

A three-dimensional framework of bis[tris(ethylenediamine)zinc] tetraiodocadmiate diiodide assisted by N—H···I hydrogen bonds

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Received 27 February 2006

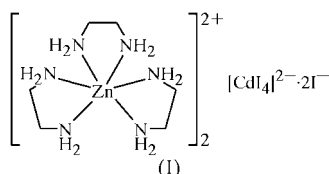
Accepted 12 May 2006

Online 15 June 2006

The title salt, $[\text{Zn}(\text{C}_2\text{N}_2\text{H}_8)_3]_2[\text{CdI}_4]\text{I}_2$, conventionally abbreviated $[\text{Zn}(\text{en})_3]_2[\text{CdI}_4]\text{I}_2$, where en is ethylenediamine, contains discrete $[\text{Zn}(\text{en})_3]^{2+}$ cations and $[\text{CdI}_4]^{2-}$ anions with distorted octahedral and nearly tetrahedral geometries, respectively, as well as uncoordinated I^- ions. The cation and the free I^- anion lie on twofold rotation axes and the $[\text{CdI}_4]^{2-}$ anion lies on a $\bar{4}$ axis in the space group $I\bar{4}2d$. The structure exhibits numerous weak inter-ionic hydrogen bonds of two types, *viz.* $\text{N}-\text{H}\cdots\text{I}^-$ (free ion) and $\text{N}-\text{H}\cdots\text{I}([\text{CdI}_4]^{2-})$, which support the resulting three-dimensional framework.

Comment

It has been shown that the preparation of complexes from zero-valent metals or metal oxides is a fascinating and promising means for the production of heterometallic compounds of unusual stoichiometry and structure (Pryma *et al.*, 2003; Nesterova *et al.*, 2005). The reaction of zinc oxide with cadmium iodide and ammonium iodide in a dimethylformamide solution of ethylenediamine (en) in the open air, using a $\text{ZnO}:\text{CdI}_2:\text{NH}_4\text{I}:\text{en}$ molar ratio of 2:1:4:6, gives colourless crystals of the title compound, $[\text{Zn}(\text{en})_3]_2[\text{CdI}_4]\text{I}_2$ (I).



Single-crystal structure analysis confirms that (I) is an ionic compound built of discrete octahedral $[\text{Zn}(\text{en})_3]^{2+}$ cations and

tetrahedral $[\text{CdI}_4]^{2-}$ and I^- anions, forming a three-dimensional framework by means of weak hydrogen bonds. The Cd atom lies on a $\bar{4}$ axis, while the cation and the free I^- ion both lie on twofold rotation axes. In the selected asymmetric unit (Fig. 1), the cation has a Δ configuration.

The Zn^{II} atom in $[\text{Zn}(\text{en})_3]^{2+}$ is coordinated by six N atoms from three bidentate en ligands, with $\text{Zn}-\text{N}$ distances ranging from 2.171 (8) to 2.229 (8) Å (Table 1). The coordination environment of the complex cation is distorted octahedral, as can be seen from the *trans* $\text{N}-\text{Zn}-\text{N}$ angles, which vary from 166.9 (4) to 169.3 (3)°, and the *cis* $\text{N}-\text{Zn}-\text{N}$ angles, which vary from 79.7 (4) to 95.1 (3)°. The observed bond distances and angles are in accordance with those found for the similar zinc(II) complexes $[\text{Zn}(\text{en})_3][\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$, $[\text{Zn}(\text{en})_3][\text{Te}_3]^{0.5\text{en}}$ and $[\text{Zn}(\text{en})_3](\text{NO}_3)_2$ (Fu *et al.*, 2004; Shreeve-Keyer *et al.*, 1997; Neill *et al.*, 1997). The Cd^{II} coordination environment

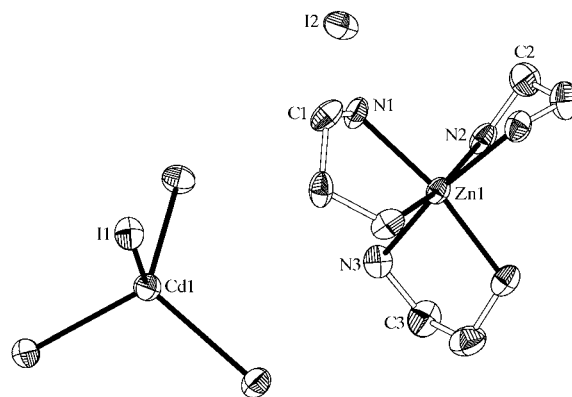


Figure 1

The main structural units in the structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

