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FULL PAPER

Metal iodides in polyiodide networks. The structural chemistry of CdI_2 with an excess of iodine*

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The reaction between $[Me_3S][I_5]$ and CdI_2 at 80 °C resulted in the compound $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$, which has been characterised by X-ray diffraction, Raman spectroscopy and EXAFS. The structure consists of layers of I_2-bridged, dimeric $Cd_2I_6^{2-}$ units interspaced with interacting I_2 molecules arranged almost perpendicularly to the cadmium-containing layers. The $Cd_2I_6^{2-}$ units consist of edge-sharing CdI_4 tetrahedra. The I_2 molecules have intramolecular distances ranging from 2.73 to 2.74 Å and intermolecular distances ranging from 3.37 to 3.56 Å. The I_2-bridged $Cd_2I_6^{2-}$ dimers create a network that can be described as infinite chains of I_2 co-ordinated in a zigzag manner to the $Cd_2I_6^{2-}$ dimers, interspaced by formal I_{10} units. The Raman spectrum is dominated by a peak at about 185 cm^{-1}, which confirms the charge-transfer interaction of I_2 with the $Cd_2I_6^{2-}$ units. The EXAFS of Cd (K shell) was determined for a 1:10 mixture of CdI_2–$[Et_3S][I_7]$ confirming the structural relationship of Cd^{II} in the liquid reaction medium and the isolated polyiodide compound. For comparison, the crystal structures of iodine-free $[Et_3S][Cd_2I_6]_{1/2}$ and two phases of polymeric $[Me_3S][CdI_3]$ were also determined.

Polyiodide networks often display low-dimensionality, with one- and two-dimensional structural motifs, and an electrical conductivity ranging from that of metals to insulators.[1–3] The polyiodides are denoted according to their stoichiometry: triiodides, pentaiodides, heptaiodides, *etc*. However, this notation seldom communicates anything about the structural properties and crystallographic repeating units. With a few exceptions, all the polyiodide structural fragments can be reductionalistically broken down into only three building blocks, I^-, I_2 and I_3^-, irrespective of whether the repeating unit along one direction in the crystal corresponds to larger units, such as I_5^-, I_8^{2-}, I_{16}^{4-}, *etc.* For a co-ordination chemist, it is interesting that both in discrete polyiodide anions and along extended one- and two-dimensional structural units, the ions I^- and I_3^- tend to be surrounded (*i.e.* solvated) by the 'neutral solvent' I_2. In the proposed Grotthus mechanism of electrical conductivity the I_2 molecules act as iodide acceptors and the iodide anions as the donors. Recently, we have studied the I^--donating properties of I_3^- in detail.[4]

In the process of substituting the iodide or triiodide fragments into polyiodide chains, we here report the results for CdI_2 in the form of $Cd_2I_6^{2-}$ dimers. The compound $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$ **1** was isolated at ambient temperature from a melt of $[Me_3S][I_5]$ and the crystal structure data were recorded at −123 °C.

Since the analogous HgI_2–polyiodide systems have displayed a structural ambiguity depending on the sulfonium cation size, we have also determined the crystal structure of the corresponding iodine-free compound $[Et_3S][Cd_2I_6]_{1/2}$ **2**. All efforts to synthesize the compound $[Me_3S][Cd_2I_6]_{1/2}$ failed and two phases of $[Me_3S][CdI_3]$, **3** and **4**, were obtained instead.

Experimental

General

The compounds CdI_2 and iodine were used as obtained from Merck. Before use $[Me_3S]I$ and $[Et_3S]I$ (Lancaster) were recrystallised from hot ethanol. Raman spectra were recorded on a Bio-Rad FT spectrometer which provides data from 70 to 4000 cm^{-1} with an Nd:YAG laser (1064 nm) as the source of the exciting radiation. X-Ray absorption (EXAFS) data were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL), using beamline 4-1 at 3.0 keV and 50–60 mA. Monochromatic radiation was obtained from an Si(220) double-crystal monochromator. High-order harmonics were rejected by 50% detuning. Incident and transmitted X-rays were monitored with argon-filled ion chambers. Seven scans were made for the cadmium sample, internally referenced to the K edge of the corresponding metal foil to 26.735 keV. The liquid sample was contained in a cell of 1 mm thickness with Kapton film as windows. The data were processed by standard procedures for pre-edge substraction, spline fit and removal.[5] The FEFF 7 program was used to calculate the Cd–I and Cd–Cd phase shift and amplitude functions, which were used in this non-linear, least-squares fit of the new EXAFS data.[6] Final data evaluation was made by a least-squares fit.[7]

