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Ethylenediammonium tetraaqua-bis(sulfato)cobaltate(II)

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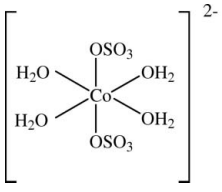
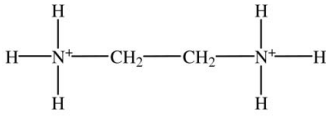
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.001 Å; R factor = 0.017; wR factor = 0.019; data-to-parameter ratio = 13.7.

In the title compound, $[NH_3(CH_2)_2NH_3][Co(SO_4)_2(H_2O)_4]$, both the cation and anion are centrosymmetric. The Co^{II} ion adopts a slightly distorted CoO_6 octahedral geometry, arising from four water molecules and two monodentate SO_4^{2-} anions. In addition to electrostatic interactions, the constituent species are linked through N—H···O and O—H···O hydrogen bonds, forming a three-dimensional network.

Related literature

The isostructural manganese(II)- and iron(II)-containing compounds were described by Chaabouni *et al.* (1996) and Held (2003), respectively. For background, see: Rao *et al.* (2006, 2004); Behera & Rao (2005); Behera *et al.* (2004). Related inorganic cobalt sulfates include $Co(SO_4)\cdot H_2O$ (Oswald, 1965), $CoSO_4\cdot 6H_2O$ (Zalkin *et al.*, 1962) and $Co_5(OH)_6(SO_4)(H_2O)_4$ (Salah *et al.*, 2006). For the refinement weighting scheme, see: Prince (1982); Watkin (1994).





Experimental

Crystal data

$(C_2H_{10}N_2)[Co(SO_4)_2(H_2O)_4]$
M_r = 385.24
Triclinic, $P\overline{1}$
a = 6.8164 (2) Å
b = 7.0862 (3) Å
c = 7.2305 (3) Å
α = 74.925 (2)°
β = 72.281 (2)°
γ = 79.183 (2)°
V = 318.99 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.74 mm^{-1}
T = 293 K
0.40 × 0.30 × 0.24 mm

Data collection

Bruker Nonius APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.499, T_{max} = 0.659
8586 measured reflections
1929 independent reflections
1698 reflections with $I > 3\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.019
S = 1.06
1698 reflections
124 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—O2	2.1079 (6)	Co1—O1	2.0707 (8)
Co1—O7	2.1140 (7)		

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

D—H···A	D—H	H···A	D—H···A
O1—H1···O5^{i}	0.81 (2)	1.94 (2)	174.8 (19)
O1—H8···O4^{ii}	0.82 (2)	1.94 (2)	175.5 (19)
O7—H4···O6^{iii}	0.823 (19)	1.928 (19)	165.1 (18)
O7—H6···O6^{ii}	0.80 (2)	2.10 (2)	163.8 (18)
N9—H2···O2^{iv}	0.883 (18)	1.932 (18)	177.3 (16)
N9—H5···O5^{iii}	0.873 (18)	2.093 (18)	153.0 (16)
N9—H7···O4	0.850 (19)	2.03 (2)	160.7 (17)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x-1, y, z$; (iv) $-x+1, -y+2, -z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2558).

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supplementary materials

Acta Cryst. (2007). E**63**, m2643-m2644 [**doi:10.1107/S1600536807047174**]

Ethylenediammonium tetraaquabis(sulfato)cobaltate(II)

P. Leyva-Bailen, A. V. Powell and P. Vaqueiro

Comment

Solvothermal synthesis is increasingly used for the preparation of organically templated metal sulfates, and a number of one-, two- and three-dimensional structures have been reported in recent years (Rao *et al.*, 2006). Examples containing transition metals include the one-dimensional structure of $[Zn(SO_4)(H_2O)_2(C_{10}N_2H_8)]$ (Behera & Rao, 2005), the layered $[H_3N(CH_2)_6NH_3][Fe_{1.5}F(SO_4)]\cdot 0.5H_2O$, which possesses an unusual Fe(II) Kagomé lattice (Rao *et al.*, 2004) and the open-framework structure of $[C_4N_2H_{12}][Ni_2F_4(SO_4)H_2O]$, which contains 10-membered channels (Behera *et al.*, 2004).

