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Note

Synthesis, structure and properties of the polychalcogenides $[M_4Te_{12}]^{4-}$ (M=Cd, Hg)

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Abstract

The cluster anions, $[M_4Te_{12}]^{4-}$ (M=Cd, Hg) are reported. $(Et_4N)_4[Cd_4Te_{12}]$ (**I**) was prepared by the reaction of CdI_2, K_2Te_2 and Et_4NBr in a 2:3:2 molar ratio, in DMF. **I** crystallizes in the orthorhombic space group *Cmca* (No. 64) with $a=15.482(5)$, $b=22.563(4)$, $c=18.027(4)$ Å, $V=6297(5)$ Å^3 and $Z=4$. The black rectangular platelet crystals of $(Me_4N)_4[Hg_4Te_{12}]$ (**II**) were obtained from the reaction of $HgCl_2$ and K_2Te in a 2:5 molar ratio in DMF. **II** crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a=10.324(3)$, $b=21.851(6)$, $c=11.125(4)$ Å, $\beta=110.63(3)$°, $V=2348(3)$ Å^3 and $Z=2$. $[M_4Te_{12}]^{4-}$ is a cluster with two Te^{2-}, two $Te_2{}^{2-}$ and two $Te_3{}^{2-}$ ligands connecting a planar array of four tetrahedral M^{2+} metal centers. Its shape may be described as a basket, consisting of an $\{M_4(Te_2)_2Te_2\}$ core with two side $Te_3{}^{2-}$ handles. The average M–Te and Te–Te distances are 2.85(8) and 2.74(2) Å for **I**, respectively, and 2.86(12) and 2.73(1) Å for **II**, respectively. The far-IR spectra show two absorptions at 173 and 160 cm^{-1} for **I** and at 167 and 148 cm^{-1} for **II**. Thermal gravimetric analysis data are reported.

Keywords: Crystal structures; Tellurium complexes; Polychalcogenide complexes

1. Introduction

Compared to metal polysulfide and polyselenide chemistry, metal polytelluride chemistry is less explored. For the late transition (Group 10, 11 and 12) metals, $[M(Te_4)_2]^{2-}$ (M=Pd, Cd, Hg) [1,2], $[Ni_4Te_{20}]^{4-}$ [3], $[Pt_4Te_{22}]^{4-}$ [3b], $[MTe_7]^{2-}$ (M=Zn, Hg) [4], $[Hg_4Te_{12}]^{4-}$ [5], $[Hg_2Te_5]^{2-}$ [5], $[M_2Te_{12}]^{4-}$ (M=Cu, Ag) [6], $[M(Te_4)]^-$ (M=Cu, Ag) [7], $[Au_2Te_4]^{2-}$ [8] and $[MTe_7]^{3-}$ (M=Ag, Au) [9] are some examples of metal polytelluride compounds. One common fascinating feature in most of these compounds is the novelty of their structures, for which sulfide or selenide analogs do not exist. The structures of metal polychalcogenide anions are often dependent on the size of organic counter-cations. A typical example can be found in silver polyselenide chemistry where different structural compounds ranging from molecular clusters to 1D polymers have been prepared using different organic cations [10]. The trend continues in mercury polytelluride chemistry where two different $[Hg_4Te_{12}]^{4-}$ and $[Hg_2Te_5]^{2-}$ complexes have been isolated from the same ethylenediamine extract of the $K_2Hg_2Te_3$ alloy as $n\text{-}Bu_4N^+$ and Ph_4P^+ salts, respectively [5]. A similar reaction with an alloy of composition KHgTe and 2,2,2-cryptand has yielded the linear $[HgTe_2]^{2-}$ anion as a salt of 2,2,2-crypt-K^+ [11]. In our search for new mercury (or cadmium) polytelluride compounds we investigated smaller organic cations such as Me_4N^+ and Et_4N^+. In addition, shorter-chain polytelluride ligands, $Te_x{}^{2-}$ ($x=1$, 2) were employed to avoid forming the stable $[M(Te_4)_2]^{2-}$ (M=Cd, Hg) anion. While this paper was in preparation, the structure of $[Cd_4Te_{12}]^{4-}$, stabilized with $[Na(15\text{-crown-}5)]^+$ as the counterion, was reported [12]. Here we report the synthesis, structural characterization and some physicochemical properties of $(Et_4N)_4[Cd_4Te_{12}]$ (**I**) and $(Me_4N)_4[Hg_4Te_{12}]$ (**II**).

