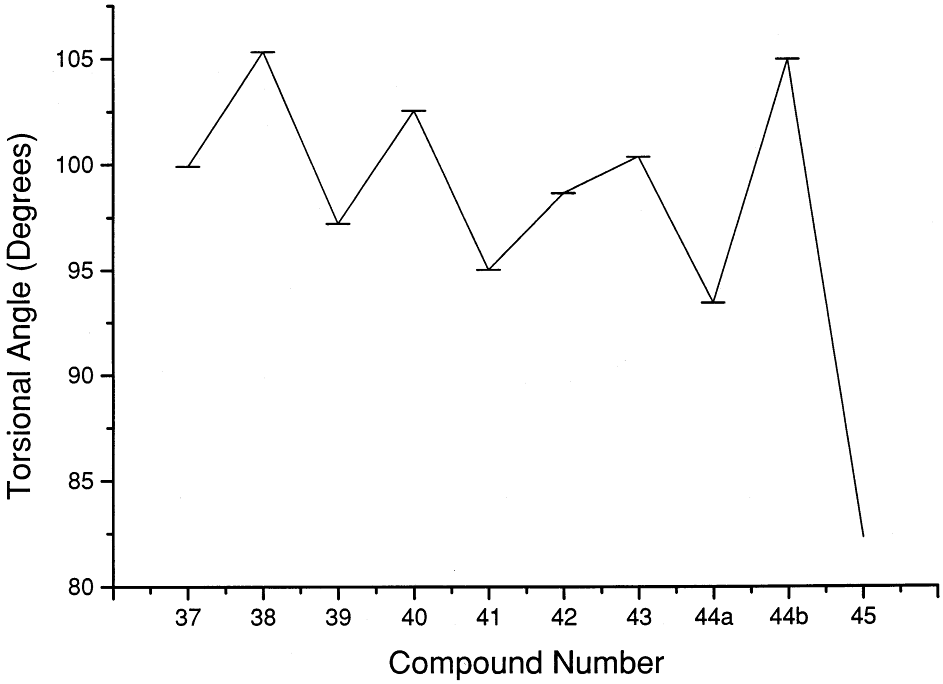

Fig. 3. Torsional angles (°) in the $[Te_4]^{2-}$ anions.

3.7. $[Te_5]^{4-}$ anion

This anion is found only in NaTe (**8**) [19], which is actually $Na_6Te(Te_5)$. Its structure contains both isolated Te^{2-} ions (closest Te···Te interaction = 4.80 Å) and $[Te_5]^{4-}$ units. The $[Te_5]^{4-}$ units are Z-shaped with an internal Te–Te distance of 3.08(1) Å and an external Te–Te distance of 2.82(1) Å. The lengthening of the internal distances is consistent with a 3-center 4-electron bond. The arrangement of $[Te_5]^{4-}$ units creates channels where the Na^+ cations are located. The closest Na–Te distance is 3.067(1) Å.

3.8. $[Te_6]^-$ anion

This anion, as an isolated entity, has not been found. Rather, the structure of $RbTe_6$ (**27**) [45] comprises two-dimensional $^2_\infty[Te_6^-]$ sheets separated by Rb^+ cations. The sheets are made up of rows of Te_6 rings (in the chair conformation with internal bond distances ranging from 2.777(3) to 3.195(3) Å) that are bonded to other rows of Te_6 rings through four of the Te atoms (Te–Te bond distances are 3.214(3) Å). In addition, Te_6 rings within a row interact through weak Te···Te contacts of 3.449(3) Å. The Rb–Te distances range from 3.672(3) to 4.059(3) Å.

