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catena-Poly[[dihydrazinecadmium(II)]-di-μ-sulfato-κ⁴O:O′]

The title compound, $\{[Cd(SO_4)_2(N_2H_5)_2]\}_n$, contains fairly regular trans-CdN$_2$O$_4$ octahedra. The Cd atoms (site symmetry $\bar{1}$) are bridged by pairs of sulfate groups into infinite chains. A network of N—H⋯O hydrogen bonds, including a well defined trifurcated N—H⋯(O,O,O) link, completes the structure, which is isostructural with its zinc(II) and chromium(II) analogues.

Comment

The divalent-metal–hydrazinium sulfates of general formula $[M(N_2H_5)_2](SO_4)_2$, where M = Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd, are readily prepared by reacting a salt of the respective metal with hydrazinium sulfate in dilute sulfuric acid (Hand & Prout, 1966). This method usually results in the formation of microcrystalline solids unsuitable for single-crystal X-ray studies, except for the zinc compound, which was obtained as twinned crystals (Prout & Powell, 1961). More recently, chromous hydrazinium sulfate, $[Cr(N_2H_5)_2](SO_4)_2$, was fortuitously isolated as single crystals from a well tried reaction (Palmer, 1954) that usually generates a powder, and its crystal structure was subsequently determined (Parkins et al., 2001). The title compound, (I), arose unexpectedly during our attempts to prepare metal complexes with the hydrazinoacetate (NH$_2$—NH—CH$_2$—COO$^-$) anion. It is isostructural with $[Zn(N_2H_5)_2](SO_4)_2$ (Prout & Powell, 1961) and $[Cr(N_2H_5)_2](SO_4)_2$ (Parkins et al., 2001).

Compound (I) contains trans-CdN$_2$O$_4$ octahedra (Fig. 1), where the N atom is part of a hydrazinium (N$_2$H$_5{}^+$) cation. The Cd atoms (site symmetry $\bar{1}$) are connected by pairs of sulfate groups into infinite chains that propagate in the [100] direc-
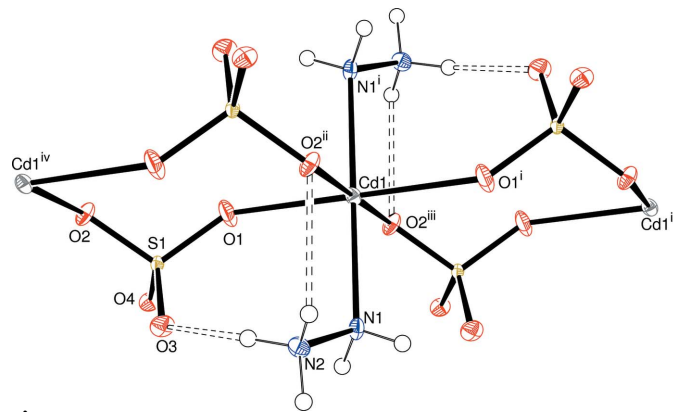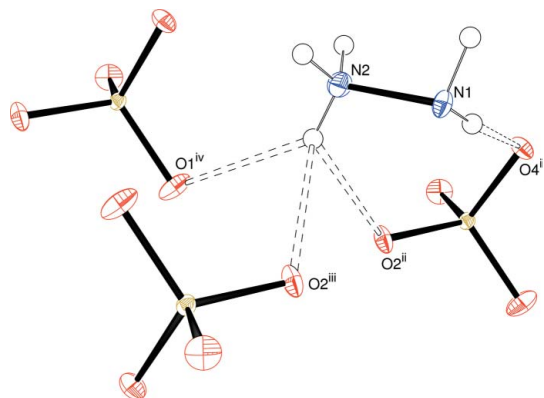

Figure 1
A view of part of the chain structure in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) −x, −y, −z; (ii) 1 − x, −y, −z; (iii) x − 1, y, z; (iv) x + 1, y, z.]