2. Experimental

2.1. Reagents

The chemicals in this research were used as obtained without further purification. All solvents, however, were distilled using standard methods.

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Table 1
Summary of crystallographic data for $(Et_4N)_4[Cd_4Te_{12}]$ (**I**) and $(Me_4N)_4[Hg_4Te_{12}]$ (**II**)

	I	**II**
Compound	$(Et_4N)_4[Cd_4Te_{12}]$	$(Me_4N)_4[Hg_4Te_{12}]$
Formula	$C_{32}H_{80}N_4Cd_4Te_{12}$	$C_{16}H_{48}N_4Hg_4Te_{12}$
Formula weight	2501.82	2630.14
Temperature (°C)	23	23
Crystal size (mm)	0.26 × 0.22 × 0.10	0.05 × 0.10 × 0.21
a (Å)	15.482(5)	10.324(3)
b (Å)	22.563(4)	21.851(6)
c (Å)	18.027(4)	11.125(4)
α (°)	90	90
β (°)	90	110.63(3)
γ (°)	90	90
V (Å^3), Z	6297(5), 4	2348(3), 2
Space group	*Cmca* (No. 64)	$P2_1/n$ (No. 14)
μ (cm^{-1}) Mo(Kα)	68.2	203.8
D_{calc} (g/cm^3)	2.639	3.719
Scan method	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{max}$ (°)	45	45
No. reflections collected	2313	3409
No. of reflections with $F_o^2 > 3\sigma(F_o)^2$	1335	1700
No. variables	70	123
Max. shift/e.s.d.	0.00	0.00
Phasing method	direct methods	direct methods
R/R_w[a] (%)	5.1/6.5	5.8/5.7

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

2.2. Physicochemical methods

Far-IR spectra were measured using CsI pellets of compounds on a Nicolet 740 FT-IR spectrometer. Thermal gravimetric analysis (TGA) was performed on a Shimadzu TGA-50. The samples were heated to 900 °C at a rate of 5 or 10 °C/min under a steady flow of dry N_2 gas.

Semi-quantitative elemental analyses were done by the SEM/EDS (scanning electron microscopy/ energy dispersive spectroscopy) technique on a JEOL JSM-35C microscope equipped with a Tracor Northern TN 5500 X-ray microanalysis attachment. The analysis results reported here are the average of three to five measurements on several different single crystals of each compound.

2.3. Syntheses

All experiments and manipulations were performed under an atmosphere of dry nitrogen. Preparations of K_2Te_2 and K_2Te were accomplished by dissolving appropriate stoichiometric ratios of elemental tellurium and potassium metal in liquid NH_3.

2.3.1. Preparation of $(Et_4N)_4[Cd_4(Te)_2(Te_2)_2(Te_3)_2]$ (I)

To a 40 ml DMF solution of 0.37 g (1.1 mmol) K_2Te_2 and 0.23 g (0.75 mmol) Et_4NBr, a 35 ml DMF solution of 0.27 g (0.74 mmol) CdI_2 was added dropwise over 20 min. When all the CdI_2 solution was added, the reaction solution turned brownish black in color. After removal of the undissolved black precipitate by filtration, the solution was placed into several long test tubes and ether was layered over it. Upon allowing the solution to stand for a week, black polyhedral chunky crystals (24% yield) were obtained. SEM/EDS analysis on these crystals showed the Cd:Te ratio as 1:3.5.