The title compound, which was prepared under solvothermal conditions, is a cobalt sulfate which contains isolated $[Co(SO_4)_2(H_2O)_4]^{2-}$ anions, separated by diprotonated $[NH_3(CH_2)_2NH_3]^{2+}$ cations. The local coordination and the atom-labelling scheme are shown in Figure 1. The environment of the cobalt(II) ion consist of six oxygen atoms in a distorted octahedral coordination. Four O atoms are associated with H_2O molecules, and the other two with monodentate SO_4^{2-} anions. The Co—O distances in (I) (Table 1) are similar to those found in inorganic cobalt sulfates such as $Co(SO_4)\cdot H_2O$ (Oswald, 1965) or $CoSO_4\cdot 6H_2O$ (Zalkin *et al.*, 1962). While in the title compound the $[Co(SO_4)_2(H_2O)_4]^{2-}$ anions are isolated, similar $[Co(SO_4)_2(H_2O)_4]^{2-}$ units have been found in the three-dimensional structure of $Co_5(OH)_6(SO_4)(H_2O)_4$ (Salah *et al.*, 2006), where they act as linkages between brucite-like layers of cobalt-centered edge-sharing octahedra. In (I), the $[Co(SO_4)_2(H_2O)_4]^{2-}$ anions are interconnected through O—H···O hydrogen bonds from the hydrogen of the water molecules to the O atoms of SO_4^{2-} groups of neighbouring anions. Additional N—H···O hydrogen bonds link the anions and cations, forming an infinite three-dimensional network (Table 2, Fig. 2). This compound is isostructural with the analogous iron (Held, 2003) and manganese (Chaabouni *et al.*, 1996) materials.

Experimental

A mixture of $Co(SO_4)\cdot 7H_2O$ (1.12 g; 4 mmol), ethylenediamine (0.135 ml; 2 mmol) and H_2SO_4 (0.11 ml; 2 mmol) was loaded into a 23 ml Teflon-lined stainless autoclave. Deionized water (0.072 ml) was added to form a mixture with a molar composition $CoSO_4\cdot 7H_2O$:en:H_2SO_4:H_2O of 2:1:1:1. After stirring the mixture, the container was closed, heated at 443 K for 5 days, and then cooled to room temperature at a cooling rate of 1 K min^{-1}. The product was filtered, washed with deionized water, methanol and acetone and dried in air at room temperature to yield many pink blocks of (I).

Refinement

The H atoms were located in difference maps and their positions and U_{iso} values were freely refined.

Figures

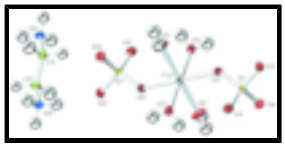

Fig. 1. The molecular structure of (I) showing displacement ellipsoids at 50% probability for non-H atoms. Primed atoms in the anion are generated by (1 − *x*, −*y*, −*z*); those in the cation by (−*x*, 2 − *y*, 1 − *z*).

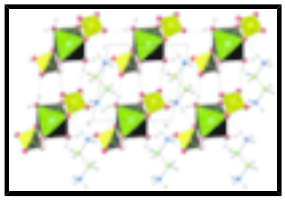

Fig. 2. View of (I) along the[100] direction, showing the SO_4 tetrahedra (yellow), $Co(H_2O)_4O_2$ octahedra (green), nitrogen (blue), carbon (light green) and hydrogen (white) atoms. (N—H···O) and (O—H···O) hydrogen bonds (red dashed lines) are shown.

Ethylenediammonium tetraaquabis(sulfato)cobaltate(II)

Crystal data

$(C_2H_{10}N_2)[Co(SO_4)_2(H_2O)_4]$	$Z = 1$
$M_r = 385.24$	$F_{000} = 199$
Triclinic, $P\overline{1}$	$D_x = 2.005$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.8164$ (2) Å	Cell parameters from 1929 reflections
$b = 7.0862$ (3) Å	$\theta = 3.0$–$30.6°$
$c = 7.2305$ (3) Å	$\mu = 1.74$ mm^{-1}
$\alpha = 74.925$ (2)°	$T = 293$ K
$\beta = 72.281$ (2)°	Block, pink
$\gamma = 79.183$ (2)°	0.40 × 0.30 × 0.24 mm
$V = 318.99$ (2) Å^3	

Data collection

Bruker Nonius APEXII CCD area-detector diffractometer	1698 reflections with $I > 3\sigma(I)$
Monochromator: graphite	$R_{int} = 0.016$
$T = 293$ K	$\theta_{max} = 30.6°$
ω/2θ scans	$\theta_{min} = 3.0°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.499$, $T_{max} = 0.659$	$k = -10 \rightarrow 10$
8586 measured reflections	$l = -10 \rightarrow 10$
1929 independent reflections	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	All H-atom parameters refined