Preparations

$[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$ 1. An equimolar mixture of $[Me_3S][I_5]$(l) and CdI_2(s) was heated to 80 °C for 10 min. Black crystals appeared when the reaction mixture reached room temperature. The yield was estimated to be about 40%. However, the crystals are not stable on storing because of loss of iodine. The salt $[Me_3S][I_5]$(l) was made by treating $[Me_3S]I$ with I_2 (1:2 molar ratio).

$[Et_3S][Cd_2I_6]_{1/2}$ 2. An equimolar mixture of $[Et_3S][I_5]$(l) and CdI_2(s) was heated to 90 °C for 10 min. The yield was estimated to be about 30%. It is interesting that the change of cation from Me_3S^+ to Et_3S^+ results in transparent crystals when the reaction mixture reaches room temperature. Possibly, iodine-containing products similar to $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$ can be isolated at lower temperatures. The salt $[Et_3S][I_5]$(l) was made by treating $[Et_3S]I$ with I_2 (1:2 molar ratio).

$[Me_3S][CdI_3]$. An equimolar mixture of $[Me_3S]I$ and CdI_2 was heated in acetone at 60 °C. After evaporation of acetone transparent crystals of salts **3** and **4** appeared. Yield at least 70%.

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* *Non-SI unit employed*: eV ≈ 1.60 × 10^{-19} J.

Table 1 Crystallographic data for compounds **1**, **2**, **3** and **4***

	1	**2**	**3**	**4**
Formula	$C_3H_9CdI_9S$	$C_6H_{15}CdI_5S$	$C_3H_9CdI_3S$	$C_3H_9CdI_3S$
M	1328.69	1224.74	570.29	570.29
Crystal size/mm	0.1 × 0.1 × 0.2	0.08 × 0.1 × 0.2	0.3 × 0.08 × 0.07	0.25 × 0.2 × 0.09
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	8.9662(8)	7.885(1)	8.941(2)	8.393(1)
b/Å	19.843(2)	13.233(6)	17.112(3)	16.714(2)
c/Å	12.896(2)	14.862(3)	8.388(2)	17.537(2)
β/°	92.778(7)	96.05(1)	105.42(1)	102.54(1)
U/Å^3	2291.8(4)	1542.2(6)	1237.3(8)	2401.4(5)
Z	4	4	4	8
D_c/g cm^{-3}	3.85	2.64	3.06	3.15
μ/cm^{-1}	131.53	75.22	93.63	96.48
$2\theta_{max}$	52.48	49.96	60.80	49.94
h,k,l Ranges	−11, −24, ±16	+9, +15, ±17	±12, −24, +11	+9, −19, ±20
T/K	150	293	293	150
Total data collected	5080	3067	4105	4682
Unique data	4784	2873	3872	4422
R_{int}	4.58	6.00	4.9	3.19
Observed data [$I \geq 3\sigma(I)$]	3499	1123	1339	3325
T_{min}, T_{max}	0.698, 1.000	0.654, 1.000	0.777, 1.000	0.545, 1.000
Data, variables	3499, 128	1123, 98	1339, 83	3325, 146
Goodness of fit	2.131	1.311	2.014	1.792
Final difference map features/e Å^{-3}	−1.60, 1.81	−0.83, 0.69	−1.24, 2.37	−1.17, 1.67
R, R'	0.0388, 0.0592	0.0411, 0.0445	0.0450, 0.0451	0.0352, 0.0426

* Details in common: CAD4 diffractometer; monoclinic, Mo-Kα radiation (λ = 0.710 69 Å); ω–2θ scans.