2.3.2. Preparation of $(Me_4N)_4[Hg_4(Te)_2(Te_2)_2(Te_3)_2]$ (II)

To a solution of 0.23 g (1.1 mmol) K_2Te in 20 ml DMF, a 15 ml DMF solution of 0.12 g (0.44 mmol) $HgCl_2$ was added dropwise over 15 min. K_2Te is not soluble in DMF, but dissolved to give a dark brownish solution upon addition of $HgCl_2$ solution. Following filtration to remove a precipitate, a 80 ml MeOH solution of 0.05 g (0.46 mmol) Me_4NCl was layered over the filtrate solution. Black rectangular platelet crystals grew upon allowing the solution to stand for a week. These crystals were isolated and washed with ether several times. The yield was 10%, based on the Hg metal ion content used. SEM/EDS analysis on these crystals showed the Hg:Te ratio as 1:2.7.

Both compounds gave satisfactory elemental analyses.

2.4. X-ray crystallographic studies

Single crystals of **I** and **II** were mounted on the tip of glass fibers with epoxy adhesive and coated with

Table 2
Fractional atomic coordinates and B_{eq} values for $(Et_4N)_4[Cd_4Te_{12}]$ (I) with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}[a] (Å^2)
Cd(1)	0.1240(1)	0.07896(7)	−0.0220(1)	4.32(8)
Te(1)	0	0.0758(1)	0.1010(1)	4.0(1)
Te(2)	0	−0.0435(1)	0.1357(1)	4.4(1)
Te(3)	0.2548(1)	0	0	4.5(1)
Te(4)	0	0.2145(1)	−0.1255(1)	5.8(1)
Te(5)	0.1445(1)	0.20230(7)	−0.0407(1)	6.3(1)
N(1)	1/4	0.118(1)	1/4	6(2)
N(2)	0	0.138(1)	−0.376(2)	9(2)
C(1)	0.2026	0.1762	0.2034	8(1)
C(2)	0.2251	0.2286	0.2448	18(2)
C(1′)	0.2174	0.0668	0.2075	9(1)
C(2′)	0.2881	0.0101	0.2229	8(1)
C(3)	0.3442	0.1233	0.2372	12(2)
C(3′)	0.2263	0.1292	0.3380	9(1)
C(4)	0.3557	0.1252	0.1470	15(1)
C(5)	0.0822	0.1248	−0.3216	12(1)
C(5′)	−0.1005	−0.1512	0.4150	11(1)
C(6)	0.1755	0.1341	−0.3315	23(2)
C(6′)	−0.1405	−0.0838	0.4318	37(1)
C(7)	0	0.0855	−0.4343	19(1)
C(7′)	0	−0.0795	0.3452	4(2)
C(8)	0	0.0300	−0.3914	14(2)
C(9)	0	0.1965	−0.4223	20(1)
C(9′)	0	−0.1821	0.2963	4(1)
C(10)	0	0.2449	−0.3502	15(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq}=(8\pi^2/3)[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$. The anisotropic temperature factor expression is $\exp[-2\pi^2(B_{11}a^{*2}h^2+\ldots+2B_{12}a^*b^*hk+\ldots)]$.

Table 3
Fractional atomic coordinates and B_{eq} values for $(Me_4N)_4[Hg_4Te_{12}]$ (II) with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}[a] (Å^2)
Hg(1)	0.0382(2)	0.03566(8)	0.2443(2)	3.34(7)
Hg(2)	−0.0959(2)	0.11111(8)	−0.1004(2)	3.39(7)
Te(1)	0.1464(2)	−0.0741(1)	0.3455(3)	3.0(1)
Te(2)	0.1879(2)	0.0847(1)	0.0793(3)	2.7(1)
Te(3)	−0.2245(2)	0.0236(1)	0.0287(3)	2.7(1)
Te(4)	−0.1391(2)	0.2253(1)	−0.0116(3)	3.0(1)
Te(5)	0.0651(2)	0.2215(1)	0.2258(3)	3.4(1)
Te(6)	−0.0235(3)	0.1388(1)	0.3625(3)	3.2(1)
N(1)	0.542(3)	0.218(1)	0.189(3)	3(1)
N(2)	0.615(3)	−0.061(2)	0.336(4)	4(2)
C(1)	0.643(4)	0.265(2)	0.222(5)	3.6(9)
C(2)	0.404(4)	0.245(2)	0.136(5)	4(1)
C(3)	0.549(5)	0.172(2)	0.299(6)	6(1)
C(4)	0.552(4)	0.173(2)	0.077(5)	5(1)
C(5)	0.609(4)	−0.081(2)	0.470(5)	6(1)
C(6)	0.761(4)	−0.050(2)	0.347(4)	3.6(9)
C(7)	0.549(6)	−0.100(3)	0.229(7)	10(1)
C(8)	0.542(4)	0.002(2)	0.296(5)	5(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq}=(8\pi^2/3)[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$. The anisotropic temperature factor expression is $\exp[-2\pi^2(B_{11}a^{*2}h^2+\ldots+2B_{12}a^*b^*hk+\ldots)]$.

