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Ethylenediammonium tetraaquabis(dichromate) dihydrate

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.070; data-to-parameter ratio = 44.4.

The crystal structure of the title compound, [NH₂(CH₂)₂NH₃][Cd(SO₄)₂(H₂O)₄], consists of [Cd(SO₄)₂(H₂O)₄]²⁻ anions that are built from octahedral Cd(H₂O)₄O₂ and SO₄ tetrahedral units linked by corner sharing. The ethylenediamminium cations are linked to the anions via N—H⋯O hydrogen bonds. The asymmetric unit contains one-half of the compound, the other half being related to the first by an inversion centre. The crystal structure presents alternate stacking of the inorganic and organic layers along the crystallographic b axis. The structure cohesion and stability is further assured by O(water)—H⋯O hydrogen bonds.

Related literature

For our previous work on the synthesis, characterization and properties of mixed metal sulfates and amines, see: Rekik et al. (2005, 2007, 2008, 2009); Naïli et al. (2006); Yahyaoui et al. (2007). For the manganese, iron, cobalt and magnesium analogs of the title compound, see: Chaabouni et al. (1996); Held (2003); Rekik et al. (2008, 2009b). For our previous work on the synthesis, characterization and properties of mixed metal sulfates and amines, see: Rekik, Naïli, Bataille & Mhiri (2006); Rekik, Naïli, Bataille, Roisnel & Mhiri (2006).

Table 1
Selected bond lengths (Å).

| Bond | Length (Å) |
|------|------------|
| Cd—O₆ | 2.2511 (12) |
| Cd—O₄ | 2.2789 (9) |

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

N—H⋯O—A | 1.93 | 2.8155 (15) | 177 |
N—H⋯O₂ | 1.99 | 2.8378 (16) | 160 |
N—H⋯O₃ | 2.03 | 2.8767 (15) | 160 |
OW₁—H₁₁—OW₂ | 1.90 (2) | 2.7542 (15) | 176 (3) |
OW₁—H₁₂—OW₃ | 1.89 (2) | 2.7293 (17) | 173 (3) |
OW₂—H₂₁—OW₃ | 2.01 (2) | 2.8177 (14) | 163 (2) |
OW₂—H₂₂—OW₃ | 1.89 (2) | 2.7150 (15) | 165 (2) |

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZo (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELX97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Berndt, 1999); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GO2021).
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supplementary materials
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Ethylenediammonium tetraaquadisulfatocadmate

W. Rekik, H. Naïli, T. Mhiri and T. Bataille

Comment

The chemistry of organic-inorganic hybrid materials has received increasing attention over the last few years, mainly with the idea of using amines as templates and associating transition metals. A great interest has been shown in some organically templated metal sulfate because of their open-framework structure and ferroelastic and ferroelectric properties. We note also that a previous work of synthesis and characterization of mixed metal sulfates and amines, leading to many important physical properties, has been realized in our laboratory (Rekik et al., 2005; Naïli, et al., 2006; Rekik et al., 2007; Yahyaoui et al., 2007; Rekik et al., 2008; Rekik et al., 2009a). In the course of our investigations on new sulfate materials having interesting properties, we report here the chemical preparation and the structural characterization of a new ethylenediammonium cadmium (II) tetraaquabis(sulfato-O)cadmate, [NH$_3$(CH$_2$)$_2$NH$_3$][Cd(SO$_4$)$_2$(H$_2$O)$_4$]. The title compound is isostructural with the manganese, iron, cobalt and magnesium related phases (Chaabouni et al., 1996; Held, 2003; Rekik et al., 2008; Rekik et al., 2009b). As it can be seen in figure 1, the crystal structure shows an alternate stacking of inorganic layers of tetraaquabis(sulfato-O)cadmium anions, [Cd(SO$_4$)$_2$(H$_2$O)$_4$]$^{2-}$, and organic layers of [NH$_3$(CH$_2$)$_2$NH$_3$]$^{2+}$ cations along the crystallographic b axis. Anions and cations are linked together through N—H···O hydrogen bonds to form a three-dimensional network. The asymmetric unit (Fig. 2) of the title compound contains only one cadmium atom located at a symmetry centre, only one sulfate tetrahedron and ethylenediammonium cation lying about inversion centre. The Cd(II) central atom is octahedrally coordinated by one oxygen atom of sulfate group, two water molecules and the corresponding centrosymmetrically located atoms. Each octahedron around Cd shares two oxygen atoms with two sulfate groups to form trimeric units. These latest are stabilized and linked via OW—H···O hydrogen bonds giving rise to a three-dimensional inorganic framework delimiting tunnels along the three crystallographic axes. The negative charge of the inorganic part is compensated by ethylenediammonium cations which are located on inversion centres in the inorganic framework cavities. The structure cohesion and stability are assured by two types of hydrogen bonds, OW—H···O and N—H···O.

Experimental

Single-crystals of the title compound were grown by slow evaporation at room temperature of an aqueous solution of CdSO$_4$.8(H$_2$O)/C$_2$H$_8$N$_2$/H$_2$SO$_4$ in a ratio 1:1:1. The product was filtered off and washed with a small amount of distilled water.

