Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Bis(μ-hexamethylenetetramine)bis(aquadibromocadmium)diaquadibromocadmium dihydrate

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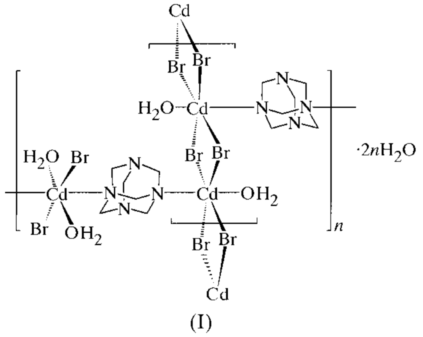
Received 31 January 2000
Accepted 18 May 2000

The title compound, poly[[diaquadibromocadmium-μ-(1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane-N^1:N^5)-aquacadmium-di-μ-bromo-aquacadmium-μ-(1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane-N^1:N^5)-di-μ-bromo] dihydrate], $[Cd_3Br_6(C_6H_{12}N_4)_2(H_2O)_4]\cdot 2H_2O$, is made up of two-dimensional neutral rectangular coordination layers. Each rectangular subunit is enclosed by a pair of $Cd_3(\mu_2\text{-}Br)_6(H_2O)_3$ fragments and a pair of $(\mu_2\text{-hmt})Cd(H_2O)_2Br_2(\mu_2\text{-hmt})$ fragments as sides (hmt is hexamethylenetetramine). The unique Cd^{II} atom in the Cd_2Br_2 ring in the $Cd_3(\mu_2\text{-}Br)_6(H_2O)_3$ fragment is in a slightly distorted octahedral $CdNOBr_4$ geometry, surrounded by one hmt ligand [2.433 (5) Å], one aqua ligand [2.273 (4) Å] and four Br atoms [2.6409 (11)–3.0270 (14) Å]. The Cd^{II} atom in the $(\mu_2\text{-hmt})Cd(H_2O)_2Br_2(\mu_2\text{-hmt})$ fragment lies on an inversion center and is in a highly distorted octahedral $CdN_2O_2Br_2$ geometry, surrounded by two *trans*-related N atoms of two hmt ligands [2.479 (5) Å], two *trans*-related aqua ligands [2.294 (4) Å] and two *trans*-related Br atoms [2.6755 (12) Å]. Adjacent two-dimensional coordination sheets are connected into a three-dimensional network by hydrogen bonds involving lattice water molecules, and the aqua, bromo and hmt ligands belonging to different layers.

Comment

Hexamethylenetetramine (hmt) as a potential polydentate ligand has been of interest in recent years (Miyamae *et al.*, 1988; Mak, 1984; Pickardt & Droas, 1985). These compounds may exhibit interesting topological structures. We and others have recently reported some interesting two- and three-dimensional non-interpenetrating open networks constructed from Ag^I ions and the μ_4-hmt ligand (Bertelli *et al.*, 1997; Carlucci *et al.*, 1997; Tong *et al.*, 1999). We describe herein the crystal structure of the title compound, (I), with a two-dimensional rectangle-like network, in which hmt acts in a μ_2-bridging mode.



(I)

The title complex is made up of two-dimensional neutral layers of rectangular subunits and lattice water molecules. As shown in Fig. 1, each rectangular subunit is enclosed by a pair of $Cd_3(\mu_2\text{-}Br)_6(H_2O)_3$ fragments and a pair of $Cd(H_2O)_2Br_2(\mu_2\text{-hmt})_2$ fragments as sides. The $Cd(H_2O)_2Br_2(\mu_2\text{-hmt})_2$ fragment has inversion symmetry with octahedral coordination by two *trans*-related monodentate Br atoms [Cd1—Br1 2.6755 (12) Å], two *trans*-related aqua ligands [Cd1—O2*W* 2.294 (4) Å] and two *trans*-related N atoms [Cd1—N2 2.479 (5) Å] from