Krylon™ to protect them from exposure to air. The crystallographic data for I and II were collected on Rigaku AFC6S four-circle automated diffractometers. Accurate unit cell parameters were determined from the 2θ, ω, ϕ and χ angles of 15 to 25 centered reflections. The intensities of three standard reflections were monitored every 150 reflections. No serious decay was observed during the data collection period. An empirical absorption correction based on ψ scans of three strong reflections with χ ~90° was applied to each data set. The structures were solved by direct methods using the SHELXS-86 software program and refined with a full-matrix least-squares technique. After isotropic refinement of all atoms, DIFABS corrections were applied [13]. All calculations were performed on a VAXstation 3100/76 computer with the TEXSAN crystallographic software package [14]. All atoms in the anions of both compounds were refined anisotropically. The hydrogen atom positions were calculated but not refined.

An asymmetric unit in the structure of the $[Cd_4Te_{12}]^{4-}$ anion of I has one Cd atom and five Te atoms. While Cd and Te(5) atoms are sitting in general positions, Te(1), Te(2) and Te(4) sit in a mirror plane (0,y,z), and Te(3) sits on a two-fold axis (x,0,0). The two independent Et_4N^+ cations in the structure of I are completely disordered and atomic coordinates of all C atoms had to be fixed during the final refinement of the structure. Atom N(1) lies on a two-fold axis ($\frac{1}{4}$,y,$\frac{1}{4}$), while atom N(2) is in a mirror plane (0,y,z). The carbon atoms associated with the N(1) atom are in general positions, but disordered except for C(4). The second Et_4N^+ cation was modeled with two orientations having a common nitrogen atom, N(2). One orientation was assigned with 4/5 occupancy while the other with only 1/5. Both N atoms were refined anisotropically and all C atoms were refined isotropically.

In the structure of II, only half of $(Me_4N)_4[Hg_4Te_{12}]$ is in the asymmetric unit and the other half can be generated by a center of symmetry situated in the center of the $[Hg_4Te_{12}]^{4-}$ cluster. For Me_4N^+ organic cations, the N atoms were refined anisotropically and all C atoms were refined isotropically. Table 1 shows the crystal data and details for the structure analyses of both compounds. The fractional coordinates and temperature factors (B_{eq}) of all atoms with their e.s.d.s are given in Tables 2 and 3. Based on the atomic coordinates from the X-ray single crystal diffraction study, X-ray powder patterns for both compounds were calculated with the software package CERIUS [15]. The good agreement between observed X-ray powder patterns and those calculated confirmed the homogeneity and purity of the compounds.

Table 4
TGA data for $(Et_4N)_4[Cd_4Te_{12}]$ (**I**) and $(Me_4N)_4[Hg_4Te_{12}]$ (**II**)

Compound	Temperature range (°C)	Weight loss (%)	Proposed formula of residue	Calculated weight loss (%)
$(Et_4N)_4[Cd_4Te_{12}]$	166–224	30.5	Cd_4Te_{10}	31.0
	465–615	26.0	Cd_4Te_5	25.5
	696–876	42.0		
$(Me_4N)_4[Hg_4Te_{12}]$	190–220	9.3	Hg_4Te_{12}	11.3
	297–405	40.6	10Te	40.2
	465–590	41.2		