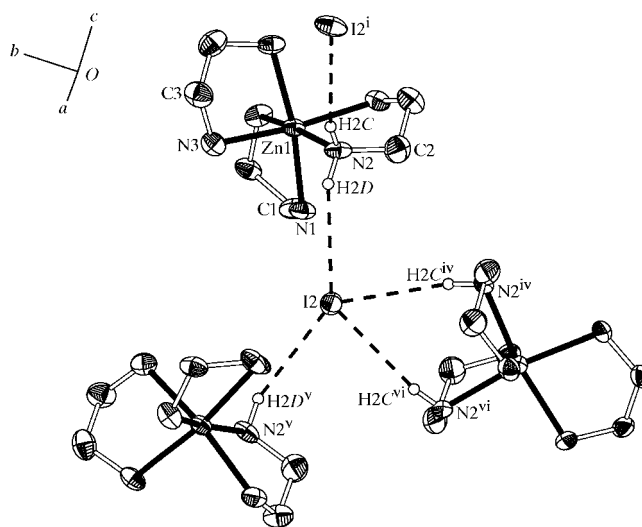


Figure 2

A view of the environment of the I^- anion, based on hydrogen bonds. [Symmetry codes: (i) $x, -1 - y, -z$; (iv) $-1 - x, y, -z$; (v) $-\frac{1}{2} - x, y, -\frac{1}{4} - z$; (vi) $-1 - x, -\frac{1}{2} - y, -\frac{1}{4} + z$.]

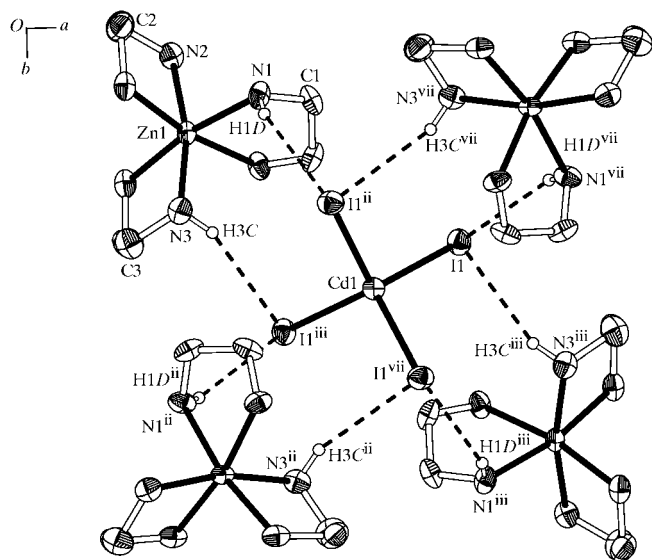


Figure 3
A view of the $[\text{CdI}_4]^{2-}$ environment, stabilized by hydrogen bonds. [Symmetry codes: (ii) $-x, y, -z$; (iii) $-x, -y, z$; (vii) $x, -y, -z$.]

has approximate tetrahedral symmetry. The Cd–I bond length in the $[\text{CdI}_4]^{2-}$ anion is approximately equal to the sum of the covalent radii for Cd (1.51 Å) and I (1.33 Å) atoms (Batsanov, 1991), and is typical of its type (Bailey & Pennington, 1995; Nieuwenhuyzen *et al.*, 1992; Kallel *et al.*, 1981).

A complex system of hydrogen bonds links the ions of (I) into a three-dimensional framework. Each I^- anion is hydrogen bonded to three different $[\text{Zn}(\text{en})_3]^{2+}$ units (Fig. 2), while each $[\text{CdI}_4]^{2-}$ unit is hydrogen bonded to four different $[\text{Zn}(\text{en})_3]^{2+}$ cations (Fig. 3). The non-coordinated I2 atom takes part in hydrogen bonding with the NH_2 groups of en in the cations, being four-coordinated by H(N) atoms (Table 2). All four I atoms in the $[\text{CdI}_4]^{2-}$ anion are two-coordinated by H(N) atoms, forming eight hydrogen bonds to $[\text{Zn}(\text{en})_3]^{2+}$ cations. The hydrogen bonds interlink the $[\text{Zn}(\text{en})_3]^{2+}$ and $[\text{CdI}_4]^{2-}$ building blocks and I^- anions into a three-dimensional framework. The nearest $\text{I} \cdots \text{I}$ distance is $\text{I1} \cdots \text{I2}^{\text{vii}}$ of 4.695 (5) Å [symmetry code: (vii) $-y, x, -z$], indicating no specific interaction between I atoms.