$R[F^2 > 2\sigma(F^2)] = 0.017$	Method, part 1, Chebychev polynomial, (Watkin, 1994; *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 0.499 0.168 0.293
$wR(F^2) = 0.019$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
1698 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}
124 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.0000	0.0145
O2	0.66383 (12)	0.68463 (11)	0.06949 (10)	0.0232
S3	0.69800 (3)	0.72331 (3)	0.24984 (3)	0.0142
O4	0.49557 (11)	0.76164 (12)	0.39107 (11)	0.0265
O5	0.80946 (12)	0.89975 (10)	0.18192 (11)	0.0225
O6	0.82269 (12)	0.55493 (11)	0.34286 (12)	0.0263
O7	0.24143 (12)	0.56705 (12)	0.23321 (12)	0.0248
C8	0.04829 (16)	1.08330 (14)	0.41936 (14)	0.0213
N9	0.17194 (14)	1.00681 (13)	0.24180 (12)	0.0221
O1	0.58219 (16)	0.25962 (12)	0.20735 (12)	0.0324
H81	0.142 (2)	1.137 (2)	0.466 (2)	0.028 (4)*
H82	−0.058 (3)	1.192 (3)	0.375 (3)	0.045 (5)*
H1	0.650 (3)	0.156 (3)	0.192 (3)	0.042 (5)*
H2	0.227 (3)	1.103 (3)	0.146 (3)	0.033 (4)*
H4	0.119 (3)	0.561 (3)	0.246 (3)	0.039 (4)*
H5	0.095 (3)	0.953 (3)	0.198 (3)	0.036 (4)*
H6	0.248 (3)	0.537 (3)	0.346 (3)	0.039 (4)*
H7	0.268 (3)	0.918 (3)	0.267 (3)	0.040 (4)*
H8	0.555 (3)	0.259 (3)	0.326 (3)	0.042 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01667 (8)	0.01479 (8)	0.01339 (8)	−0.00381 (5)	−0.00494 (6)	−0.00292 (5)
O2	0.0306 (4)	0.0290 (4)	0.0151 (3)	−0.0159 (3)	−0.0065 (3)	−0.0045 (2)
S3	0.01444 (9)	0.01676 (10)	0.01245 (9)	−0.00355 (7)	−0.00478 (7)	−0.00235 (7)
O4	0.0191 (3)	0.0383 (4)	0.0181 (3)	0.0006 (3)	−0.0010 (2)	−0.0066 (3)
O5	0.0269 (3)	0.0199 (3)	0.0248 (3)	−0.0093 (3)	−0.0100 (3)	−0.0037 (2)
O6	0.0227 (3)	0.0244 (3)	0.0279 (4)	−0.0002 (3)	−0.0101 (3)	0.0034 (3)
O7	0.0178 (3)	0.0379 (4)	0.0199 (3)	−0.0042 (3)	−0.0038 (2)	−0.0090 (3)
C8	0.0268 (4)	0.0201 (4)	0.0162 (4)	−0.0074 (3)	−0.0025 (3)	−0.0030 (3)

N9	0.0233 (4)	0.0257 (4)	0.0153 (3)	−0.0052 (3)	−0.0029 (3)	−0.0022 (3)
O1	0.0543 (5)	0.0227 (4)	0.0200 (4)	0.0087 (3)	−0.0171 (3)	−0.0054 (3)

Geometric parameters (Å, °)

