A woven structure of hexaacetamidecadmium(II) polyiodide

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The coordination of the $[Cd(acetamide)_6]^{2+}$ cation in the title compound, hexaacetamidecadmium(II) bis(triiodide) bis-(diiodine), $[Cd(C_2H_5NO)_6](I_3)_2 \cdot 2I_2$, is octahedral. The I atoms form a woven structure consisting of alternating triiodide anions and iodine molecules. Cd atoms and triiodide anions lie on inversion centres.

Comment

Polyiodides have earned much deserved attention because of their fascinating structural chemistry (Svensson & Kloo, 2003). Interest in polyiodides has also focused on materials with unusually high electrical conductivity, in which polyiodide species are involved in conduction processes. For example, transition metal complex polyiodides with acetamide were found to have a specific electrical conductivity of 10^{-4} S cm^{-1} (Savinkina *et al.*, 1998). In this work, we report the crystal structure of (I), a cadmium polyiodide complex with acet-amide (Fig. 1).
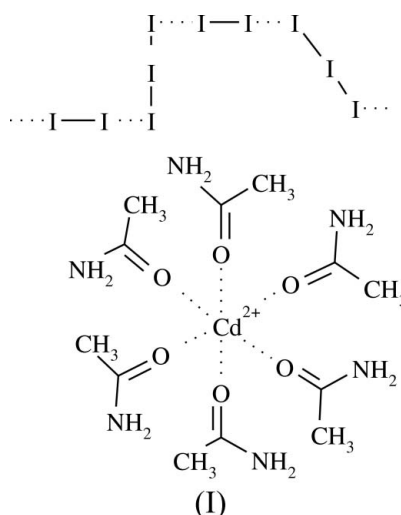
In this compound, acetamide molecules coordinate to Cd to yield $[Cd(acetamide)_6]^{2+}$ cations with an octahedral CdO_6 coordination geometry. The acetamide ligands form hydrogen bonds with two neighbouring complex cations (Table 2) to give infinite chains. The I atoms form infinite zigzag chains to give a woven structure (Fig. 2). Consideration of the bond lengths (Table 1) in the iodine chain suggests the presence of triiodide anions (I3—I4—I3[ii] and I5—I6—I5[iii]; symmetry codes as in Table 1) alternating with iodine molecules (I1—I2). The I1···I5 and I2···I3 distances are somewhat longer, 3.4680 (18) and 3.4371 (18) Å, respectively. They are greater than the sum of covalent radii (2.66 Å) but less than the sum of
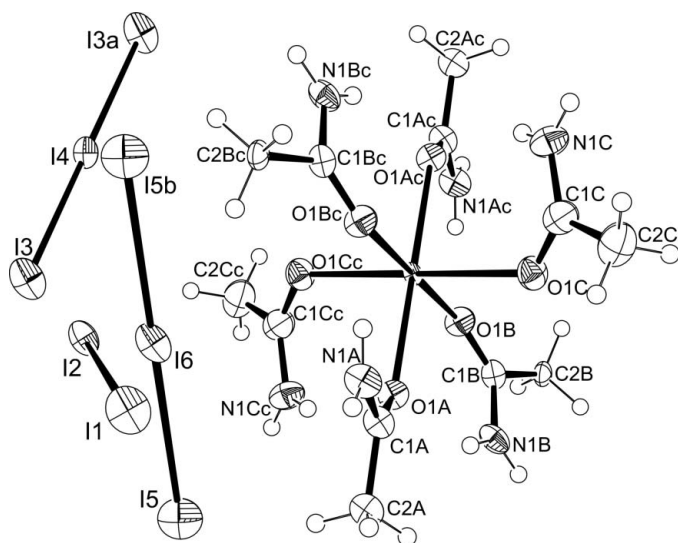
Figure 1
ORTEP-3 (Farrugia, 1997) view and numbering scheme of compound (I). Displacement ellipsoids are drawn at the 50% probability level. The suffixes a, b and c correspond to symmetry codes (i), (ii) and (iii), respectively, in Table 1.

van der Waals radii (4.3 Å), indicative of weak bonding interactions.

Compound (I) represents a rare example of a cadmium polyiodide that contains no Cd—I bonds. In the structure of [Cd(12-crown-4)]$_2$I$_{10}$ (Wieczorrek, 2000), the isolated I$_{10}^{2-}$ ion is found; it can be described as a dimer of V-shaped I$_5^-$ ions. In all other reported cadmium polyiodides, iodine molecules are linked to iodide ions that are bonded to Cd atoms.

Experimental

Cadmium iodide (1 g), acetamide (1 g) and iodine (1.4 g) were powdered in a porcelain mortar. The mixture was dissolved in water (15 ml) and heated to 333 K. Excess iodine was removed. Cooling the solution to room temperature gave green crystals decomposing in air (yield 10%). Crystals suitable for the X-ray diffraction study were prepared by crystallization from ethanol at room temperature.