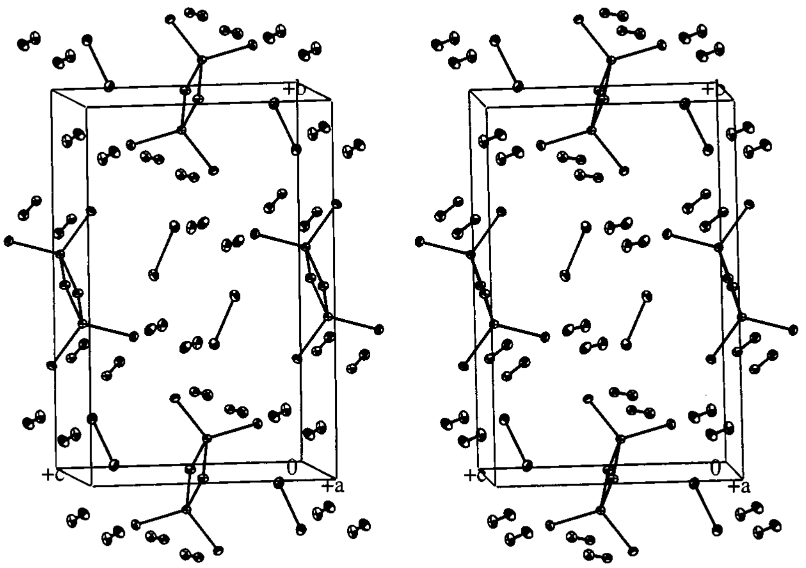

Fig. 1 Stereoscopic view of the crystal structure of $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$. The cations are omitted for clarity

Crystallography

A summary of the crystallographic data is provided in Table 1. All data were corrected for Lorentz-polarisation effects and an empirical absorption correction was applied using DIFABS[8] (compound **1**) or ψ-scan[9] methods (**2**–**4**). All the structures were solved by direct methods (SIR 92).[10] Hydrogen atoms were not located and not included at calculated positions. The final cycle of full-matrix least-squares refinement, $\Sigma w(|F_o| - |F_c|)$, was based on the observed reflections [$I \geq 3\sigma(I)$] and the number of variable parameters, using neutral atom scattering factors and anomalous dispersion corrections. All calculations were performed with the TEXSAN crystallographic software package.[11] Crystals of compound **1** were mounted on glass fibres and stored in liquid nitrogen, since iodine tends to be lost under ambient conditions. The data were collected at 150 K. Crystals of **2**, **3** and **4** were mounted on a glass fibre at room temperature. The data collections for **2** and **3** were performed under ambient conditions, that for **4** at 150 K. The carbon atoms closest to the sulfur atom in the cation of compound **2** exhibit a disorder over two distinct positions. The sulfur atom of the cation in **3** is disordered over two distinct positions.

CCDC reference number 186/893.

See http://www.rsc.org/suppdata/dt/1998/1425/ for crystallographic files in .cif format.

Results and Discussion

The structure of $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$ (Fig. 1) consists of layers of I_2-bridged, dimeric $Cd_2I_6^{2-}$ units interspaced with I_2 molecules arranged almost perpendicularly to the cadmium-containing layers. The $Cd_2I_6^{2-}$ units consist of edge-sharing CdI_4 tetrahedra with central Cd–I distances of 2.835(1) and 2.858(1) Å and terminal Cd–I distances of 2.728(1) and 2.750(2) Å. The corresponding dimers in $[Et_3S][Cd_2I_6]_{1/2}$ (Fig. 2), which we have studied for comparison, are very similar with central Cd–I distances of 2.854(2) and 2.872(2) Å and terminal

Table 2 Selected bond distances (Å) and angles (°) in compounds **1**, **2**, **3** and **4**

