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Piperazinium hexaaquacobalt(II) disulfate

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Key indicators

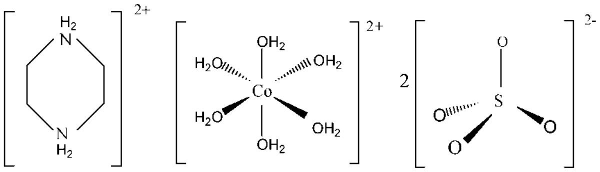
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 11.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the title compound, $(C_4H_{12}N_2)[Co(H_2O)_6](SO_4)_2$, is built of $[Co(H_2O)_6]^{2+}$ cations, diprotonated piperazinium cations (each of the two crystallographically independent piperazinium cations occupies a special position on an inversion centre) and sulfate anions. The Co atom is coordinated by six water molecules in a slightly distorted octahedral geometry. The cations are linked to anions by N—H···O and O—H···O hydrogen bonds, forming an extensive three-dimensional hydrogen-bond network in the crystal structure.

Comment

Intermolecular interactions, such as hydrogen bonds or aromatic π–π stacking, play a dominant role in molecular recognition in nature, and in the design of molecular aggregates (Juan *et al.*, 2002). One of the important aspects of cobalt sulfate hydrate structures is the existence of extensive hydrogen-bonding interactions. Hitherto, a series of such compounds has been reported in the literature, *e.g.* $CoSO_4·7D_2O$ (Olovsson *et al.*, 1991), $CoSO_4·4D_2O$ (Kellersohn, 1992) and $CoSO_4·6D_2O$ (Kellersohn *et al.*, 1993). In the course of our studies of transition metal borophosphates, we tried to prepare a novel cobalt borophosphate containing piperazine as a template. Unfortunately, the borophosphate salt was not isolated; instead, single crystals of the title double salt, (I), were obtained.



(I)

The crystal structure of (I) consists of discrete $[Co(H_2O)_6]^{2+}$ cations, diprotonated piperazinium cations and sulfate anions. All crystallographically independent chemical residues in the crystal of the title compound are shown in Fig. 1. Within the $[Co(H_2O)_6]^{2+}$ cation, the Co atom is coordinated by six water molecules at the vertices of a slightly distorted octahedron. The Co—O bond lengths range from 2.052 (4) to 2.124 (3) Å and the O—Co—O bond angles span the ranges 84.7–93.8 and 177.3–178.8°.

The anions and cations in the crystal are linked *via* N—H···O and O—H···O hydrogen bonds into an extensive three-dimensional infinite framework. Each cation acts as a donor of hydrogen bonds and each anion acts as an acceptor. A packing diagram of the title compound, showing the hydrogen-bonding framework, is presented in Fig. 2. Inter-

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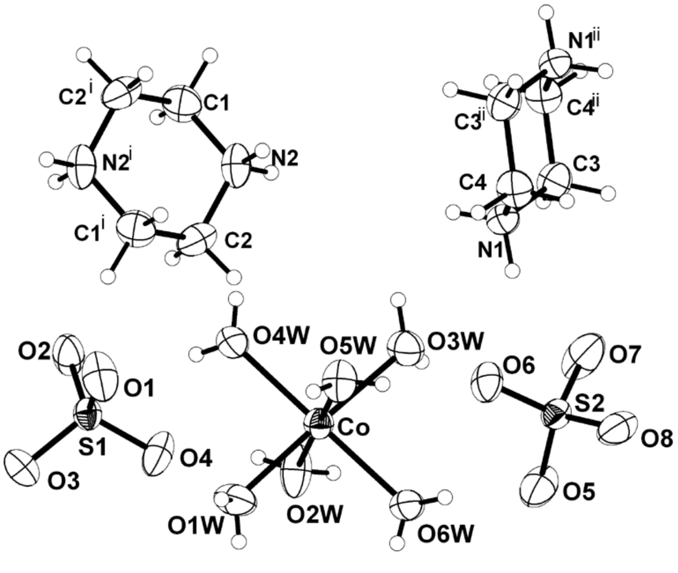

Figure 1
The cations and anions in the structure of the title compound, with the atom-numbering scheme and displacement ellipsoids shown at the 50% probability level [symmetry codes: (i) $1 - x$, $2 - y$, $-z$; (ii) $1 - x$, $2 - y$, $1 - z$].

