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## Key indicators

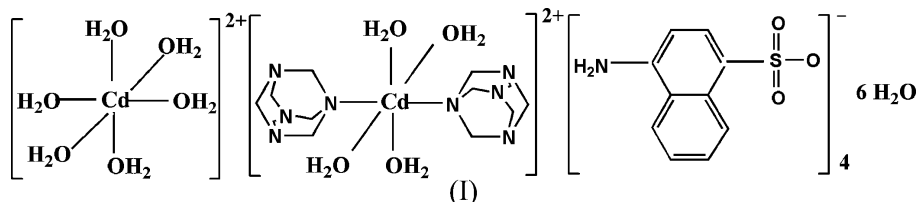
Single-crystal X-ray study  
 $T = 292$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.038  
 $wR$  factor = 0.087  
Data-to-parameter ratio = 14.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hexaaquacadmium(II) tetraaquabis-  
(hexamethylenetetramine)cadmium(II)  
tetrakis(4-aminonaphthalene-1-sulfonate)  
hexahydrate

In the title complex,  $[\text{Cd}(\text{C}_6\text{H}_{12}\text{N}_4)_2(\text{H}_2\text{O})_4][\text{Cd}(\text{H}_2\text{O})_6] \cdot (\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_4 \cdot 6\text{H}_2\text{O}$ , there are two types of distorted octahedrally coordinated Cd centers in the cations. The first Cd center is coordinated by two N atoms from two hexamethylenetetramine molecules and four water O atoms; the second Cd atom is coordinated by six water O atoms. Both cations are centrosymmetric. The 4-aminonaphthalene-1-sulfonate anions are antiparallel. The crystal structure is stabilized by  $\pi-\pi$  interactions and hydrogen bonds.

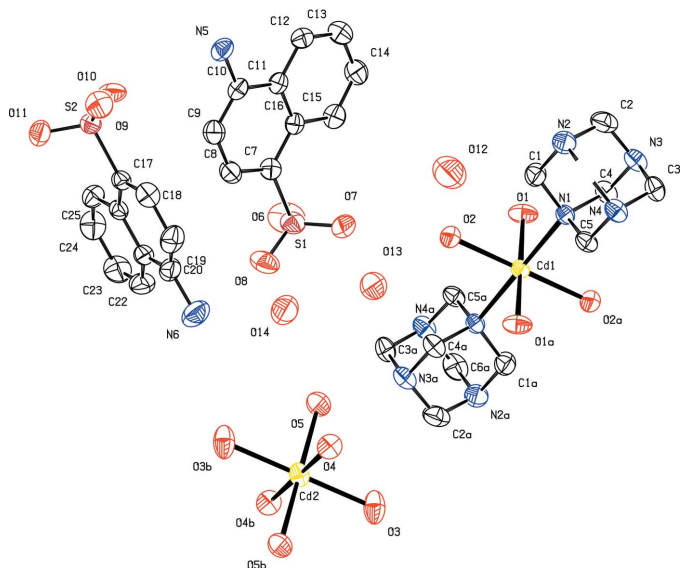
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## Comment

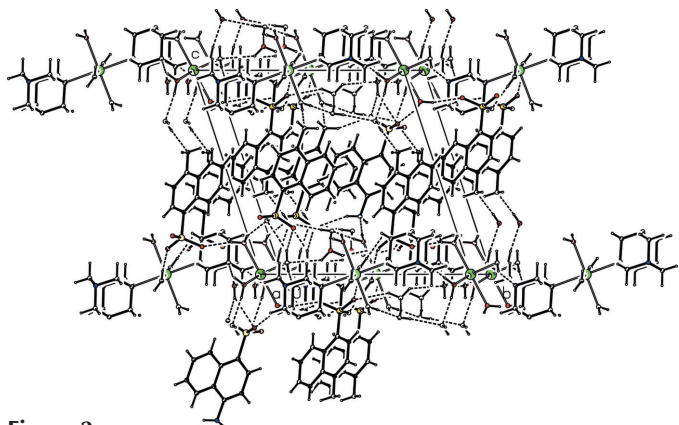
Due to the weak coordination strength of sulfonate anions with transition metal anions, sulfonates usually act to counterbalance the charge (Chen *et al.*, 2002; Li *et al.*, 2005a; Li *et al.*, 2005b). As part of an investigation of the coordinating ability of the sulfonate anion, we present here the crystal structure of the title compound,  $[\text{Cd}(\text{hmt})_2(\text{H}_2\text{O})_4][\text{Cd}(\text{H}_2\text{O})_6](\text{ans})_4 \cdot 6\text{H}_2\text{O}$ , (I), (hmt = hexamethylenetetramine; ans = 4-aminonaphthalene-1-sulfonate).