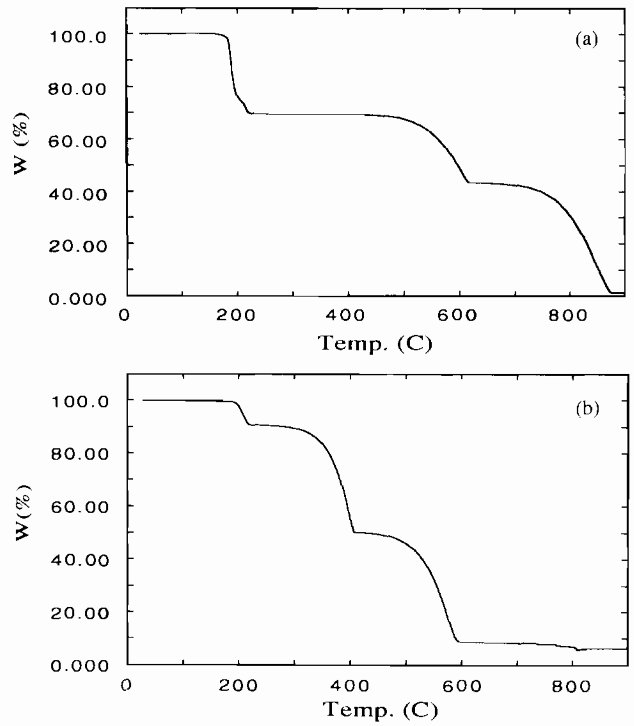


Fig. 1. TGA diagrams of (a) $(Et_4N)_4[Cd_4Te_{12}]$ (**I**) and (b) $(Me_4N)_4[Hg_4Te_{12}]$ (**II**).

3. Results and discussion

3.1. Properties

DMF and CH_3CN solutions of **I** show a dark brown color and give featureless UV–Vis spectra. They slowly decompose to give black precipitates in several hours. Compound **II** is insoluble in most solvents, including DMF.

The far-IR spectra of **I** and **II** show two peaks at 160 and 173 cm^{-1}, and at 148 and 167 cm^{-1}, respectively. These peaks are assigned to Te–Te and M–Te (M = Cd, Hg) vibration modes. Frequencies of some previously assigned Te–Te vibration modes range from 188 to 219 cm^{-1}, as found in metal polytelluride and free polytelluride complexes such as $[PdTe_8]^{2-}$ (ν(Te–Te) = 200 cm^{-1}) [1c], $[Au_2Te_4]^{2-}$ (ν(Te–Te) = 188 cm^{-1}) [16] and $[Te_4]^{2-}$ (ν(Te–Te) = 219, 188 cm^{-1}) [17].