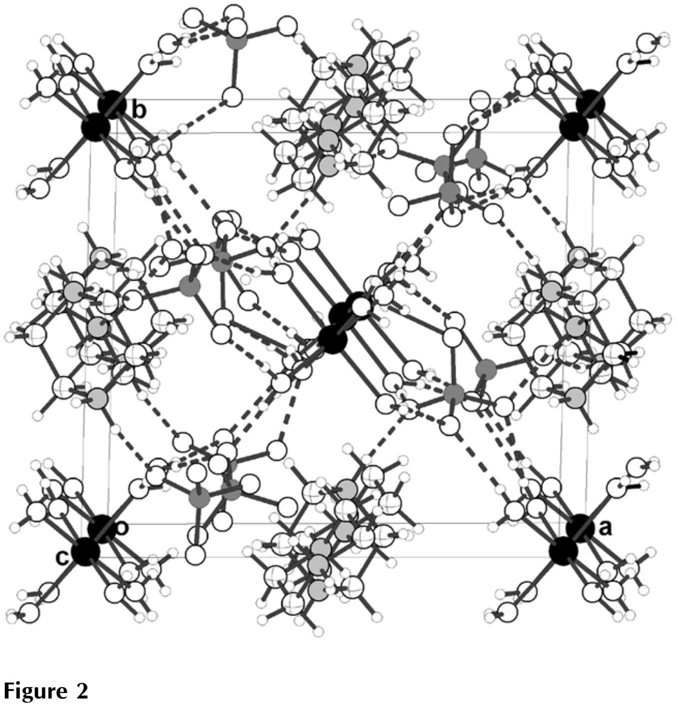

Figure 2
A packing diagram, viewed down the *c* axis of the unit cell, showing N—H···O and O—H···O hydrogen bonds.

molecular N—H···O and O—H···O hydrogen bonds lengths are in the ranges 2.720 (5)–3.239 (5) and 2.689 (5)–3.049 (6) Å, respectively.

Experimental

The title compound was prepared by hydrothermal synthesis from a mixture of $CoSO_4 \cdot 7H_2O$ (0.562 g, 2 mmol), H_3BO_3 (0.124 g, 2 mmol), piperazine (0.172 g, 2 mmol), 85% H_3PO_4 (0.27 ml, 4 mmol) and 37% HCl (1 ml) in H_2O (5 ml). The mixture was sealed in a Teflon autoclave, heated at 438 K for 5 d, and cooled. After filtration, the red filtrate was allowed to stand in air for 2 d, whereupon red crystals were obtained.

Crystal data

$(C_4H_{12}N_2)[Co(H_2O)_6](SO_4)_2$
$M_r = 447.30$
Monoclinic, $P2_1/n$
$a = 12.8796$ (6) Å
$b = 10.6984$ (6) Å
$c = 13.3098$ (7) Å
$\beta = 114.118$ (2)°
$V = 1673.88$ (15) Å^3
$Z = 4$

$D_x = 1.775$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 68 reflections
$\theta = 1.8$–25.1°
$\mu = 1.34$ mm^{-1}
$T = 293$ (2) K
Polyhedron, red
0.34 × 0.26 × 0.24 mm

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.639$, $T_{max} = 0.724$
5044 measured reflections

2914 independent reflections
2163 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.1°$
$h = -6 \rightarrow 15$
$k = -8 \rightarrow 12$
$l = -15 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.112$
$S = 1.07$
2914 reflections
256 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 3.1275P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—O1*W*	2.057 (4)	S2—O5	1.449 (3)
Co—O2*W*	2.087 (4)	S2—O6	1.472 (3)
Co—O3*W*	2.124 (3)	S2—O7	1.458 (3)
Co—O4*W*	2.052 (4)	S2—O8	1.463 (3)
Co—O5*W*	2.105 (4)	N1—C3	1.486 (5)
Co—O6*W*	2.085 (3)	N1—C4	1.481 (6)
S1—O1	1.451 (3)	N2—C1	1.477 (6)
S1—O2	1.473 (3)	N2—C2	1.472 (6)
S1—O3	1.467 (3)	C1—C2^i	1.494 (6)
S1—O4	1.463 (3)	C3—C4^{ii}	1.509 (6)