Figure 2
Detail of (I), showing the trifurcated N2—H2$C\cdots$(O,O,O) hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes are as in Table 2.

tion. In the previously studied compounds, a different setting of the triclinic cell was used and the equivalent chains in these materials propagate in the [010] direction. The separation of the Cd nodes in (I) is equal to the a unit-cell dimension, *i.e.* 5.4835 (2) Å. The equivalent metal$\cdots$metal separations for the Zn and Cr compounds are 5.33 and 5.4568 (5) Å, respectively.

Unlike the situation in the zinc and chromium analogues, where there is a substantial asymmetry in the two distinct M—O bond lengths [2.10 and 2.38 Å for Zn, and 2.0535 (17) and 2.3791 (19) Å for Cr], the two distinct Cd—O bond lengths in (I) are very similar (Table 1). The N—N bond length in (I) of 1.450 (2) Å is much shorter than the equivalent value of 1.56 Å reported for the Zn compound, but is almost identical to the value of 1.453 (3) Å found for $[Cr(N_2H_5)_2](SO_4)_2$ (Parkins *et al.*, 2001).

The crystal packing in (I) is influenced by N—H$\cdots$O hydrogen bonds (Table 2). It appears to be similar to the scheme proposed for $[Zn(N_2H_5)_2](SO_4)_2$ and is the same as that observed in $[Cr(N_2H_5)_2](SO_4)_2$. Four of the N—H bonds participate in simple N—H$\cdots$O interactions [mean N—H = 0.88 (3), mean H$\cdots$O = 2.03 (3) and mean N$\cdots$O = 2.853 (3) Å; mean N—H$\cdots$O = 159 (3)°]. The other H atom, H2C, is involved in a well defined trifurcated (four-centre) N—H$\cdots$(O,O,O) bond (Fig. 2); the bond-angle sum about H2C is 107°. The packing for (I) involves the Cd/sulfate chains propagating in the [100] direction, with crosslinking in the [010] and [001] directions *via* the N—H$\cdots$O hydrogen bonds (Fig. 3).

Experimental

In an attempt to synthesize ethyl hydrazinoacetate, 99%+ hydrazine hydrate ($N_2H_4 \cdot H_2O$; 0.50 g, 10 mmol) and ethyl bromoacetate (1.671 g, 10 mmol) were reacted together in dry ethanol (5 ml), resulting in a white solid. The white solid (0.236 g, 2 mmol) was dissolved in water (30 ml) and mixed with an aqueous solution (30 ml) of $3CdSO_4 \cdot 8H_2O$ (0.769 g, 1 mmol). The resulting clear solution, with a pH of 3, was kept for crystallization at room temperature. Within 1 d, many faceted block-shaped crystals of (I)
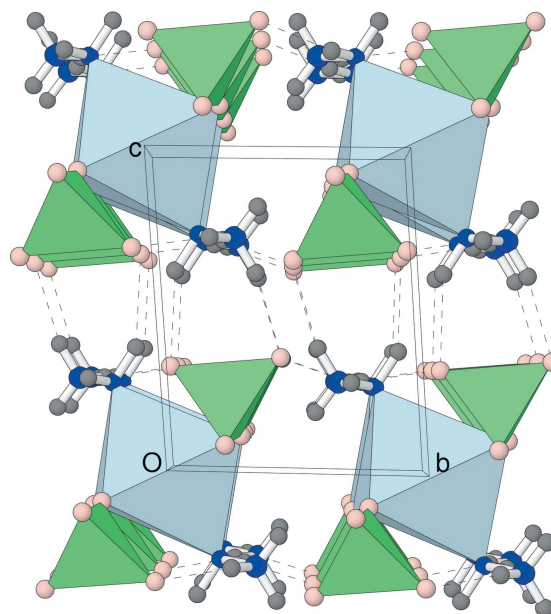
Figure 3
The packing in (I) in a polyhedral representation, with N—H$\cdots$O hydrogen bonds indicated by dashed lines. Colour key: CdN_2O_4 octahedra are blue–grey, SO_4 tetrahedra green, N atoms blue, O atoms beige and H atoms dark grey.