3.9. $[Te_6]^{2-}$ anion

Similarly, this isolated anion has not been found. Rather, the structure of $LiTe_3$ (**23**) [46], solved from a combination of powder X-ray and neutron diffraction data, comprises infinite ${}^{1}_{\infty}[Te_6^{2-}]$ chains separated by channels of Li^+ cations. The chains are helical. Te–Te distances range from 2.86(1) to 3.02(1) Å, only slightly shorter than the inter-chain interactions of 3.14(1) to 3.32(2) Å. The Li–Te distances average 3.08(2) Å. The structure of $NaTe_3$ (**24**) [47], solved from single-crystal X-ray diffraction data, also contains $[Te_6]^{2-}$ chains linked together via their terminal Te atoms (inter-chain Te–Te distance, 3.164(1) Å) to produce infinite helical strings. Te–Te distances within the $[Te_6]^{2-}$ anion range from 2.767(1) to 2.979(1) Å. If 3.16 Å is taken as a covalent bonding interaction, then the description of the structure changes from $[Te_6]^{2-}$ anions to $[Te_{12}]^{6-}$ anions bound together to form one-dimensional strands of ${}^{1}_{\infty}[(Te_{12}^{6-})(Te_2)_3]$. If the next closest Te–Te interaction at 3.326(1) Å is also considered bonding, then the structure may be described as three-dimensional and it is isostructural to $AgTe_3$ [48]. And so the difficulty of describing polytelluride anions continues! Na–Te distances range from 3.070(3) to 3.314(3) Å.

3.10. $[Te_6]^{3-}$ anion

$[Cr(en)_3][Te_6]$ (**49**) [20] is unique and difficult to categorize. Nominally, the structure contains a polymeric $[Te_6]^{3-}$ anion whose pores are filled with isolated

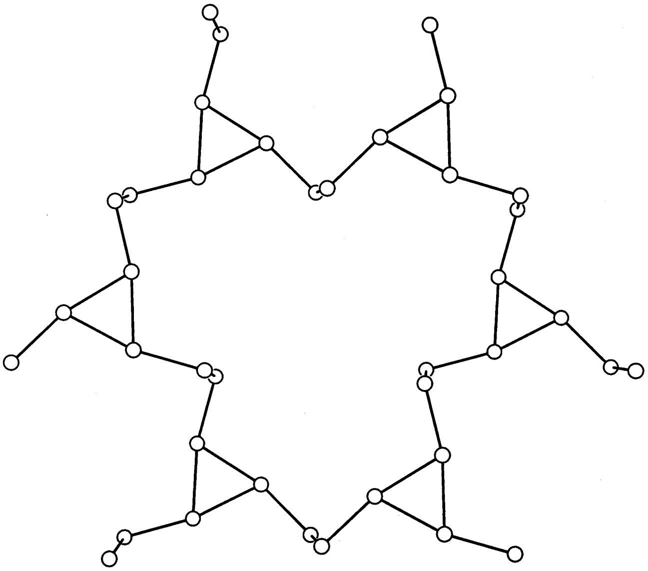

Fig. 4. Structure of the anion in $[Cr(en)_3][Te_6]$ (**49**) [20] showing covalent bonds between 2.763(1) and 3.138(1) Å.

$[Cr(en)_3]^{3+}$ cations. The $[Te_6]^{3-}$ anion (Fig. 4) contains a central Te_3 ring with one exocyclic Te atom attached to each atom of the ring. The Te_6 fragments are connected by single Te–Te bonds (2.763(1) Å) to form puckered sheets. These sheets, in turn, are connected to adjacent layers through longer Te–Te interactions of 3.376(1) Å. The bond distances connecting the Te atoms in the ring are rather long at 3.138(1) Å. The bond distances from the ring atoms to the exocyclic atoms are also long at 2.918(1) Å. If only 'classical' bond distances of 2.7–3.0 Å are considered, then the structure can be described in terms of isolated $[Te_4]^{2-}$ chains.

3.11. $[Te_8]^{2-}$ anions

$[K(15\text{-}C\text{-}5)_2]_2[Te_8]$ (**50**) [16] does not contain isolated $[Te_8]^{2-}$ anions, nor does it contain chains. Instead its structure consists of a central Te^{2+} atom coordinated in a distorted square-planar fashion to a $[Te_4]^{2-}$ and a $[Te_3]^{2-}$ chelating ring (Fig. 5). The Te–Te bond distances in the planar $[Te_3]^{2-}$ ring (2.770(3) and 2.754(5) Å) and the envelope-shaped $[Te_4]^{2-}$ ring (2.713(3)–2.746(4) Å) are approximately 0.3 Å shorter than the distances to the central Te atom (2.919(4)–3.112(4) Å).

