

Diaquabis(ethylenediamine)cadmium(II) bis(4-aminonaphthalene-1-sulfonate) dihydrate

 Ming-Tian Li,^a Cheng-Gang Wang^{a*} and Xu-Cheng Fu^b

^aDepartment of Chemistry, Central China Normal University, Wuhan, Hubei 430079, People's Republic of China, and ^bChemistry and Biology Department, West Anhui University, Liu an, Anhui 237000, People's Republic of China
Correspondence e-mail: wangcg23@yahoo.com.cn

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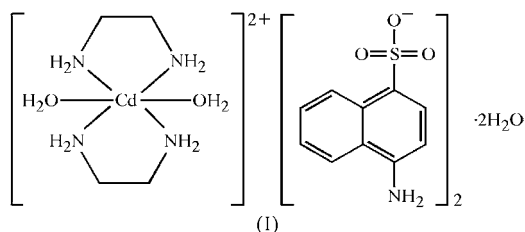
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In the title compound, $[\text{Cd}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_2 \cdot 2\text{H}_2\text{O}$, the Cd^{II} atom, located on an inversion centre, has a distorted octahedral coordination geometry formed by two ethylenediamine and two water molecules. 4-Aminonaphthalene-1-sulfonate acts as a counter-ion to balance the charge, and two antiparallel anions showing strong π - π stacking interactions are linked by paired $\text{N}-\text{H} \cdots \text{O}(\text{sulfonate})$ hydrogen bonds into an isolated $R_2^2(16)$ dimer. The crystal structure is stabilized by the π - π stacking interactions and hydrogen bonds.

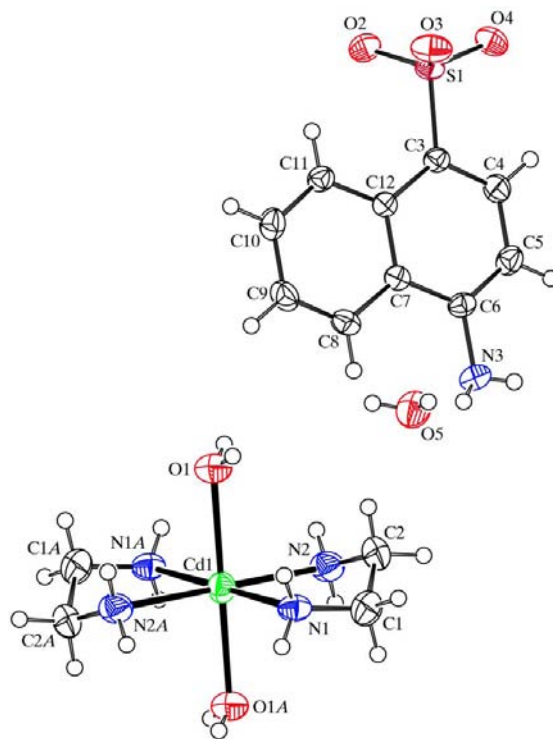
Comment

Organosulfonates are widely used industrially as surfactants and dyes. Recently, they have been studied as potential liquid crystalline (Huo *et al.*, 1994) and non-linear optical materials (Marder *et al.*, 1994; Russell *et al.*, 1994), and as complexing agents in the form of sulfonated macrocycles (Steed *et al.*, 1995). However, because of their weak coordination abilities with transition metal ions, most of the reported complexes containing sulfonate are aqua-metal salts in which the sulfonate only acts as a counter-anion to balance the charge (Kosnic *et al.*, 1992; Shubnell *et al.*, 1994; Gunderman *et al.*, 1997). As part of an investigation of the coordination behavior of the sulfonate anion, we present here the crystal structure of the title compound, $[\text{Cd}(\text{en})_2(\text{H}_2\text{O})_2](\text{ans})_2 \cdot 2\text{H}_2\text{O}$, (I) (en is ethylenediamine and ans is 4-aminonaphthalene-1-sulfonate).