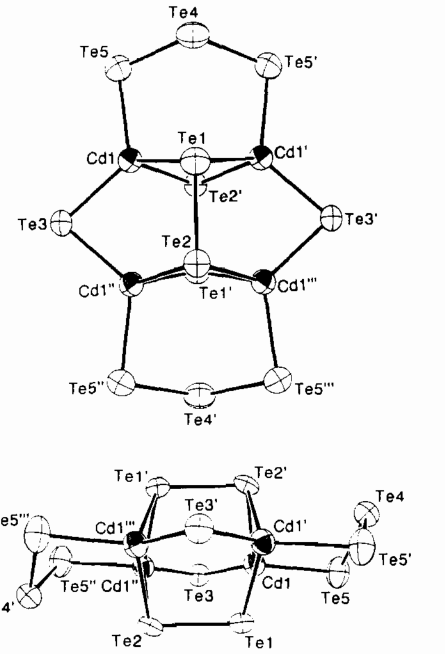
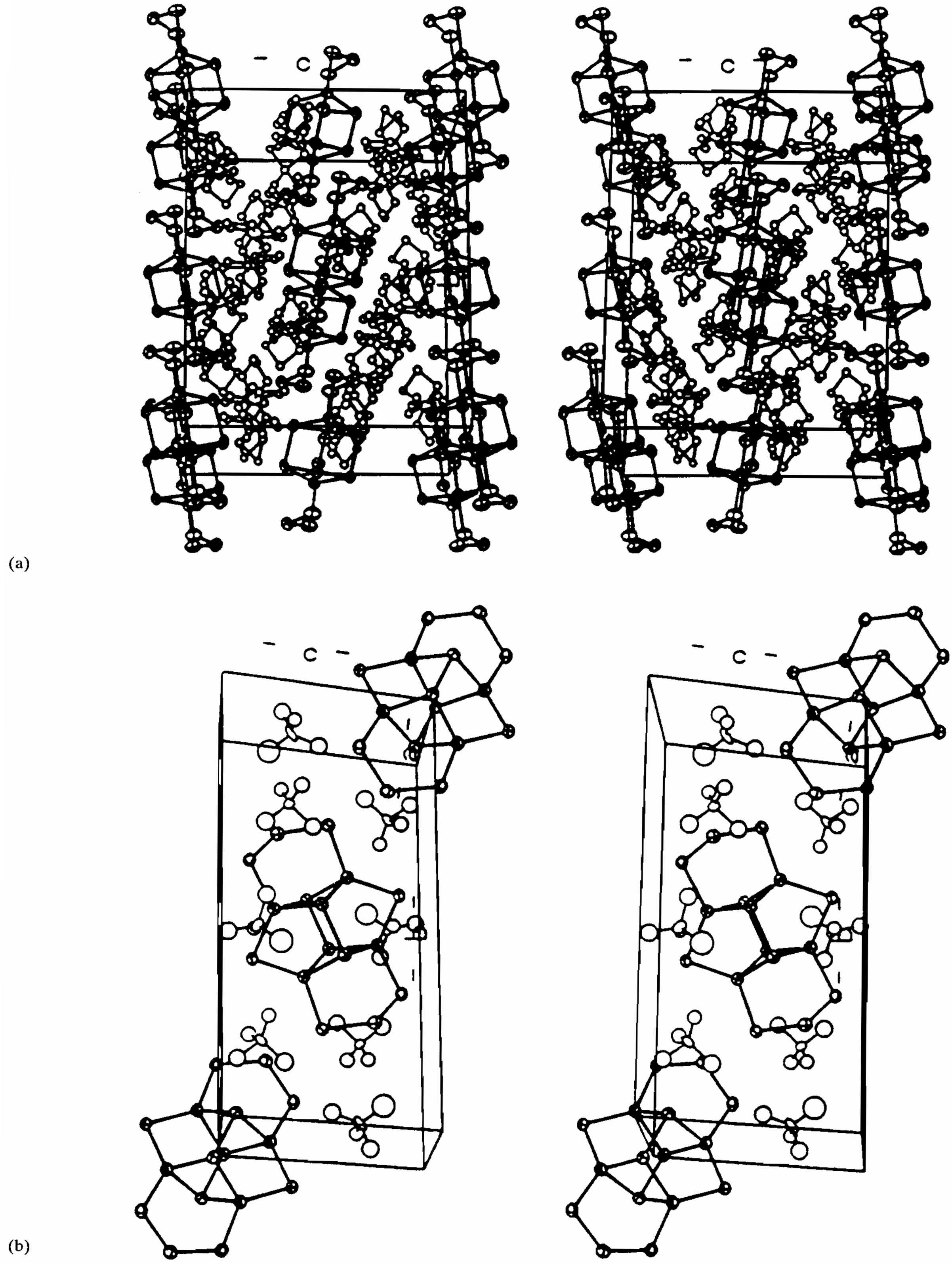


Fig. 2. ORTEP representation (two views) of the $[Cd_4Te_{12}]^{4-}$ cluster with the labeling scheme. The Hg analog has a similar structure.

TGA results for both compounds are summarized in Table 4 and shown in Fig. 1. Compound **I** begins to lose Et_2Te, Et_3N and other products in the temperature range 166–224 °C. Some Te is lost in the next step of weight loss (465–615 °C) to give an intermediate of CdTe, which evaporates in the final step of weight loss (696–876 °C). The thermal decomposition behavior of $(Me_4N)_4[Hg_4Te_{12}]$ (**II**) is similar to **I**. Loss of Me_2Te and Me_3N occurs at 190–220 °C, followed by the evaporation of Hg metal and some Te at 297–405 °C. Finally, most Te evaporates in the temperature range 465–590 °C.