Co1—O7^{i}	2.1140 (7)	O7—H6	0.80 (2)
Co1—O2^{i}	2.1079 (6)	C8—C8^{ii}	1.5150 (18)
Co1—O1^{i}	2.0707 (8)	C8—N9	1.4779 (13)
Co1—O2	2.1079 (6)	C8—H81	0.972 (15)
Co1—O7	2.1140 (7)	C8—H82	1.012 (19)
Co1—O1	2.0707 (8)	N9—H2	0.883 (18)
O2—S3	1.4915 (7)	N9—H5	0.873 (18)
S3—O4	1.4719 (7)	N9—H7	0.850 (19)
S3—O5	1.4804 (7)	O1—H1	0.81 (2)
S3—O6	1.4656 (7)	O1—H8	0.82 (2)
O7—H4	0.823 (19)		
O7^{i}—Co1—O2^{i}	88.63 (3)	O4—S3—O6	110.21 (5)
O7^{i}—Co1—O1^{i}	86.51 (3)	O5—S3—O6	110.15 (4)
O2^{i}—Co1—O1^{i}	92.44 (3)	Co1—O7—H4	127.5 (13)
O7^{i}—Co1—O2	91.37 (3)	Co1—O7—H6	120.9 (13)
O2^{i}—Co1—O2	180.0	H4—O7—H6	102.4 (18)
O1^{i}—Co1—O2	87.56 (3)	C8^{ii}—C8—N9	109.46 (10)
O7^{i}—Co1—O7	180.0	C8^{ii}—C8—H81	109.5 (9)
O2^{i}—Co1—O7	91.37 (3)	N9—C8—H81	107.8 (9)
O1^{i}—Co1—O7	93.49 (4)	C8^{ii}—C8—H82	113.1 (11)
O2—Co1—O7	88.63 (3)	N9—C8—H82	106.8 (11)
O7^{i}—Co1—O1	93.49 (3)	H81—C8—H82	110.0 (14)
O2^{i}—Co1—O1	87.56 (3)	C8—N9—H2	110.3 (11)
O1^{i}—Co1—O1	180.0	C8—N9—H5	111.0 (12)
O2—Co1—O1	92.44 (3)	H2—N9—H5	108.5 (16)
O7—Co1—O1	86.51 (3)	C8—N9—H7	111.9 (12)
Co1—O2—S3	138.29 (4)	H2—N9—H7	109.1 (16)
O2—S3—O4	109.01 (4)	H5—N9—H7	106.0 (16)
O2—S3—O5	106.54 (4)	Co1—O1—H1	130.2 (13)
O4—S3—O5	110.29 (5)	Co1—O1—H8	123.1 (13)
O2—S3—O6	110.56 (5)	H1—O1—H8	106.6 (18)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
O1—H1···O5^{iii}	0.81 (2)	1.94 (2)	174.8 (19)
O1—H8···O4^{iv}	0.82 (2)	1.94 (2)	175.5 (19)
O7—H4···O6^{v}	0.823 (19)	1.928 (19)	165.1 (18)
O7—H6···O6^{iv}	0.80 (2)	2.10 (2)	163.8 (18)

N9—H2···O2^{vi}	0.883 (18)	1.932 (18)	177.3 (16)
N9—H5···O5^{v}	0.873 (18)	2.093 (18)	153.0 (16)
N9—H7···O4	0.850 (19)	2.03 (2)	160.7 (17)

Symmetry codes: (iii) *x*, *y*−1, *z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*−1, *y*, *z*; (vi) −*x*+1, −*y*+2, −*z*.

Fig. 1

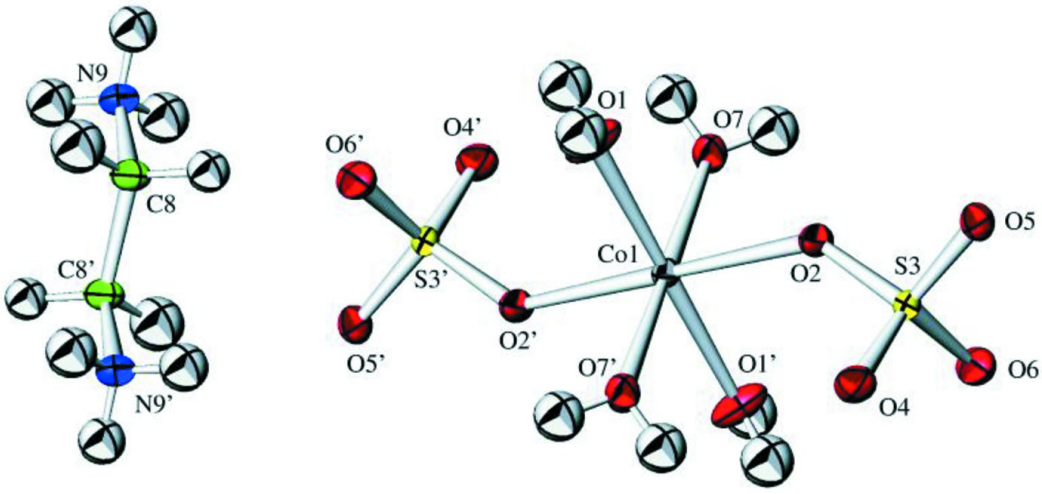

Fig. 2