were visible. These were recovered by filtration, washed with cold water and dried in air. Later analysis of the previously obtained white solid suggested the presence of hydrazinium bromide as well as ethyl hydrazinoacetate. The detailed mechanism that results in the formation of large single crystals of (I) rather than the usual powder is unknown, but the reaction is reproducible and may also be used to prepare single crystals of other $[M^{II}(N_2H_5)_2](SO_4)_2$ compounds.

Crystal data

$[Cd(SO_4)_2(N_2H_5)_2]$	$V = 227.61$ (1) Å^3
$M_r = 370.64$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 2.704$ Mg m^{-3}
$a = 5.4835$ (2) Å	Mo $K\alpha$ radiation
$b = 5.9034$ (1) Å	$\mu = 2.90$ mm^{-1}
$c = 7.3624$ (2) Å	$T = 120$ (2) K
$\alpha = 92.116$ (2)°	Block, colourless
$\beta = 103.5206$ (16)°	$0.52 \times 0.38 \times 0.20$ mm
$\gamma = 99.7984$ (18)°	

Data collection

Nonius KappaCCD area-detector diffractometer	5260 measured reflections
	1036 independent reflections
φ and ω scans	1032 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	$R_{int} = 0.023$
$T_{min} = 0.314$, $T_{max} = 0.595$	$\theta_{max} = 27.5°$
(expected range = 0.296–0.560)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.002P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.013$	$+ 0.3006P]$
$wR(F^2) = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} = 0.001$
1036 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
91 parameters	$\Delta\rho_{min} = -0.52$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXL97* (Sheldrick, 1997)
	Extinction coefficient: 0.176 (5)

Table 1
Selected geometric parameters (Å, °).

Cd1—O2[i]	2.2890 (12)	Cd1—O1	2.3058 (12)
Cd1—N1	2.3018 (15)		
S1—O1—Cd1	141.72 (8)	S1—O2—Cd1[ii]	123.18 (7)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O3[iii]	0.93 (3)	2.17 (3)	2.988 (2)	146 (2)
N1—H1$B\cdots$O4[iv]	0.82 (3)	2.09 (3)	2.8949 (19)	167 (3)
N2—H2$A\cdots$O4[iii]	0.88 (3)	1.92 (3)	2.776 (2)	164 (2)
N2—H2$B\cdots$O3	0.87 (3)	1.93 (3)	2.753 (2)	158 (2)
N2—H2$C\cdots$O2[v]	0.83 (3)	2.34 (3)	2.876 (2)	123 (2)
N2—H2$C\cdots$O2[iv]	0.83 (3)	2.44 (3)	2.964 (2)	121 (2)
N2—H2$C\cdots$O1[vi]	0.83 (3)	2.47 (3)	3.127 (2)	136 (2)

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

The H atoms were located in difference maps and their positions and U_{iso} values were freely refined. N—H distances are listed in Table 2.

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supporting information

catena-Poly[[dihydrazinecadmium(II)]-di-*μ*-sulfato-*κ⁴O:O′*]

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catena-Poly[[dihydrazinecadmium(II)]-di-*μ*-sulfato-*κ²O:O′*]