Refinement

The aqua H atoms were located in difference map and refined with O—H distance restraints of 0.85 (2) Å and H—H distance restraints of 1.35 (2) Å. H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atom, with C—H = 0.97 Å, N—H = 0.89 Å and $U_{iso} = 1.2U_{eq}$(C, N). The 1 1 3 reflection has been omitted, (Iobs/Ical)/sigma greater than 10.
Figures

Fig. 1. Projection of the crystal structure of the title compound along the $a$ axis, with hydrogen bonds indicated as dashed lines.

Fig. 2. A part of the crystal structure of the title compound showing the asymmetric unit (expanded by symmetry to give complete organic cation and trimeric unit) and atom numbering. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines.[Symmetry codes: (I) -x + 1, -y + 1, -z + 2; (II) -x + 2, -y + 2, -z + 1.]

Ethylenediammonium tetraaquadisulfatocadmate

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Cd}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$  
$M_r = 438.70$  
$Z = 1$  
$F(000) = 220$  
$D_x = 2.166 \text{ Mg m}^{-3}$  
$\text{Hall symbol: } -P 1$  
$\text{Mo K}\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å}$  
$a = 6.9114 (2) \text{ Å}$  
$\theta = 2.9–42.2^\circ$  
$b = 7.3056 (2) \text{ Å}$  
$\mu = 1.99 \text{ mm}^{-1}$  
$c = 7.3629 (1) \text{ Å}$  
$T = 293 \text{ K}$  
$\alpha = 74.013 (2)^\circ$  
$\beta = 71.731 (1)^\circ$  
$\gamma = 78.043 (1)^\circ$  
$V = 336.39 (1) \text{ Å}^3$  

Data collection

Nonius KappaCCD diffractometer  
4684 independent reflections  
Radiation source: fine-focus sealed tube  
4352 reflections with $I > 2\sigma(I)$  
horizontally mounted graphite crystal  
$R_{int} = 0.040$  
Detector resolution: 9 pixels mm$^{-1}$  
$\theta_{max} = 42.2^\circ$, $\theta_{min} = 2.9^\circ$  
CCD rotation images, thick slices scans  
$h = -13 \rightarrow 13$  
Absorption correction: analytical  
$k = -9 \rightarrow 13$  
(de Meulenaer & Tompa, 1965)  
$l = -9 \rightarrow 13$  
8732 measured reflections  

sup-2
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Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.070$

$S = 1.04$

$4684$ reflections

$105$ parameters

$6$ restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0105P)^2 + 0.0726P]$

where $P = (F_o^2 + 2F_c^2)/3$

$\Delta \rho_{\text{max}} = 0.90 \text{ e Å}^{-3}$

$\Delta \rho_{\text{min}} = -1.49 \text{ e Å}^{-3}$

Extinction correction: SHELXL97 (Sheldrick, 2008), $\text{Fc}^* = \text{kFc}[1+0.001\text{xFe}^2\lambda^2/\sin(2\theta)]^{1/4}$

Primary atom site location: structure-invariant direct methods

Experimental. Data were corrected for Lorentz-polarization effects and an analytical absorption correction (dc Meulenaer & Tompa, 1965) was applied. The structure was solved in the P -1 space group by the direct methods (Cd and S) and subsequent difference Fourier syntheses (all other atoms), with an exception for H atoms bonded to C and N atoms which are positioned geometrically.

Geometry. All e.s.d.’s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.’s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.

Refinement. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(ggt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|    | x   | y   | z   | $U_{iso}$/$U_{eq}$ |
|----|-----|-----|-----|-------------------|
| Cd | 0.5000 | 0.5000 | 1.0000 | 0.01899 (4) |
| OW1 | 0.5857 (3) | 0.24405 (19) | 1.22634 (18) | 0.0483 (4) |
| OW2 | 0.77475 (16) | 0.43008 (19) | 0.74717 (15) | 0.0293 (2) |
| S  | 0.69724 (4) | 0.72895 (4) | 1.24802 (4) | 0.01654 (5) |
| O1  | 0.81539 (17) | 0.55801 (17) | 1.34097 (15) | 0.02945 (19) |
| O2  | 0.49364 (16) | 0.76868 (19) | 1.38281 (14) | 0.0302 (2) |
| O3  | 0.81079 (17) | 0.89591 (15) | 1.18806 (15) | 0.02517 (18) |
| O4  | 0.66952 (18) | 0.69978 (16) | 1.06591 (13) | 0.0285 (2) |
| N  | 0.83624 (18) | 0.99858 (18) | 0.75717 (15) | 0.02352 (18) |
| H0A  | 0.7789 | 0.9054 | 0.8533 | 0.035* |
| H0B  | 0.7386 | 1.0923 | 0.7270 | 0.035* |
| H0C  | 0.9219 | 1.0448 | 0.7964 | 0.035* |
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|     | U^11     | U^22     | U^33     | U^12     | U^13     | U^23     |
|-----|----------|----------|----------|----------|----------|----------|
| Cd  | 0.02244  | 0.01866  | 0.01811  | -0.00551 | -0.00646 | -0.00462 |
| OW1 | 0.0878   | 0.0283   | 0.02277  | 0.0176   | -0.0281  | -0.0090  |
| OW2 | 0.0206   | 0.0431   | 0.0245   | -0.0046  | -0.0047  | -0.0096  |
| S   | 0.01696  | 0.01998  | 0.01439  | -0.00478 | -0.00561 | -0.00337 |
| O1  | 0.0256   | 0.0265   | 0.0308   | -0.0015  | -0.0096  | 0.0031   |
| O2  | 0.0200   | 0.0437   | 0.0221   | -0.0006  | -0.0016  | -0.0069  |
| O3  | 0.0289   | 0.0231   | 0.0292   | -0.0102  | -0.0118  | -0.0056  |
| O4  | 0.0410   | 0.0350   | 0.0168   | -0.0214  | -0.0087  | -0.0045  |
| N   | 0.0244   | 0.0274   | 0.0175   | -0.0054  | -0.0040  | -0.0036  |
| C   | 0.0275   | 0.0220   | 0.0178   | -0.0080  | -0.0036  | -0.0032  |