$[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$ **1**			
I(1)–Cd	2.728(1)	I(8)–I(9)	2.730(1)
I(2)–Cd	2.750(2)	I(1)···I(4*)	3.510(2)
I(3*)–Cd	2.835(1)	I(1)···I(9)	3.465(1)
I(3)–Cd	2.858(1)	I(2)···I(5*)	3.367(2)
I(4)–I(5)	2.740(2)	I(2)···I(7*)	3.415(1)
I(4)···I(6)	3.561(1)	I(2)···I(8*)	3.500(1)
I(6)–I(7)	2.731(2)	Cd···Cd*	3.830(2)
I(1)–Cd–I(2)	111.37(5)	I(2)–Cd–I(3)	114.86(5)
I(1)–Cd–I(3)	112.49(5)	I(2)–Cd–I(3*)	107.72(5)
I(1)–Cd–I(3*)	114.01(5)	I(3)–Cd–I(3*)	95.44(4)
$[Et_3S][Cd_2I_6]_{1/2}$ **2**			
I(1)–Cd	2.723(2)	I(3*)–Cd	2.872(2)
I(2)–Cd	2.722(2)	Cd···Cd*	3.829(3)
I(3)–Cd	2.854(2)		
Cd–I(3)–Cd*	83.93(6)	I(2)–Cd–I(3)	112.62(7)
I(1)–Cd–I(2)	114.22(7)	I(2)–Cd–I(3*)	111.42(7)
I(1)–Cd–I(3)	111.56(7)	I(3)–Cd–I(3*)	96.07(6)
I(1)–Cd–I(3*)	109.51(6)		
$[Me_3S][CdI_3]$ **3**			
I(1)–Cd	2.824(2)	I(3)–Cd	2.702(2)
I(1*)–Cd	2.939(2)	Cd···Cd*	4.410(6)
I(2)–Cd	2.722(2)		
I(1)–Cd–I(2)	114.35(5)	I(2)–Cd–I(1*)	100.07(5)
I(1)–Cd–I(3)	112.09(5)	I(2)–Cd–I(3)	121.82(6)
I(1)–Cd–I(1*)	97.56(5)	I(3)–Cd–I(1*)	106.57(5)
$[Me_3S][CdI_3]$ **4**			
I(1)–Cd(1)	2.845(1)	I(4)–Cd(2)	2.844(1)
I(1)–Cd(2)	2.892(1)	I(5)–Cd(2)	2.730(1)
I(2)–Cd(1)	2.699(1)	I(6)–Cd(2)	2.713(1)
I(3)–Cd(1)	2.745(1)	Cd(1)···Cd(2)	4.502(1)
I(4)–Cd(1)	2.899(1)	Cd(1)···Cd(2*)	4.314(1)
Cd(1)–I(1)–Cd(2)	97.51(3)	I(3)–Cd(1)–I(4)	101.33(3)
Cd(1)–I(4)–Cd(2)	103.24(3)	I(1*)–Cd(2)–I(4)	98.66(3)
I(1)–Cd(1)–I(2)	111.40(3)	I(1*)–Cd(2)–I(5)	102.91(3)
I(1)–Cd(1)–I(3)	115.49(3)	I(1*)–Cd(2)–I(6)	109.23(3)
I(1)–Cd(1)–I(4)	96.11(3)	I(4)–Cd(2)–I(5)	113.65(3)
I(2)–Cd(1)–I(3)	118.99(4)	I(4)–Cd(2)–I(6)	108.25(3)
I(2)–Cd(1)–I(4)	110.23(3)	I(5)–Cd(2)–I(6)	121.45(4)