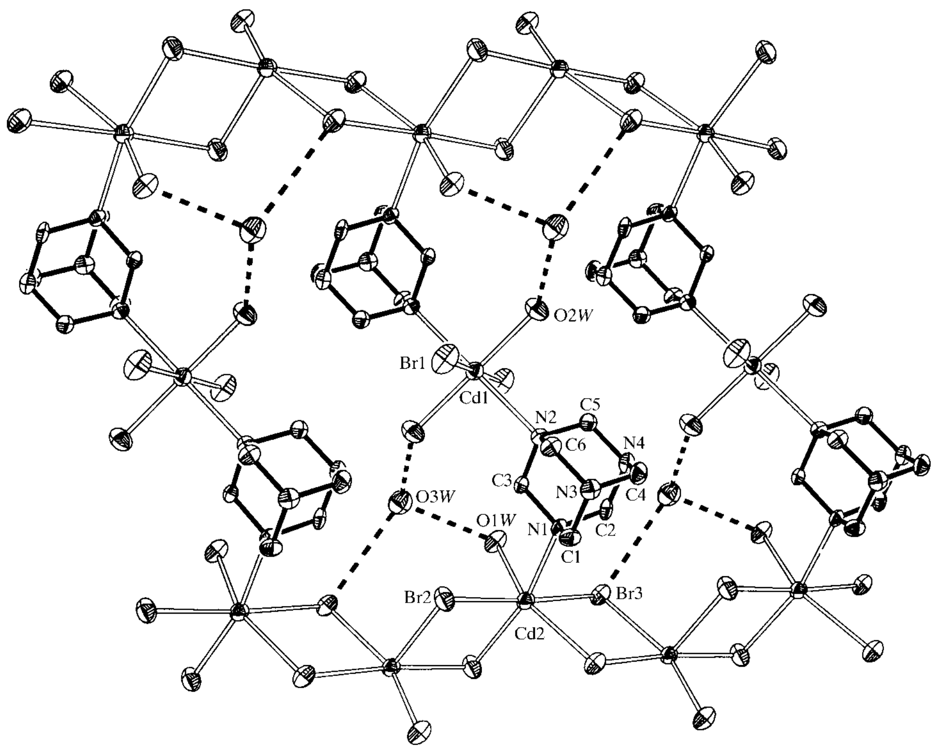


Figure 1
ORTEP (Sheldrick, 1998) plot (35% probability displacement ellipsoids) of the coordination layer with rectangular cavities in (I).

different hmt ligands. The Cd2 atom in the $Cd_3(\mu_2\text{-Br})_6(H_2O)_3$ fragment is in a highly distorted octahedral geometry and coordinated by four Br atoms [2.6409 (11)–3.0270 (14) Å], one aqua [2.273 (4) Å] and one hmt ligand [2.433 (5) Å]. Along the *a* direction, the Cd^{II} atoms share common Br atoms at the corners to form $Cd(\mu_2\text{-Br})_2(H_2O)$ infinite chains, similar to related compounds (Rogers *et al.*, 1993; Rogers & Bond, 1996; Krishnan *et al.*, 1991). These chains are further interlinked by $(\mu_2\text{-hmt})\text{–}CdBr_2(H_2O)_2\text{–}(\mu_2\text{-hmt})$ fragments, resulting in a two-dimensional coordination rectangular layer. The hmt ligand acts in a μ_2-mode and bridges two Cd^{II} atoms belonging to two types of Cd^{II} atoms. The Cd—Br(μ_2-mode) bonds are largely unequivalent compared with those [2.668 (3) and 2.780 (4) Å] found in a related compound, *catena*-[(μ_2-nicotinato-*O*,*O*′,*N*)-μ_2-aquacadmium(II)] (Zhang *et al.*, 1996).

The structure of (I) differs significantly from that of a closely related compound, bis(μ_2-hexamethylenetetramine)-bis(diiodocadmium)diaquadiiodocadmium dihydrate, in which the Cd^{II} atoms have an octahedral or tetrahedral coordinate geometry, resulting in a three-dimensional coordination network (Mak, 1981, 1982; Pickardt, 1981).

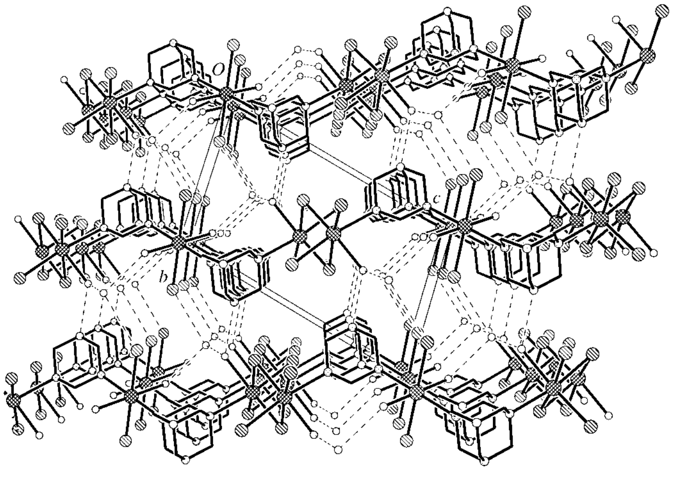


Figure 2
Perspective view of the molecular packing of (I).