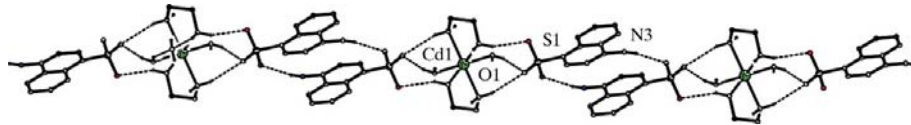


The crystal structure of (I) consists of Cd^{II} complex cations, ans anions and solvent water molecules. The molecular

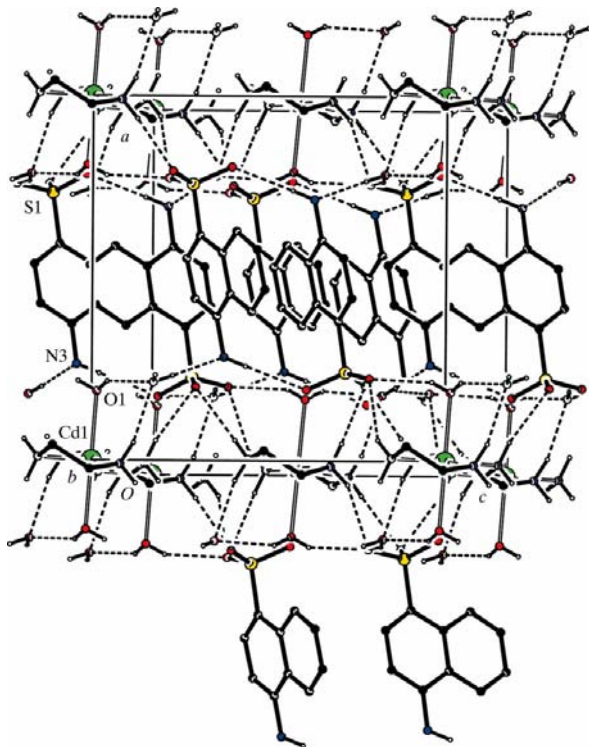
structure of (I) is shown in Fig. 1. The Cd atom, lying on an inversion center, has a distorted octahedral environment and is coordinated by four N atoms from two diethylenediamine ligands, which lie in the equatorial plane, and by two water O atoms occupying the axial sites. The Cd–N distances [average 2.259 (11) Å; Table 1] are slightly shorter than the Cd–N distances in $[\text{Cd}(\text{en})_3](\text{NO}_3)_2$ [Cd–N = 2.355 (3)–2.400 (3) Å; Prior, 2006]. The Cd–O distance is longer than the equivalent Cd–O distances in the complex $[\text{Cd}(\text{hmt})_2(\text{H}_2\text{O})_4]$ – $[\text{Cd}(\text{H}_2\text{O})_6](\text{ans})_4 \cdot 6\text{H}_2\text{O}$ [Cd–O = 2.2804 (18)–2.3025 (19) Å; hmt is hexamethylenetetramine; Zhou *et al.*, 2005]. The naphthalene ring is essentially planar (the r.m.s. deviation is 0.002 Å), the greatest deviation from the mean plane being 0.024 (2) Å for atom C6. The S and N atoms deviate slightly [0.1730 (5) and 0.012 (2) Å, respectively] from the naphthalene plane. The centroid–centroid distance between the C3–C7/C12 benzene ring (centroid Cg1) belonging to the naphthalene ring system in one anion and the C7–C12 benzene ring (Cg2) of the neighboring naphthalene ring system at (1 – x, –y, 1 – z) is 3.5384 (13) Å, and the dihedral angles α (between planes Cg1 and Cg2) and β (between the Cg1–Cg2 vector and the normal to the C3–C7/C12 ring) are 1.03 and 15.94°, respectively; these values indicate the existence of significant π - π stacking interactions between adjacent ans ions. Two antiparallel ans anions are linked by paired $\text{N}-\text{H} \cdots \text{O}(\text{sulfonate})$ hydrogen bonds into an isolated $R_2^2(16)$ dimer (Bernstein *et al.*, 1995). The formed anionic dimers are packed along the [011] direction with their mean naphthalene


Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 50% probability level [symmetry code: (A) $-x, -y, 1 - z$].


Figure 2

The one-dimensional chain constructed from the cations and anions, with hydrogen bonds shown as dashed lines.