Geometric parameters (Å, °)

| Bond | Distance | Angle   |
|------|----------|---------|
| Cd—OW1 | 2.2511 (12) | S—O2 1.4708 (10) |
| Cd—OW1 | 2.2511 (12) | S—O3 1.4770 (10) |
| Cd—O4 | 2.2789 (9)   | S—O4 1.4884 (8) |
| Cd—O4i | 2.2789 (9)   | N—C 1.4803 (16) |
| Cd—OW2i | 2.2887 (10) | N—H0A 0.8900 |
| Cd—OW2 | 2.2887 (10) | N—H0B 0.8900 |
| OW1—H12 | 0.846 (16)   | N—H0C 0.8900 |
| OW1—H11 | 0.833 (15)   | C—Cii 1.514 (2) |
| OW2—H21 | 0.833 (15)   | C—H1D 0.9700 |
| OW2—H22 | 0.842 (15)   | C—H1E 0.9700 |
| S—O1  | 1.4669 (11)  |         |
| OW1—Cd—OW1 | 180.0   | H21—OW2—H22 107.2 (19) |
| OW1—Cd—O4 | 85.76 (5)   | O1—S—O2 110.44 (7) |
| OW1—Cd—O4 | 94.24 (5)   | O1—S—O3 110.09 (7) |
| OW1—Cd—O4i | 94.24 (5)   | O2—S—O3 110.47 (7) |
| OW1—Cd—O4i | 85.76 (5)   | O1—S—O4 110.31 (7) |
| O4—Cd—O4i | 180.0       | O2—S—O4 108.81 (6) |
| OW1—Cd—OW2i | 95.02 (5)   | O3—S—O4 106.63 (6) |
| OW1—Cd—OW2i | 84.98 (5)   | S—O4—Cd 134.68 (6) |
| O4—Cd—OW2i | 87.96 (4)   | C—N—H0A 109.5 |
| O4—Cd—OW2i | 92.04 (4)   | C—N—H0B 109.5 |
| OW1—Cd—OW2 | 84.98 (5)   | H0A—N—H0B 109.5 |
supplementary materials

OW1—Cd—OW2  95.02 (5)  C—N—H0C  109.5
O4—Cd—OW2  92.04 (4)  H0A—N—H0C  109.5
O41—Cd—OW2  87.96 (4)  H0B—N—H0C  109.5
OW21—Cd—OW2  180.000 (1)  N—C—Cii  109.62 (13)
Cd—OW1—H12  127.0 (18)  N—C—H1D  109.7
Cd—OW1—H11  127.6 (18)  Cii—C—H1D  109.7
H12—OW1—H11  105 (2)  N—C—H1E  109.7
Cd—OW2—H21  121.2 (16)  Cii—C—H1E  109.7
Cd—OW2—H22  123.0 (15)  H1D—C—H1E  108.2

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

Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H  | H···A | D···A       | D—H···A |
|---------------|-------|-------|-------------|---------|
| N—H0A···O4    | 0.89  | 1.93  | 2.8155 (15) | 177.0   |
| N—H0B···O2iii | 0.89  | 1.99  | 2.8378 (16) | 160.0   |
| N—H0C···O3iv  | 0.89  | 2.03  | 2.8767 (15) | 160.0   |
| OW1—H11···O2v | 0.83 (2) | 1.90 (2) | 2.7342 (15) | 176 (3) |
| OW1—H12···O3vi| 0.85 (2) | 1.89 (2) | 2.7293 (17) | 173 (3) |
| OW2—H21···O1vii| 0.83 (2) | 2.01 (2) | 2.8177 (14) | 163 (2) |
| OW2—H22···O1viii| 0.84 (2) | 1.89 (2) | 2.7150 (15) | 165 (2) |

Symmetry codes: (iii) −x+1, −y+2, −z+2; (iv) −x+2, −y+2, −z+2; (v) −x+1, −y+1, −z+3; (vi) x, y−1, z; (vii) x, y, z−1; (viii) −x+2, −y+1, −z+2.
supplementary materials

Fig. 1