O1*W*—Co—O2*W*	84.7 (2)	O1—S1—O4	110.3 (2)
O1*W*—Co—O3*W*	177.5 (2)	O3—S1—O2	107.4 (2)
O1*W*—Co—O5*W*	92.9 (2)	O4—S1—O2	108.0 (2)
O1*W*—Co—O6*W*	93.4 (2)	O4—S1—O3	111.1 (2)
O2*W*—Co—O3*W*	93.2 (2)	O5—S2—O6	111.4 (2)
O2*W*—Co—O5*W*	177.3 (2)	O5—S2—O7	110.4 (3)
O4*W*—Co—O1*W*	87.6 (2)	O5—S2—O8	108.5 (2)
O4*W*—Co—O2*W*	93.2 (2)	O7—S2—O6	107.4 (2)
O4*W*—Co—O3*W*	93.8 (2)	O7—S2—O8	109.0 (2)
O4*W*—Co—O5*W*	87.9 (2)	O8—S2—O6	110.1 (2)
O4*W*—Co—O6*W*	178.8 (2)	C4—N1—C3	111.8 (3)
O5*W*—Co—O3*W*	89.3 (2)	C2—N2—C1	112.3 (4)
O6*W*—Co—O2*W*	86.1 (2)	N2—C1—C2^i	110.1 (4)
O6*W*—Co—O3*W*	85.2 (2)	N2—C2—C1^i	110.5 (4)
O6*W*—Co—O5*W*	92.8 (2)	N1—C3—C4^{ii}	111.0 (4)
O1—S1—O2	109.3 (2)	N1—C4—C3^{ii}	110.4 (3)
O1—S1—O3	110.6 (2)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2$^{\mathrm{iii}}$	0.90	1.89	2.768 (5)	163
N1—H1*B*···O6	0.90	2.53	3.239 (5)	136
N1—H1*B*···O7	0.90	1.92	2.741 (5)	151
N2—H2*A*···O2$^{\mathrm{iii}}$	0.90	1.84	2.733 (4)	171
N2—H2*B*···O8$^{\mathrm{iv}}$	0.90	1.83	2.720 (5)	170
O1*W*—H11···O1$^{\mathrm{v}}$	0.83 (6)	1.87 (7)	2.698 (5)	169 (6)
O1*W*—H12···O8$^{\mathrm{vi}}$	0.73 (5)	2.01 (5)	2.716 (5)	166 (6)
O2*W*—H21···O4	0.81 (6)	1.95 (7)	2.742 (5)	164 (6)
O2*W*—H22···O7$^{\mathrm{vii}}$	0.83 (5)	1.87 (6)	2.689 (5)	168 (5)
O3*W*—H31···O3$^{\mathrm{iii}}$	0.88 (8)	1.94 (9)	2.808 (5)	171 (7)
O3*W*—H32···O5$^{\mathrm{vii}}$	0.70 (6)	2.41 (6)	3.049 (6)	152 (6)
O4*W*—H41···O4$^{\mathrm{iii}}$	0.76 (6)	1.95 (6)	2.715 (5)	176 (6)
O4*W*—H42···O1	0.77 (6)	1.95 (6)	2.710 (5)	174 (6)
O5*W*—H51···O3$^{\mathrm{v}}$	0.79 (6)	2.11 (6)	2.888 (5)	173 (7)
O5*W*—H52···O6	0.77 (6)	1.96 (6)	2.726 (5)	172 (6)
O6*W*—H61···O6$^{\mathrm{vi}}$	0.69 (6)	2.08 (6)	2.760 (5)	170 (6)
O6*W*—H62···O5	0.81 (6)	1.91 (6)	2.719 (5)	174 (5)

Symmetry codes: (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $1-x, 1-y, -z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $1-x, 1-y, 1-z$.

The aqua H atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. H atoms bonded to C and N atoms were positioned geometrically (the C—H and N—H bonds were fixed at 0.97 and 0.90 Å, respectively) and allowed to ride on their parent atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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