3.2. Description of structures

In **I** and **II**, the $[M_4Te_{12}]^{4-}$ (M = Cd, Hg) anions are well separated from non-interacting organic counter-

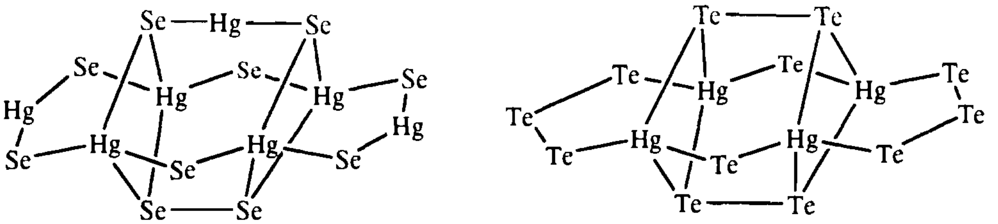


(a)

(b)

Fig. 3. The packing diagrams (stereo view) of (a) $(Et_4N)_4[Cd_4Te_{12}]$ (**I**) and (b) $(Me_4N)_4[Hg_4Te_{12}]$ (**II**) in the unit cell.

cations. These anions are structurally similar to the Bu_4N^+ salt [5]. As shown in Fig. 2, $[M_4Te_{12}]^{4-}$ are clusters in which four M^{2+} metal ion centers are connected through three different kinds of $Te_x{}^{2-}$ ligands, two Te^{2-}, two $Te_2{}^{2-}$ and two $Te_3{}^{2-}$. It is tempting to describe the shape of the cluster as a basket having



Scheme 1.

Table 5
Selected bond distances (Å) and bond angles (°) in the [Cd$_4$Te$_{12}$]$^{4-}$ anion; standard deviations are given in parentheses[a]

Cd–Te(1)	2.933(2)	Te(1)–Te(2)	2.764(3)
Cd–Te(2)	2.920(2)	Te(4)–Te(5)	2.725(2)
Cd–Te(3)	2.727(2)		
Cd–Te(5)	2.821(2)	Te–Te (mean)	2.74(3)
Cd–Te (mean)	2.85(10)		
Te(1)–Cd–Te(2)	95.37(7)	Cd–Te(1)–Cd	81.74(8)
Te(1)–Cd–Te(3)	111.13(7)	Cd–Te(2)–Cd	82.21(9)
Te(1)–Cd–Te(5)	100.81(7)	Cd–Te(3)–Cd	84.0(1)
Te(2)–Cd–Te(3)	114.29(7)	Cd–Te(1)–Te(2)	101.21(7)
Te(2)–Cd–Te(5)	105.13(8)	Cd–Te(2)–Te(1)	96.22(7)
Te(3)–Cd–Te(5)	125.31(8)	Cd–Te(5)–Te(4)	94.22(8)
		Te(5)–Te(4)–Te(5)	110.4(1)

[a] The e.s.d.s in the mean bond distances were calculated by the equation $\sigma_l = \{\Sigma_n(l_n - l)^2/n(n-1)\}^{1/2}$, where l_n is the distance of the nth bond, l is the mean bond distance, and n is the number of bonds.

Table 6
Selected bond distances (Å) and bond angles (°) in the [Hg$_4$Te$_{12}$]$^{4-}$ anion; standard deviations are given in parentheses[a]