Crystal data

$[Cd(SO_4)_2(N_2H_5)_2]$	$Z = 1$
$M_r = 370.64$	$F(000) = 182$
Triclinic, $P\bar{1}$	$D_x = 2.704$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.4835$ (2) Å	Cell parameters from 1033 reflections
$b = 5.9034$ (1) Å	$\theta = 1.0$–27.5°
$c = 7.3624$ (2) Å	$\mu = 2.90$ mm^{-1}
$\alpha = 92.116$ (2)°	$T = 120$ K
$\beta = 103.5206$ (16)°	Block, colourless
$\gamma = 99.7984$ (18)°	0.52 × 0.38 × 0.20 mm
$V = 227.61$ (1) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	5260 measured reflections
Radiation source: fine-focus sealed tube	1036 independent reflections
Graphite monochromator	1032 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.9°$
$T_{min} = 0.314$, $T_{max} = 0.595$	$h = -7\rightarrow7$
	$k = -7\rightarrow7$
	$l = -9\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.013$	All H-atom parameters refined
$wR(F^2) = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.002P)^2 + 0.3006P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	
1036 reflections	$(\Delta/\sigma)_{max} = 0.001$
91 parameters	$\Delta\rho_{max} = 0.38$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.52$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 1997), Fc*=kFc[1+0.001xFc²λ^3/sin(2θ)]$^{-1/4}$
	Extinction coefficient: 0.176 (5)

Special details

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(gt) *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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cd1	0.0000	0.0000	0.0000	0.00581 (10)
S1	0.64505 (7)	0.26136 (7)	0.22259 (6)	0.00434 (11)
O1	0.3921 (2)	0.2413 (2)	0.09232 (19)	0.0115 (3)
O2	0.8452 (2)	0.2967 (2)	0.11515 (17)	0.0078 (3)
O3	0.6639 (2)	0.0524 (2)	0.32514 (18)	0.0091 (3)
O4	0.6894 (2)	0.4654 (2)	0.35697 (17)	0.0074 (2)
N1	0.0764 (3)	−0.1853 (3)	0.2717 (2)	0.0067 (3)
H1A	0.129 (5)	−0.089 (4)	0.382 (4)	0.017 (6)*
H1B	−0.049 (5)	−0.275 (5)	0.284 (4)	0.020 (6)*
N2	0.2749 (3)	−0.3221 (3)	0.2844 (2)	0.0073 (3)
H2A	0.293 (5)	−0.392 (4)	0.389 (4)	0.013 (6)*
H2B	0.418 (5)	−0.231 (5)	0.287 (4)	0.019 (6)*
H2C	0.238 (5)	−0.415 (5)	0.190 (4)	0.014 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.00511 (12)	0.00545 (12)	0.00648 (12)	0.00149 (6)	0.00025 (7)	0.00081 (6)
S1	0.0034 (2)	0.0045 (2)	0.0050 (2)	0.00012 (15)	0.00116 (15)	0.00009 (15)
O1	0.0054 (6)	0.0120 (6)	0.0139 (6)	−0.0008 (5)	−0.0023 (5)	0.0016 (5)
O2	0.0081 (6)	0.0072 (6)	0.0098 (6)	0.0010 (5)	0.0058 (5)	−0.0005 (5)
O3	0.0111 (6)	0.0062 (6)	0.0099 (6)	0.0009 (5)	0.0026 (5)	0.0027 (5)
O4	0.0097 (6)	0.0060 (6)	0.0067 (6)	0.0013 (5)	0.0030 (5)	−0.0014 (4)
N1	0.0042 (7)	0.0069 (7)	0.0092 (8)	0.0012 (6)	0.0023 (6)	0.0011 (6)
N2	0.0076 (7)	0.0070 (7)	0.0075 (8)	0.0027 (6)	0.0011 (6)	0.0014 (6)

Geometric parameters (Å, º)

Cd1—O2[i]	2.2890 (12)	S1—O2	1.4880 (12)
Cd1—O2[ii]	2.2890 (12)	O2—Cd1[iv]	2.2890 (12)
Cd1—N1	2.3018 (15)	N1—N2	1.450 (2)
Cd1—N1[iii]	2.3018 (15)	N1—H1A	0.93 (3)
Cd1—O1[iii]	2.3058 (12)	N1—H1B	0.82 (3)
Cd1—O1	2.3058 (12)	N2—H2A	0.88 (3)
S1—O1	1.4735 (13)	N2—H2B	0.87 (3)
S1—O3	1.4759 (13)	N2—H2C	0.83 (3)