It is also noteworthy that the extensive interlayer hydrogen bonds between the adjacent layers may play a role in consolidating the crystal architecture. Each O1*W* ligand forms one hydrogen bond with a lattice water molecule and one interlayer hydrogen bond with the hmt ligand belonging to the adjacent layer. Each O2*W* ligand donates only one hydrogen bond, which is the lattice water molecule. Interestingly, each lattice water molecule forms two acceptor hydrogen bonds with two aqua ligands and two donor hydrogen bonds with two bromo ligands [$O1W\cdots O3W$ 2.812 (7), $O2W\cdots O3W^{i}$ 2.837 (7), $O3W\cdots Br1^{ii}$ 3.332 (5), $O3W\cdots Br3^{iii}$ 3.415 (5), $O1W\cdots N3^{ii}$ 2.771 (7) and $O2W\text{—}Br1^{i}$ 3.522 (5) Å; symmetry codes: (i) $-x, -y, -z$; (ii) $x, y-1, z$; (iii) $x-1, y, z$]. These hydrogen bonds extend the two-dimensional coordination layers into three-dimensional molecular networks (Fig. 2).

Experimental

To a solution (5 ml) of $CdBr_2\cdot 4H_2O$ (1 mmol), a solution (5 ml) of hmt (1 mmol) was added slowly with stirring at 323 K for 15 min. The resulting solution was allowed to stand in air at room temperature and colorless crystals were deposited within several days (90% yield).

Crystal data

$[Cd_3Br_6(C_6H_{12}N_4)_2(H_2O)_4]\cdot 2H_2O$
$M_r = 1205.15$
Triclinic, $P\bar{1}$
$a = 7.577$ (2) Å
$b = 8.030$ (2) Å
$c = 13.464$ (3) Å
$\alpha = 76.60$ (3)°
$\beta = 89.17$ (3)°
$\gamma = 82.60$ (3)°
$V = 790.2$ (3) $Å^3$
$Z = 1$
$D_x = 2.533$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5\text{–}15.0°$
$\mu = 9.625$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.30 × 0.20 × 0.16 mm

Data collection

Siemens *R3M* diffractometer
ω scans
Absorption correction: semi-empirical absorption based on ψ scans (North *et al.*, 1968)
$T_{min} = 0.112$, $T_{max} = 0.214$
3630 measured reflections
3630 independent reflections
2716 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.57°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$
2 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.104$
$S = 1.025$
3630 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.0981P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.00$ e $Å^{-3}$
$\Delta\rho_{min} = -0.93$ e $Å^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0046 (5)

Table 1
Selected geometric parameters (Å, °).

Cd1—O2*W*	2.294 (4)	$Cd2\text{—}Br3^{i}$	2.6409 (11)
Cd1—N2	2.479 (5)	$Cd2\text{—}Br2^{ii}$	2.7287 (13)
Cd1—Br1	2.6755 (12)	Cd2—Br2	2.7482 (13)
Cd2—O1*W*	2.273 (4)	Cd2—Br3	3.0270 (14)
Cd2—N1	2.433 (5)		
O2*W*—Cd1—N2	88.47 (17)	$Br3^{i}\text{—}Cd2\text{—}Br2^{ii}$	99.99 (4)
O2*W*—Cd1—Br1	90.06 (13)	O1*W*—Cd2—Br2	96.00 (13)
N2—Cd1—Br1	91.75 (13)	N1—Cd2—Br2	85.88 (13)
O1*W*—Cd2—N1	83.48 (17)	$Br3^{i}\text{—}Cd2\text{—}Br2$	106.02 (4)
$O1W\text{—}Cd2\text{—}Br3^{i}$	157.16 (13)	$Br2^{ii}\text{—}Cd2\text{—}Br2$	87.17 (4)
$N1\text{—}Cd2\text{—}Br3^{i}$	91.96 (12)	O1*W*—Cd2—Br3	76.72 (13)
$O1W\text{—}Cd2\text{—}Br2^{ii}$	86.88 (12)	N1—Cd2—Br3	95.03 (13)
$N1\text{—}Cd2\text{—}Br2^{ii}$	167.46 (11)		

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

Data collection: *R3M Software* (Siemens, 1990); cell refinement: *R3M Software*; data reduction: *R3M Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL*97.

We acknowledge financial support by the NSFC (29625102 and 29971033). We are also indebted to the Chemistry Department of the Chinese University of Hong Kong for donation of the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1139). Services for accessing these data are described at the back of the journal.

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