The molecular structure of (I) is shown in Fig. 1. Both cations are centrosymmetric. The Cd atom in the first cation has a distorted octahedral coordination geometry, bonded to two N atoms from two hmt molecules and four water O atoms. The Cd—N distance (Table 1) is similar to that observed in the equivalent part of  $[\text{Cd}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_2(\mu_2\text{-hmt})]_n$  [2.378 (2) Å; Liu *et al.*, 2002]. The Cd1—O distances to O1 and O2 (Table 1) are shorter than the Cd—O(W) distance in  $\text{Cd}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_2(\mu_2\text{-hmt})_n$  [2.325 (3) Å; Liu *et al.*, 2002]. The second cation contains a Cd center bonded to six O atoms from water molecules, showing a slightly distorted octahedral coordination geometry. The average bond length of Cd—O is 2.275 (2) Å, which is slightly shorter than the Cd—O distances in the first cation. As shown in Fig. 2, the adjacent 4-aminonaphthalene-1-sulfonate anions are antiparallel, showing significant  $\pi-\pi$  interactions. The distance between centroids of neighboring parallel naphthalene rings is 3.5432 (17) Å. These interactions together with the hydrogen bonds (Table 2) stabilize the crystal structure.



**Figure 1**  
View of (I), showing the atom labeling, with 50% probability ellipsoids. H atoms have been omitted. [Symmetry codes: (a)  $1 - x, 1 - y, -z$ ; (b)  $x + 2, -y, -z$ .]



**Figure 2**  
A view of the crystal packing. Hydrogen bonds are shown as dashed lines.

## Experimental

Hexamethylenetetramine (0.145 g, 1 mmol) was added to an aqueous solution (20 ml) of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.263 g, 1 mmol). After the mixture was stirred for 2 h at room temperature, the solution was then treated with 4-aminonaphthalene-1-sulfonic acid sodium salt tetrahydrate (0.645 g, 2 mmol) in methanol (10 ml). After filtration, the colorless solution was allowed to stand at room temperature. Well shaped colorless crystals were obtained by slow evaporation of the solvent in about one week.

### Crystal data

$[\text{Cd}(\text{C}_6\text{H}_{12}\text{N}_4)_2(\text{H}_2\text{O})_4] \cdot [\text{Cd}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_4 \cdot 6\text{H}_2\text{O}$   
 $M_r = 1682.38$   
 Triclinic,  $P\bar{1}$   
 $a = 9.5324$  (9) Å  
 $b = 13.6579$  (12) Å  
 $c = 14.4179$  (13) Å  
 $\alpha = 109.400$  (1)°  
 $\beta = 103.369$  (1)°  
 $\gamma = 90.738$  (1)°  
 $V = 1714.3$  (3) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.630$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 7772 reflections  
 $\theta = 2.2$ – $28.1$ °  
 $\mu = 0.83$  mm<sup>-1</sup>  
 $T = 292$  (2) K  
 Block, colorless  
 $0.26 \times 0.16 \times 0.12$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.813, T_{\max} = 0.907$   
 19824 measured reflections

7762 independent reflections  
 6037 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.082$   
 $\theta_{\max} = 27.5$ °  
 $h = -12 \rightarrow 12$   
 $k = -17 \rightarrow 17$   
 $l = -18 \rightarrow 18$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.087$   
 $S = 0.96$   
 7762 reflections  
 525 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0429P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.12$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.58$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cd1—O2	2.2804 (18)	Cd2—O4	2.257 (2)
Cd1—O1	2.3025 (19)	Cd2—O5	2.280 (2)
Cd1—N1	2.3732 (19)	Cd2—O3	2.289 (2)
O2 <sup>i</sup> —Cd1—O2	180.0	O4—Cd2—O5	91.16 (8)
O2 <sup>i</sup> —Cd1—N1	90.69 (7)	O4—Cd2—O3	86.17 (8)
O2—Cd1—N1	89.31 (7)	O5—Cd2—O3	93.01 (9)
O1—Cd1—N1	89.37 (7)		

Symmetry code: (i)  $-x + 1, -y + 1, -z$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O14—H14B <sup>ii</sup> ···O8	0.81 (3)	2.01 (3)	2.826 (4)	174 (6)
O14—H14A···N6	0.80 (3)	2.15 (3)	2.950 (4)	176 (4)
O13—H13B···O14	0.82 (2)	2.14 (3)	2.906 (4)	154 (4)
O13—H13A···O12 <sup>ii</sup>	0.87 (2)	1.89 (2)	2.755 (5)	170 (4)
O12—H12A···O9 <sup>iii</sup>	0.86 (3)	2.42 (6)	3.071 (4)	133 (7)
N5—H5A···O7 <sup>iii</sup>	0.84 (2)	2.29 (3)	3.094 (4)	160 (3)
O2—H2D···O13	0.85 (2)	1.88 (2)	2.722 (3)	172 (3)
O2—H2C···N5 <sup>iii</sup>	0.86 (2)	1.90 (2)	2.753 (3)	171 (3)
O1—H1D···O9 <sup>iv</sup>	0.82 (2)	1.94 (2)	2.753 (3)	174 (3)
O1—H1C···O10 <sup>iii</sup>	0.83 (2)	1.88 (2)	2.706 (3)	175 (3)

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

All H atoms were initially located in a difference Fourier map. H atoms attached to O and N atoms were refined with distance restraints of  $\text{O}-\text{H} = 82$  (3) Å and  $\text{N}-\text{H} = 86$  (3) Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  or  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances of 0.93 or 0.97 Å, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The highest density peak is located 0.86 Å from atom Cd1.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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