S1—O4	1.4793 (12)		
O2ⁱ—Cd1—O2ⁱⁱ	180.0	O1—S1—O2	109.26 (8)
O2ⁱ—Cd1—N1	96.98 (5)	O3—S1—O2	109.43 (7)
O2ⁱⁱ—Cd1—N1	83.02 (5)	O4—S1—O2	107.98 (7)
O2ⁱ—Cd1—N1ⁱⁱⁱ	83.02 (5)	S1—O1—Cd1	141.72 (8)
O2ⁱⁱ—Cd1—N1ⁱⁱⁱ	96.98 (5)	S1—O2—Cd1^{iv}	123.18 (7)
N1—Cd1—N1ⁱⁱⁱ	180.0	N2—N1—Cd1	113.54 (10)
O2ⁱ—Cd1—O1ⁱⁱⁱ	94.68 (5)	N2—N1—H1A	103.8 (16)
O2ⁱⁱ—Cd1—O1ⁱⁱⁱ	85.32 (5)	Cd1—N1—H1A	115.3 (16)
N1—Cd1—O1ⁱⁱⁱ	88.39 (5)	N2—N1—H1B	105.4 (18)
N1ⁱⁱⁱ—Cd1—O1ⁱⁱⁱ	91.61 (5)	Cd1—N1—H1B	112.8 (19)
O2ⁱ—Cd1—O1	85.32 (5)	H1A—N1—H1B	105 (2)
O2ⁱⁱ—Cd1—O1	94.68 (5)	N1—N2—H2A	109.8 (15)
N1—Cd1—O1	91.61 (5)	N1—N2—H2B	108.9 (17)
N1ⁱⁱⁱ—Cd1—O1	88.39 (5)	H2A—N2—H2B	108 (2)
O1ⁱⁱⁱ—Cd1—O1	180.0	N1—N2—H2C	108.8 (17)
O1—S1—O3	111.11 (8)	H2A—N2—H2C	112 (2)
O1—S1—O4	109.22 (8)	H2B—N2—H2C	109 (2)
O3—S1—O4	109.79 (7)		
O3—S1—O1—Cd1	4.06 (16)	O1—S1—O2—Cd1^{iv}	−92.03 (9)
O4—S1—O1—Cd1	−117.19 (13)	O3—S1—O2—Cd1^{iv}	29.82 (10)
O2—S1—O1—Cd1	124.90 (12)	O4—S1—O2—Cd1^{iv}	149.29 (8)
O2ⁱ—Cd1—O1—S1	116.20 (14)	O2ⁱ—Cd1—N1—N2	−154.09 (11)
O2ⁱⁱ—Cd1—O1—S1	−63.80 (14)	O2ⁱⁱ—Cd1—N1—N2	25.91 (11)
N1—Cd1—O1—S1	19.33 (14)	O1ⁱⁱⁱ—Cd1—N1—N2	111.39 (12)
N1ⁱⁱⁱ—Cd1—O1—S1	−160.67 (14)	O1—Cd1—N1—N2	−68.61 (12)

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···O3^v	0.93 (3)	2.17 (3)	2.988 (2)	146 (2)
N1—H1*B*···O4^{vi}	0.82 (3)	2.09 (3)	2.8949 (19)	167 (3)
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N2—H2*B*···O3	0.87 (3)	1.93 (3)	2.753 (2)	158 (2)
N2—H2*C*···O2ⁱⁱ	0.83 (3)	2.34 (3)	2.876 (2)	123 (2)
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N2—H2*C*···O1^{vii}	0.83 (3)	2.47 (3)	3.127 (2)	136 (2)

Symmetry codes: (ii) −*x*+1, −*y*, −*z*; (v) −*x*+1, −*y*, −*z*+1; (vi) *x*−1, *y*−1, *z*; (vii) *x*, *y*−1, *z*.