The structure of $CsTe_4$ (**26**) [49] comprises Cs^+ cations each surrounded by eight Te atoms at distances ranging from 3.858(2) to 4.046(2) Å. Te–Te distances range from 2.754(1) to 3.378(2) Å. How should this compound be described? If only Te–Te bond distances less than 2.92 Å are considered, then the structure contains isolated $[Te_8]^{2-}$ chains separated by Cs^+ cations. If Te–Te distances less than 3.15 Å are considered, then the structure contains $[Te_{18}]^{4.5-}$ rings. In such a ring every third Te atom is pseudo trigonal bipyramidal implying that the ring is composed of joined $[Te_4]^-$ units. If Te–Te bond distances up to 3.38 Å are considered, then the structure contains chains of edge-shared Te_5 rings (represented as $[Te^cTe^t_2Te^t_{2/2}]^-$, where c = central and t = terminal atoms). Once again the propensity of Te atoms toward intermolecular bonding often makes the description of the resulting compounds ambiguous.

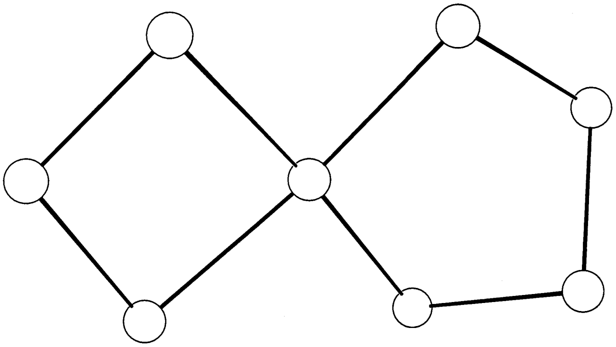

Fig. 5. Structure of the anion in $[K(15\text{-}C\text{-}5)_2][Te_8]$ (**50**) [16].

3.12. $[Te_{12}]^{2-}$ anion

Only $[N(C_2H_5)_4]_2[Te_{12}]$ (**51**) [17] contains what may be described as isolated $[Te_{12}]^{2-}$ anions, but even these are weakly bound into pseudo two-dimensional sheets sandwiched between layers of $[N(C_2H_5)_4]^+$ cations. The result is the alternation of organic and inorganic layers within the solid. The structure of this puckered anion (Fig. 6) is comparable to elemental Te in that it has short, long, and non-bonded Te–Te interactions. The short distances appear in the chain itself and range from 2.713(2) to 2.881(2) Å. Longer Te–Te interactions ranging from 3.144(2) to 3.504(2) Å weakly bind the $[Te_{12}]^{2-}$ anions into two-dimensional sheets. These longer contacts are distributed almost exclusively among the ends of the adjacent $[Te_{12}]^{2-}$ chains with the central atoms of each chain possessing short covalent Te–Te single bonds.

3.13. $[Te_{13}]^{2-}$ anion

The longest isolated tellurium anionic chain can be found in Cs_2Te_{13} (**28**) [50] providing secondary Te–Te interactions longer than 3.17 Å are ignored. The bond lengths in the $[Te_{13}]^{2-}$ chain range from 2.755(2) to 2.910(2) Å. The chains are connected in undulating sheets through Te···Te interactions of 3.181(2) and 3.261(2) Å to create a ladder of Te_4 rectangles and chair-shaped Te_6 rings.

3.14. Cs_4Te_{28} and Cs_3Te_{22}

These two compounds have unique structures. That of the anionic portion of Cs_4Te_{28} (**29**) [50] contains a Te_8 crown and, ignoring secondary Te–Te distances longer than 3.15 Å, isolated $[Te_6]^{2-}$ anions and Te_4 square rings. Te–Te distances

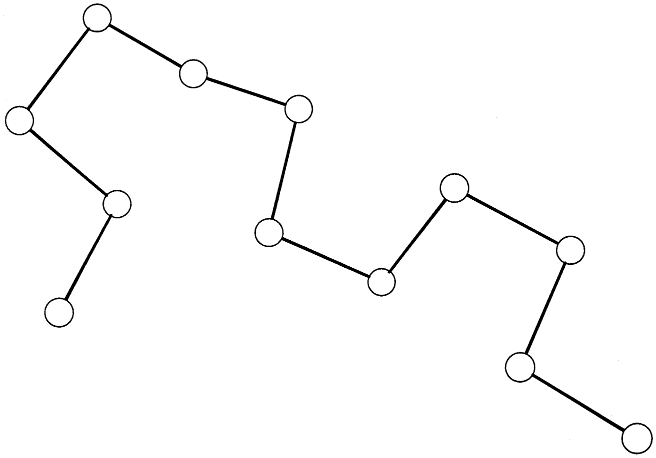

Fig. 6. Structure of the anion in $[N(C_2H_5)_4]_2[Te_{12}]$ (**51**) [17].