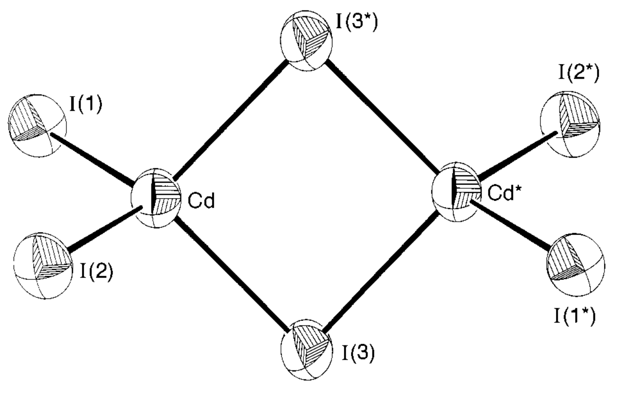

Fig. 2 The $Cd_2I_6^{2-}$ dimer in $[Et_3S][Cd_2I_6]_{1/2}$

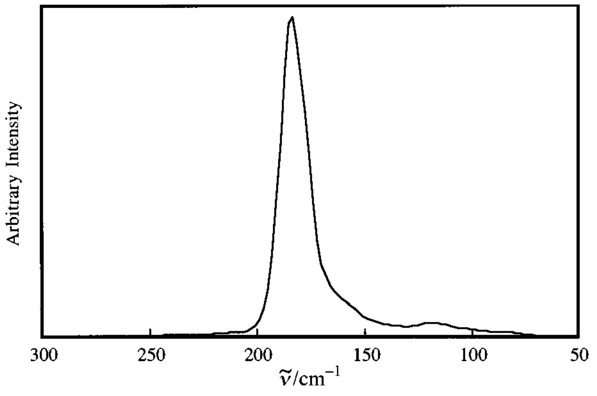

Fig. 3 Raman spectrum of $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$

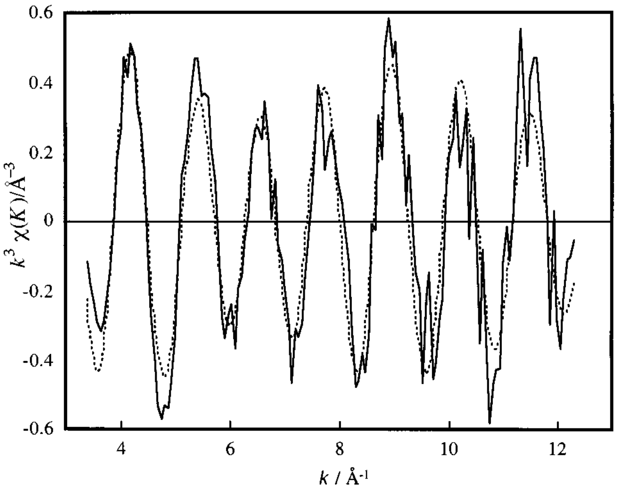

Fig. 4 Experimental EXAFS data (——) and structural model (- - -) of the cadmium K edge for the reaction medium $[Et_3S][I_7]$–CdI_2 (10 : 1)

distances of 2.722(2) and 2.723(2) Å. Selected bond lengths and angles are given in Table 2.

The iodine molecules in $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$ are divided into two groups: one in the plane of the terminal iodides of $Cd_2I_6^{2-}$, and one intercalated between the cadmium-containing layers. The I_2 molecules within the plane exclusively interact with the terminal iodides of the dimeric units and are at distances typically found in polyiodides [3.367(2) and 3.510(2) Å]. The I–I distances within the I_2 molecules, 2.730(1), 2.731(2) and 2.740(2) Å, are longer than those found for pure iodine in the solid state [2.715(6) Å][12] and in the gas phase [2.667(2) Å].[13] This indicates a significant interaction with the donor, the cadmate(II) anions, since they donate electron density into the σ* antibonding orbital of the I_2 molecule and consequently cause an elongation of the bond length. The intercalated iodine molecules are also placed in proximity to the iodide ligands, but on average at slightly longer distances: 3.41–3.56 Å. The intercalated I_2 molecules are arranged very similarly to Br_2 in the recently reported $Br_2\cdot CsF$ compounds.[14,15] The Br_2 molecules were shown to interact weakly with the F^- ions in the CsF host.[16]

The interaction of the I_2 molecules with the anionic iodide is confirmed by the Raman spectrum of the crystals (Fig. 3). The spectrum, recorded at ambient temperature in a sealed ampoule, is dominated by a peak at about 185 cm^{-1}. Polyiodides have spectral features in the range of 60 to 220 cm^{-1}. At about 180 cm^{-1} weakly co-ordinated I_2 has a symmetrical stretch mode.[17] The spectrum also contains a feature typical of a $Cd_2I_6^{2-}$ unit, the Cd–I stretching band at approximately 120 cm^{-1}.[18]

We are also interested in the predominant iodide species in the reaction medium CdI_2–$[R_3S][I_7]$ (R = Me or Et), and therefore vibrational spectroscopy of various compositions of the mixtures has been recorded. These indicate the presence of Cd^{II} in the form of nearly regular CdI_4^{2-} tetrahedra analogous to those in $Cd_2I_6^{2-}$ in $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$. The EXAFS of Cd (K shell) was determined for a 1 : 10 mixture of CdI_2–$[Et_3S][I_7]$. The scattering path can adequately be modelled (Fig. 4) with