Hg(1)–Te(1)	2.716(3)	Te(2)–Te(3)	2.740(4)
Hg(1)–Te(2)	2.984(3)	Te(4)–Te(5)	2.740(4)
Hg(1)–Te(3)	2.932(3)	Te(5)–Te(6)	2.719(4)
Hg(1)–Te(6)	2.794(3)		
Hg(2)–Te(1)	2.713(4)	Te–Te (mean)	2.73(1)
Hg(2)–Te(2)	2.964(3)		
Hg(2)–Tc(3)	2.970(3)		
Hg(2)–Te(4)	2.778(3)		
Hg–Te (mean)	2.86(12)		
Te(1)–Hg(1)–Te(2)	110.22(9)	Hg(1)–Te(1)–Hg(2)	86.6(1)
Te(1)–Hg(1)–Te(3)	112.7(1)	Hg(1)–Te(2)–Hg(2)	83.21(8)
Te(1)–Hg(1)–Te(6)	130.2(1)	Hg(1)–Te(2)–Te(3)	98.1(1)
Te(2)–Hg(1)–Te(3)	93.39(9)	Hg(2)–Te(2)–Te(3)	97.4(1)
Te(2)–Hg(1)–Te(6)	104.68(9)	Hg(1)–Te(3)–Hg(2)	84.01(8)
Te(3)–Hg(1)–Te(6)	99.13(9)	Hg(1)–Te(3)–Te(2)	101.9(1)
Te(1)–Hg(2)–Te(2)	114.5(1)	Hg(2)–Te(3)–Te(2)	100.9(1)
Te(1)–Hg(2)–Te(3)	109.5(1)	Hg(2)–Te(4)–Te(5)	98.6(1)
Te(1)–Hg(2)–Te(4)	128.9(1)	Hg(1)–Te(6)–Te(5)	95.5(1)
Te(2)–Hg(2)–Te(3)	93.01(9)	Te(4)–Te(5)–Te(6)	105.3(1)
Te(2)–Hg(2)–Te(4)	100.36(9)		
Te(3)–Hg(2)–Te(4)	104.6(1)		

[a] The e.s.d.s in the mean bond distances were calculated by the equation $\sigma_l = \{\Sigma_n(l_n - l)^2/n(n-1)\}^{1/2}$, where l_n is the distance of the nth bond, l is the mean bond distance, and n is the number of bonds.

an {M$_4$(Te$_2$)$_2$Te$_2$} core with two side Te$_3$$^{2-}$ handles. In the cluster, four metal centers are in a planar arrangement and have distorted tetrahedral coordination. [Cd$_4$Te$_{12}$]$^{4-}$ possesses both a crystallographic center of symmetry and a mirror plane, bisecting it through Te1,Te2,Te4,Te4′,Te2′ and Te1′ atoms. Only a crystallographic center of symmetry is present in [Hg$_4$Te$_{12}$]^4 . Fig. 3 shows the packing of anions and cations in the unit cell of **I** and **II**. Some selected bond distances and angles in the [M$_4$Te$_{12}$]$^{4-}$ clusters of **I** and **II** are given in Tables 5 and 6.

We view [M$_4$Te$_{12}$]$^{4-}$ as structurally related to [Hg$_7$Se$_{10}$]$^{4-}$, by replacing the side Te$_3$$^{2-}$ ligands with Se–Hg–Se units and one of the μ_4-Te$_2$$^{2-}$ ligands with a linear Se–Hg–Se unit [18]. This is shown in Scheme 1.

In the [Cd$_4$Te$_{12}$]$^{4-}$ cluster, the average Cd–Te and Te–Te bond distances are 2.85(10) and 2.74(3) Å, respectively. There are two different sets of Cd–Te bonds, that is, shorter bonds to two-coordinate Te (2.77(7) Å) and longer bonds to three-coordinate Te (2.93(1) Å). This behavior was first seen in Haushalter's [Hg$_4$Te$_{12}$]$^{4-}$ cluster. It is also present in the [Hg$_4$Te$_{12}$]$^{4-}$ cluster of **II**, which contains shorter Hg–Te bonds to two-coordinate Te (2.75(4) Å) and longer bonds to three-coordinate Te (2.96(2) Å). The average Hg–Te and Te–Te bond distances are 2.86(12) and 2.73(1) Å, respectively. These distances in **I** and **II** compare reasonably well with those found in (Bu$_4$N)$_4$[Hg$_4$Te$_{12}$] and [Na(15-Crown-5)]$_4$[Cd$_4$Te$_{12}$]·8DMF.

4. Supplementary material

Tables of detailed crystallographic data, atomic coordinates of all atoms, anisotropic thermal parameters and bond distances and angles for (Et$_4$N)$_4$[Cd$_4$Te$_{12}$] and (Me$_4$N)$_4$[Hg$_4$Te$_{12}$] are available from author M.G.K. on request.

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