range from 2.778(2) to 2.829(2) Å in the Te_8 crown, 2.774(2)–2.797(2) Å in the Te_6^{2-} chains, and 2.911(2)–2.955(2) Å in the Te_4 rings. The Te_6^{2-} chains and Te_4 rings are linked together through Te–Te interactions of 3.153(2) and 3.194(2) Å to form a ${}^3_\infty[Te_{20}^{4-}]$ network structure.

The structure of the anionic portion of Cs_3Te_{22} (**30**) [51] consists of a two-dimensional 2,3-connected defect square Te-sheet and Te_8 rings. The Te-sheet is composed of Te_4 square-planar rings (Te–Te bond distance, 3.003(1) Å) connected to each other via a linear Te atom with a Te–Te bond distance of 3.077(1) Å. The chain layers alternate with layers of Te_8 crowns and Cs^+ cations. The closest contact between the Te atoms of the sheet and the crowns is 3.424(1) Å.

4. Conclusions

In most of the accounts of the structures of polytelluride anions the authors have offered various arguments to explain why the metrical parameters they found differed from those in other published accounts. In this present comparison of the ensemble of such structures, we conclude that no one factor is responsible for these differences. Each possible 'explanation' has exceptions. Moreover, given the problems of assessing the strength and nature of non-bonded interactions, whether covalent or Coulombic, it is not only difficult in most instances to decide if such interactions are important but often it is even difficult to decide on the correct formulation for a given polytelluride anion. If we couple these with experimental problems — disorder, vibrational foreshortening, differing temperatures of data collection — it is no wonder that we conclude that no conclusions are possible. We trust that the presentation of this body of data will encourage others to examine and reconsider the interesting nature of polytelluride anions as they appear in the solid state.

Acknowledgements

This research was supported by the US National Science Foundation, Grants CHE98-19385 and CHE95-31232.

References

[1] M.A. Ansari, J.M. McConnachie, J.A. Ibers, Acc. Chem. Res. 26 (1993) 574.
[2] L.C. Roof, J.W. Kolis, Chem. Rev. 93 (1993) 1037.
[3] J. Beck, Angew. Chem. Int. Ed. Engl. 33 (1994) 163.
[4] W.S. Sheldrick, M. Wachhold, Angew. Chem. Int. Ed. Engl. 36 (1997) 206.
[5] C. Hugot, Ann. Chim. Phys. 21 (1900) 1.
[6] C.A. Kraus, J. Am. Chem. Soc. 44 (1922) 1216.
[7] E. Zintl, J. Goubeau, W. Dullenkopf, Z. Phys. Chem. Abt. A 154 (1931) 1.
[8] A. Cisar, J.D. Corbett, Inorg. Chem. 16 (1977) 632.