Figure 3

The molecular packing of (I), with hydrogen bonds shown as dashed lines.

planes perpendicular to those of their neighbors, which is different from the packing mode within the complex $[\text{Zn}(\text{en})_2(\text{H}_2\text{O})_2](\text{ans})_2 \cdot 2\text{H}_2\text{O}$ (Li & Wang, 2006). Within the latter, four parallel dimers encircle one dimer with a different orientation. The cations and anionic dimers in (I) are linked by intra- and intermolecular hydrogen bonds formed by O atoms from the dimers and H atoms belonging to the en ligands and water molecules, thus forming an infinite one-dimensional chain along the [001] direction (Fig. 2). As shown in Fig. 3, a cationic layer is linked to an anionic layer through a series of N—H...O, O—H...O and O—H...N hydrogen bonds. The extensive hydrogen bonds together with the strong π - π stacking interaction stabilize the crystal structure, forming a three-dimensional network (Table 2).

Experimental

Ethylenediamine (0.06 g, 1 mmol) was added to an aqueous solution (20 ml) of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.133 g, 0.5 mmol). After the mixture had been stirred for 2 h at room temperature, the solution was treated

with sodium 4-aminonaphthalene-1-sulfonate tetrahydrate (0.32 g, 1 mmol) in ethanol (10 ml). After filtration, the colorless solution was allowed to stand at room temperature. Colorless block-shaped crystals of the title complex were obtained by slow evaporation of the solvent for about one week.

Crystal data

$[\text{Cd}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot (\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 749.14$
 Monoclinic, $P2_1/c$
 $a = 12.4386$ (8) Å
 $b = 9.8579$ (7) Å
 $c = 12.2872$ (8) Å
 $\beta = 90.604$ (1)°

$V = 1506.55$ (17) Å³
 $Z = 2$
 $D_x = 1.651$ Mg m⁻³
 Mo K α radiation
 $\mu = 0.93$ mm⁻¹
 $T = 292$ (2) K
 Block, colorless
 0.48 × 0.40 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.664$, $T_{\max} = 0.708$

17152 measured reflections
 3590 independent reflections
 3254 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$
 $\theta_{\max} = 28.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.118$
 $S = 1.11$
 3590 reflections
 226 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 0.5785P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.019$
 $\Delta\rho_{\max} = 0.57$ e Å⁻³
 $\Delta\rho_{\min} = -0.92$ e Å⁻³

H atoms treated by a mixture of independent and constrained refinement

Table 1

Selected geometric parameters (Å, °).

Cd1—N1	2.240 (2)	Cd1—O1	2.361 (2)
Cd1—N2	2.280 (2)		
N1—Cd1—N2	78.81 (10)	N1—Cd1—O1	90.67 (8)
N1—Cd1—N2 ⁱ	101.19 (10)	N2—Cd1—O1	90.25 (8)

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5B...N3	0.77 (3)	2.13 (3)	2.900 (3)	177 (4)
O5—H5A...O4 ⁱⁱⁱ	0.80 (3)	2.13 (3)	2.906 (3)	163 (4)
O1—H1F...O5	0.78 (3)	2.16 (3)	2.858 (3)	150 (4)
O1—H1E...O4 ⁱⁱⁱ	0.73 (4)	2.14 (4)	2.815 (3)	154 (5)
N3—H3A...O3 ^{iv}	0.84 (3)	2.24 (3)	3.073 (3)	171 (3)
N1—H1B...O5	0.86 (2)	2.17 (2)	3.009 (3)	166 (3)
N1—H1A...O2 ^v	0.84 (2)	2.27 (2)	3.073 (3)	159 (4)
N2—H2B...O2 ^{vi}	0.87 (2)	2.56 (3)	3.322 (3)	148 (4)
N2—H2A...O4 ⁱⁱⁱ	0.87 (2)	2.42 (2)	3.232 (3)	154 (3)

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

The water and amine H atoms were located in a difference Fourier map and refined with the restraints O—H = 0.73 (4)–0.80 (3) Å, N—H = 0.77 (2)–0.871 (18) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O,N})$. H atoms on C atoms were placed in geometrically idealized positions and refined as riding [C—H = 0.93 or 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3025). Services for accessing these data are described at the back of the journal.

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