The title salt represents a suitable system for a comparison of the strengths of two types of $\text{N}-\text{H} \cdots \text{I}$ hydrogen bonds. Thus, the bonds involving the free I^- anions are *ca* 0.11 Å shorter than those involving the I atoms in the $[\text{CdI}_4]^{2-}$ anion. Moreover, the mean value of all hydrogen bonds observed in $[\text{Zn}(\text{en})_3]_2[\text{CdI}_4]_2$ (3.81 Å), compared with the mean value found in $[\text{Cd}(\text{en})_3]_2[\text{CdI}_4]_2$ (3.76 Å) (Wieczorrek & Tebbe, 1998), indicates donor properties for the NH_2 group somewhat stronger in $[\text{Cd}(\text{en})_3]^{2+}$ than in $[\text{Zn}(\text{en})_3]^{2+}$.

Experimental

Zinc oxide (0.2 g, 0.0025 mol), CdI_2 (0.455 g, 0.00125 mol), NH_4I (0.72 g, 0.005 mol), dimethylformamide (20 ml) and ethylenediamine

(0.5 ml, 0.0075 mol) were heated to 323–333 K and stirred magnetically for about 50 min. The solution was filtered and propan-2-ol (10 ml) was added to the resulting colourless solution. Colourless crystals of (I) suitable for single-crystal X-ray diffraction separated over a period of one day; these were washed with dry propan-2-ol and dried *in vacuo* at room temperature (yield 1.32 g, 78%). An additional amount of product was obtained from the filtrate. Analysis calculated for $\text{C}_{12}\text{H}_{48}\text{CdI}_6\text{N}_{12}\text{Zn}_2$: C 10.6, H 3.5, Cd 8.2, I 55.8, N 12.3, Zn 9.6%; found: C 10.6, H 3.7, Cd 8.3, I 55.4, N 12.5, Zn 9.6%.

Crystal data

$[\text{Zn}(\text{C}_2\text{H}_8\text{N}_2)_3][\text{CdI}_4]_2$
 $M_r = 1365.16$
Trigonal, $I\bar{4}2d$
 $a = 14.803$ (2) Å
 $c = 16.991$ (4) Å
 $V = 3723.2$ (11) Å³
 $Z = 4$

$D_x = 2.435$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 6.84$ mm⁻¹
 $T = 294$ (2) K
Block, colourless
0.4 × 0.2 × 0.2 mm

Data collection

Siemens P3/PC diffractometer
 $\theta/2\theta$ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
 $T_{\text{min}} = 0.127$, $T_{\text{max}} = 0.255$
3556 measured reflections
916 independent reflections

825 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 25.1^\circ$
2 standard reflections
every 95 reflections
intensity decay: 5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.062$
 $S = 1.07$
916 reflections
76 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2 + 14.3589P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³
Absolute structure: Flack (1983)
Flack parameter: -0.07 (7)

Table 1

Selected geometric parameters (Å, °).

Cd1–I1	2.7934 (9)	Zn1–N1	2.186 (7)
Zn1–N2	2.171 (8)	Zn1–N3	2.229 (8)
I1 ⁱ –Cd1–I1	109.40 (2)	N2–Zn1–N3 ⁱⁱⁱ	79.9 (3)
I1–Cd1–I1 ⁱⁱ	109.61 (3)	N1–Zn1–N3 ⁱⁱⁱ	95.1 (3)
N2–Zn1–N2 ⁱⁱⁱ	98.0 (4)	N2–Zn1–N3	91.5 (3)
N2–Zn1–N1 ⁱⁱⁱ	169.3 (3)	N1–Zn1–N3	94.9 (3)
N2–Zn1–N1	91.4 (3)	N3 ⁱⁱⁱ –Zn1–N3	166.9 (4)
N1 ⁱⁱⁱ –Zn1–N1	79.7 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N2}-\text{H2C} \cdots \text{I2}^{\text{iv}}$	0.90	2.90	3.758 (8)	160
$\text{N2}-\text{H2D} \cdots \text{I2}$	0.90	2.92	3.746 (7)	153
$\text{N1}-\text{H1D} \cdots \text{I1}^{\text{i}}$	0.90	3.09	3.904 (9)	150
$\text{N3}-\text{H3C} \cdots \text{I1}^{\text{ii}}$	0.90	2.99	3.827 (8)	156

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

All H atoms were located in difference maps and then treated as riding atoms, with $\text{C}-\text{H} = 0.97$ Å, $\text{N}-\text{H} = 0.90$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The absolute axis assignment (Jones, 1986) was established by means of the Flack (1983) parameter.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *SHELXL97*.

This work was supported in part by the INTAS (Project No. 03–51–4532) and the ‘Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich’ (Project No. 15874-N03).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3008). Services for accessing these data are described at the back of the journal.

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