[9] E. Canadell, S. Jobic, R. Brec, J. Rouxel, J. Solid State Chem. 98 (1992) 59.
[10] A. Mar, J.A. Ibers, J. Am. Chem. Soc. 115 (1993) 3227.
[11] R. Zagler, B. Eisenmann, H. Schäfer, Z. Naturforsch. B Chem. Sci. 42 (1987) 151.
[12] D. Fenske, G. Baum, H. Wolkers, B. Schreiner, F. Weller, K. Dehnicke, Z. Anorg. Allg. Chem. 619 (1993) 489.
[13] L.A. Devereux, G.J. Schrobilgen, J.F. Sawyer, Acta Crystallogr. Sect. C Cryst. Struct. Commun. 41 (1985) 1730.
[14] J.C. Huffman, R.C. Haushalter, Z. Anorg. Allg. Chem. 518 (1984) 203.
[15] H. Wolkers, B. Schreiner, R. Staffel, U. Müller, K. Dehnicke, Z. Naturforsch. B Chem. Sci. 46 (1991) 1015.
[16] B. Schreiner, K. Dehnicke, K. Maczek, D. Fenske, Z. Anorg. Allg. Chem. 619 (1993) 1414.
[17] C.J. Warren, R.C. Haushalter, A.B. Bocarsly, J. Alloys Compd. 233 (1996) 23.
[18] K.W. Klinkhammer, P. Böttcher, Z. Naturforsch. B Chem. Sci. 45 (1990) 141.
[19] P. Böttcher, R. Keller, J. Less-Common Met. 109 (1985) 311.
[20] C. Reisner, W. Tremel, J. Chem. Soc. Chem. Commun. (1997) 387.
[21] M. Björgvinsson, G.J. Schrobilgen, Inorg. Chem. 30 (1991) 2540.
[22] C. Adenis, V. Langer, O. Lindqvist, Acta Crystallogr. Sect. C Cryst. Struct. Commun. 45 (1985) 941.
[23] E. Zintl, A. Harder, B. Dauth, Z. Elektrochem. 40 (1934) 588.
[24] I. Schewe-Miller, P. Böttcher, Z. Kristallogr. 196 (1991) 137.
[25] I. Oftedal, Z. Phys. Chem. 128 (1927) 154.
[26] K. Spangenberg, Naturwissenschaften 15 (1927) 266.
[27] I. Schewe, P. Böttcher, Z. Naturforsch. B Anorg. Chem. Org. Chem. 45 (1990) 417.
[28] R.J. Batchelor, F.W.B. Einstein, I.D. Gay, C.H.W. Jones, R.D. Sharma, Inorg. Chem. 32 (1993) 4378.
[29] K.-H. Thiele, A. Steinicke, U. Dümichen, B. Neumüller, Z. Anorg. Allg. Chem. 622 (1996) 231.
[30] P. Böttcher, J. Getzschmann, R. Keller, Z. Anorg. Allg. Chem. 619 (1993) 476.
[31] J. Getzschmann, P. Böttcher, W. Kaluza, Z. Kristallogr. 211 (1996) 90.
[32] S. Yanagisawa, M. Tashiro, S. Anzai, J. Inorg. Nucl. Chem. 31 (1969) 943.
[33] J. Li, H.-Y. Guo, D.M. Proserpio, A. Sironi, J. Solid State Chem. 117 (1995) 247.
[34] J. Li, H.-Y. Guo, J.R. Carey, S. Mulley, D.M. Proserpio, A. Sironi, Mater. Res. Bull. 29 (1994) 1041.
[35] S.-J. Kim, H.-S. Bae, K.-A. Yee, J.-H. Choy, D.-K. Kim, N.-H. Hur, J. Solid State Chem. 115 (1995) 427.
[36] G. Cordier, C. Schwidetzky, H. Schäfer, Z. Naturforsch. B Anorg. Chem. Org. Chem. 39 (1984) 833.
[37] B. Eisenmann, H. Schäfer, Angew. Chem. Int. Ed. Engl. 17 (1978) 684.
[38] P. Böttcher, J. Less-Common Met. 70 (1980) 263.
[39] B. Schreiner, B. Neumuller, K. Dehnicke, Chemiker-Zeitung 115 (1991) 326.
[40] A. Hordvik, Acta Chem. Scand. 20 (1966) 1885.
[41] R.G. Teller, L.J. Krause, R.C. Haushalter, Inorg. Chem. 22 (1983) 1809.
[42] D.M. Smith, S.S. Schwulst, J.A. Ibers, unpublished results.
[43] P. Böttcher, U. Kretschmann, J. Less-Common Met. 95 (1983) 81.
[44] P. Böttcher, U. Kretschmann, Z. Anorg. Allg. Chem. 491 (1982) 39.
[45] W.S. Sheldrick, B. Schaaf, Z. Naturforsch. B Chem. Sci. 49 (1994) 993.
[46] D.Y. Valentine, O.B. Cavin, H.L. Yakel, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 33 (1977) 1389.
[47] P. Böttcher, R. Keller, Z. Anorg. Allg. Chem. 542 (1986) 144.
[48] K.-J. Range, M. Zabel, F. Rau, F. von Krziwanek, R. Marx, B. Panzer, Angew. Chem. Int. Ed. Engl. 21 (1982) 706.
[49] P. Böttcher, U. Kretschmann, Z. Anorg. Allg. Chem. 523 (1985) 145.
[50] W.S. Sheldrick, M. Wachhold, J. Chem. Soc. Chem. Commun. (1996) 607.
[51] W.S. Sheldrick, M. Wachhold, Angew. Chem. Int. Ed. Engl. 34 (1995) 450.