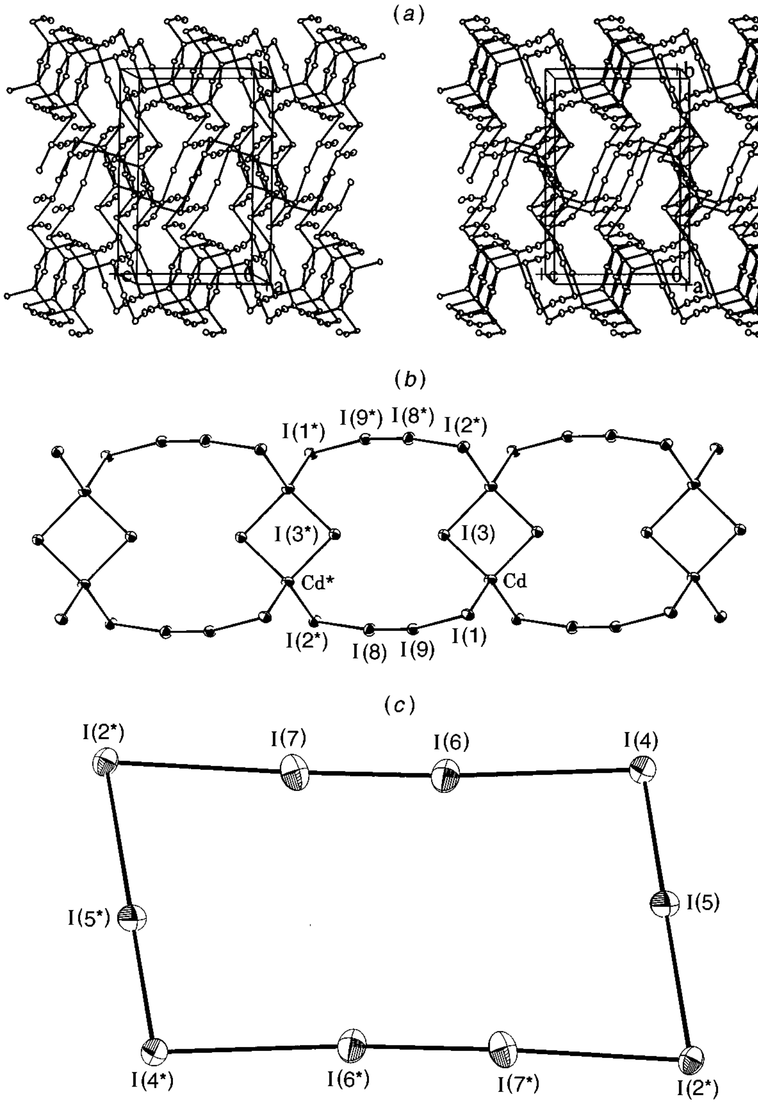

Fig. 5 (*a*) The network of $[Me_3S][Cd_2I_6]_{1/2}\cdot 3I_2$, (*b*) the infinite zigzag chain in the network and (*c*) the I_{10} unit in the network

four Cd–I contacts at an average distance of 2.77 Å. The inclusion of a Cd···Cd contact slightly improves the overall fit, giving the following parameters from a least-squares fit: d(Cd–I) = 2.77(1) Å, n(Cd–I) = 3.7(2), d(Cd···Cd) = 3.8(2) Å, n(Cd···Cd) = 1.0(1), thus confirming the structural relationship of Cd^{II} in the liquid reaction medium and the isolated polyiodide compound.

Of most interest to us is the mode of iodine bridging between the $Cd_2I_6^{2-}$ dimers. The I_2 molecules co-ordinating to the $Cd_2I_6^{2-}$ dimers create a network shown in Fig. 5(*a*). The network can be seen as infinite chains (in the *a* direction) of I_2 co-ordinated to the terminal iodides of $Cd_2I_6^{2-}$ [Fig. 5(*b*)], which are interspaced by formal I_{10} units [Fig. 5(*c*)], in which the I(2) atoms are incorporated into the chain structure. The longest I···I interaction in the network can be found within the I_{10} unit [3.561(1) Å] and it is between two I_2 units [I(6)···I(4)]. It should be pointed out that the description of the network is very dependent on where you more or less arbitrarily assign the cut-off for an I···I interaction. Intermolecular distances of 3.4–3.7 Å have been interpreted as secondary bonds (van der Waals radius of iodine 2.15 Å). Consequently, the I···I interactions in the network should be regarded as strong.