Crystal data

[Cd(C$_2$H$_5$NO)$_6$](I$_3$)$_2$·2I$_2$	$Z = 1$
$M_r = 1735.82$	$D_x = 2.911$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.666$ (4) Å	Cell parameters from 25
$b = 11.9817$ (19) Å	reflections
$c = 12.426$ (3) Å	$\theta = 12$–13°
$\alpha = 65.747$ (15)°	$\mu = 8.38$ mm^{-1}
$\beta = 80.79$ (5)°	$T = 293$ (2) K
$\gamma = 72.25$ (3)°	Prism, dark green
$V = 990.3$ (6) Å^3	$0.11 \times 0.10 \times 0.09$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2051 reflections with $I > 2\sigma(I)$
ω scans	$\theta_{max} = 25.7°$
Absorption correction: ψ scan	$h = -8 \rightarrow 9$
(North *et al.*, 1968)	$k = -12 \rightarrow 14$
$T_{min} = 0.386$, $T_{max} = 0.481$	$l = 0 \rightarrow 15$
3644 measured reflections	1 standard reflections
3644 independent reflections	frequency: 60 min
	intensity decay: 2%
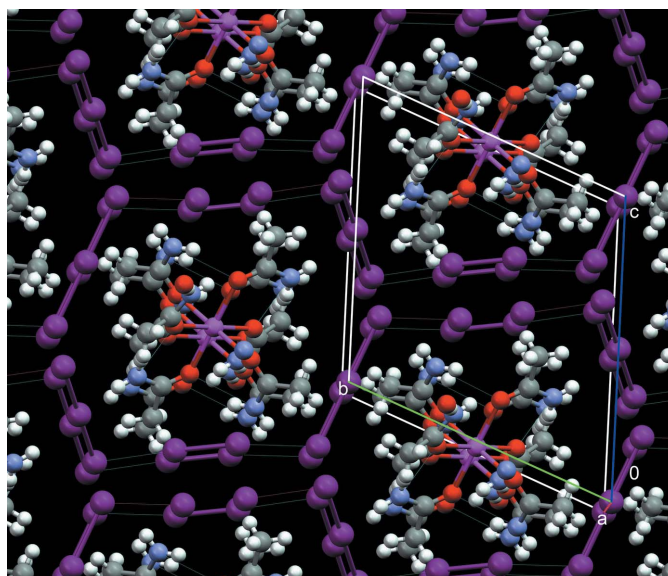
Figure 2
MERCURY (Bruno *et al.*, 2002) view of the woven structure.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.017P)^2]$
$wR(F^2) = 0.083$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.87$	$(\Delta/\sigma)_{max} < 0.001$
3644 reflections	$\Delta\rho_{max} = 1.77$ e Å^{-3}
166 parameters	$\Delta\rho_{min} = -1.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O1B	2.220 (11)	I3—I4	2.9081 (17)
Cd1—O1A	2.285 (9)	I5—I6	2.927 (2)
Cd1—O1C	2.357 (11)	I1···I5	3.4680 (18)
I1—I2	2.7398 (17)	I2···I3	3.4371 (18)
O1B—Cd1—O1B^i	180	O1A^i—Cd1—O1C	92.5 (4)
O1B—Cd1—O1A	89.2 (3)	O1C—Cd1—O1C^i	180
O1B^i—Cd1—O1A	90.8 (3)	I1—I4—I3^{ii}	180
O1B^i—Cd1—O1A^i	89.2 (3)	I5—I6—I5^{iii}	180
O1A—Cd1—O1A^i	180	I1···I5—I6	80.49 (5)
O1B—Cd1—O1C	93.4 (4)	I2···I3—I4	116.69 (5)
O1B^i—Cd1—O1C	86.6 (4)	I2—I1···I5	176.51 (6)
O1A—Cd1—O1C	87.5 (4)	I1—I2···I3	172.93 (5)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+2, -y+2, -z$; (iii) $-x+2, -y, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H11A···O1B^i	0.86	2.13	2.912 (17)	151
N1B—H11B···O1A	0.86	2.32	3.095 (18)	149
N1B—H12B···O1C^{iv}	0.86	2.18	3.024 (19)	168
N1C—H11C···O1A^i	0.86	2.26	3.05 (2)	154

Symmetry codes: (i) $-x+1, -y+1, -z$; (iv) $-x, -y+1, -z$.

H atoms were included in calculated positions and refined as riding, with U_{iso}(H) values set equal to 1.2U_{eq} (NH) and 1.5U_{eq} (CH) of the parent atoms. The N—H and C—H bond lengths are 0.86 and 0.96 Å, respectively. The highest peak is 0.70 Å from I3 and the deepest hole is 0.53 Å from Cd1.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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