To our knowledge only two other crystal structures of binary metal iodide–iodine compounds have been published, $[Et_3S][Hg_2I_6]_{1/2}\cdot 3I_2$[19] and $[NH_4][AuI_4]\cdot \frac{1}{2}I_2$.[20] In spite of the fact that the mercury(II) compound has the same stoichiometry (disregarding that the cation is Et_3S^+ instead of Me_3S^+) the structures differ significantly. The network of $[Et_3S][Hg_2I_6]_{1/2}\cdot 3I_2$ also contain infinite chains but the $Hg_2I_6^{2-}$ units are co-ordinated by I_2 molecules directly from terminal to terminal iodide instead of the zigzag way as in **1**. The chains are co-ordinated perpendicularly to each other by I_2 molecules directly between the terminal iodides of $Hg_2I_6^{2-}$ and consequently the network becomes less complicated than in **1**.

On the other hand, the gold(III) compound consists of square-planar AuI_4^- complexes, where every second complex is bridged by I_2 molecules, forming I_4^{2-} units with 'ligand' iodides. Bridging I_2 units can also be found in metal iodide complexes screened by other ligands, such as $[M(NH_3)_4I_2]^{-/0}$ (M = Cu^I or Cd^{II}), $4[(Ph_3SbI)_2O]\cdot I_2$ and $[Pt_2(Me_2CHCS_2)_4I_2]\cdot I_2$. The iodides in these complexes are found in the axial position with respect to the other ligands and it can be argued whether the iodides should be regarded as co-ordinated to the metal complexes or to the I_2 molecules, forming I_4^{2-} units.[21–25]

Both phases of $[Me_3S][CdI_3]$ belong to the space group $P2_1/c$ and consist of corner-sharing CdI_4 tetrahedra, which form polymeric chains (Fig. 6). These chains run in different directions in **3** and **4**, *c* and *a* respectively. The bridging Cd–I distances in the two phases range from 2.82 to 2.94 Å and the terminal ones from 2.70 to 2.75 Å. Selected bond lengths and angles are shown in Table 2. A major difference between the two phases is that the former has two parallel chains per unit cell, while the latter has two parallel pairs of chains. This seems to be a consequence of compound **4** having a *c* axis which is approximately twice the length of that of the former.

In the corresponding iodine-free compounds of Hg^{II} the tri-

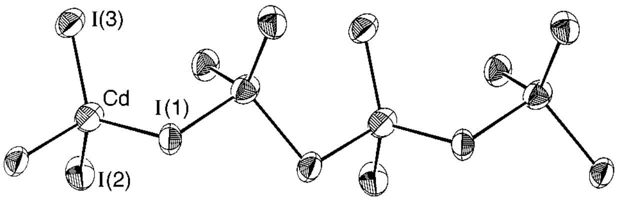

Fig. 6 Chain structure in [Me_3S][CdI_3]

ethylsulfonium compound forms $Hg_2I_6^{2-}$ dimers, whereas the trimethylsulfonium compound consists of discrete trigonal HgI_3^- units stacked in one crystallographic direction.[26] There is thus a strong relationship with the triethyl- and trimethylsulfonium compounds of cadmium iodide, where the former also forms dimeric anions but the latter exhibits CdI_3^- chains that can be visualised as an intermediate between the two mercury structures.

The addition of a metal iodide acceptor exposes I_2 to competition for the iodide ions. In this way the properties of polyiodide compounds can be modified. The distances observed indicate that terminal iodide ligands in the cadmate(II) anions interact with iodine as I^- and/or I_3^- does in ordinary polyiodides. This fact provides us with two important possibilities: (1) to check the proposed Grotthus mechanism of electrical conductivity, since the cadmate(II) anion has different I^--donating properties as compared to I_3^-; (2) to modify the polyiodide chains in order to obtain new macroscopic properties, such as direct electronic conductivity or photoconductivity.

Recently, we have isolated several metal iodide–iodine phases of the Group 11 metals, which are presently under investigation. The iodide-accepting power of the coinage metals in oxidation state +I is considerably lower than that of the metal ions of Group 12, and the iodide-accepting balance hopefully more subtle and structurally more exciting.

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