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Crystal structure of bis(dimethylammonium) hexaaquacobalt(II) bis(sulfate) dihydrate

Peter Held

Institut für Kristallographie, Universität zu Köln, Greinstr. 6, D-50939 Köln, Germany. *Correspondence e-mail: peter.held@uni-koeln.de

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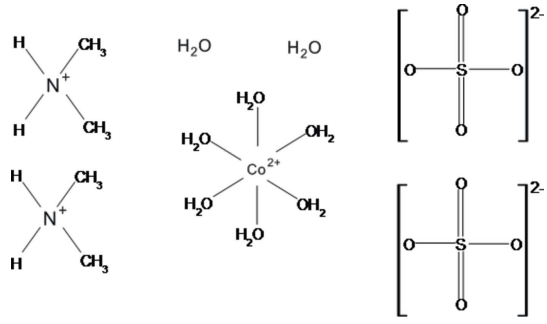
The title salt, $(C_2H_8N)_2[Co(H_2O)_6](SO_4)_2\cdot2H_2O$, is isotypic with $(C_2H_8N)_2[Ni(H_2O)_6](SO_4)_2\cdot2H_2O$. The Co—O bond lengths in the $[Co(H_2O)_6]^{2+}$ complex cation show very similar distances as in the related Tutton salt $(NH_4)_2[Co(H_2O)_6](SO_4)_2$ [average 2.093 (17) Å], but are significantly longer than in the isotypic Ni^{II} compound ($\Delta d \simeq 0.04$ Å). The cobalt cation reaches an overall bond-valence sum of 1.97 valence units. The S—O distances are nearly equal, ranging from 1.454 (4) to 1.470 (3) Å [mean 1.465 (12) Å]; however, the O—S—O angles vary clearly from 108.1 (2) to 110.2 (2)° [average bond angle 109.5 (9)°]. The non-coordinating water molecules and dimethylammonium cations connect the sulfate tetrahedra and the $[Co(H_2O)_6]^{2+}$ octahedron *via* O—H···O and N—H···O hydrogen bonds of weak up to medium strength into a three-dimensional framework whereby the complex metal cations and sulfate anions are arranged in sheets parallel to (001).

Keywords: crystal structure; dimethylammonium salt; hexaaquacobalt(II) salt; sulfate; hydrogen bonding.

CCDC reference: 1050102

1. Related literature

For the synthesis and coordination geometry of the isotypic structure $(C_2H_8N)_2[Ni(H_2O)_6](SO_4)_2\cdot2H_2O$, see: Held (2014). For the related Tutton salt $(NH_4)_2[Co(H_2O)_6](SO_4)_2$, see: Grimes *et al.* (1963). For the bond-valence-sum method, see: Brown & Altermatt (1985).



2. Experimental

2.1. Crystal data

$(C_2H_8N)_2[Co(H_2O)_6](SO_4)_2\cdot2H_2O$
M_r = 487.37
Orthorhombic, *Pbca*
a = 8.975 (5) Å
b = 13.268 (5) Å
c = 16.528 (5) Å
V = 1968.2 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.16 mm^{-1}
T = 295 K
0.30 × 0.27 × 0.24 mm

2.2. Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.903, T_{max} = 1.000
3383 measured reflections
1733 independent reflections
936 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
3 standard reflections every 100 reflections
intensity decay: 1.5%

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.111
S = 0.98
1733 reflections
148 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O2^{i}	0.82 (6)	1.91 (6)	2.724 (6)	169 (5)
O5—H52···O8	0.84 (7)	1.97 (8)	2.806 (7)	171 (7)
O6—H61···O3^{ii}	0.85 (7)	1.85 (7)	2.687 (6)	173 (6)
O6—H62···O1	0.69 (5)	2.08 (5)	2.740 (6)	161 (6)
O7—H71···O4^{iii}	0.74 (6)	2.01 (6)	2.740 (6)	173 (6)
O7—H72···O1^{iv}	0.72 (4)	2.04 (4)	2.756 (6)	176 (5)
O8—H81···O3^{iii}	0.71 (6)	2.32 (6)	2.975 (7)	154 (7)
O8—H82···O2^{v}	0.83 (6)	2.02 (6)	2.849 (6)	169 (7)
N3—H3*A*···O6^{iv}	0.90	2.63	3.265 (6)	128
N3—H3*B*···O4^{vi}	0.90	2.00	2.823 (6)	152

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2011); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

Supporting information for this paper is available from the IUCr electronic archives (Reference: FK2085).

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supporting information

Acta Cryst. (2015). E**71**, m77–m78 [doi:10.1107/S2056989015003400]

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S1. Refinement

All H atoms were clearly discernible from difference Fourier maps. However, to all hydrogen atoms riding model contraints were applied in the least squares refinement, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and with N—H = 0.90 Å and U_{iso}(H) = 1.2U_{eq}(N) for ammonium H atoms. The H atoms of water molecules were refined with a distance restraint of O—H = 0.84 Å and individual U_{iso} values for each H atom.

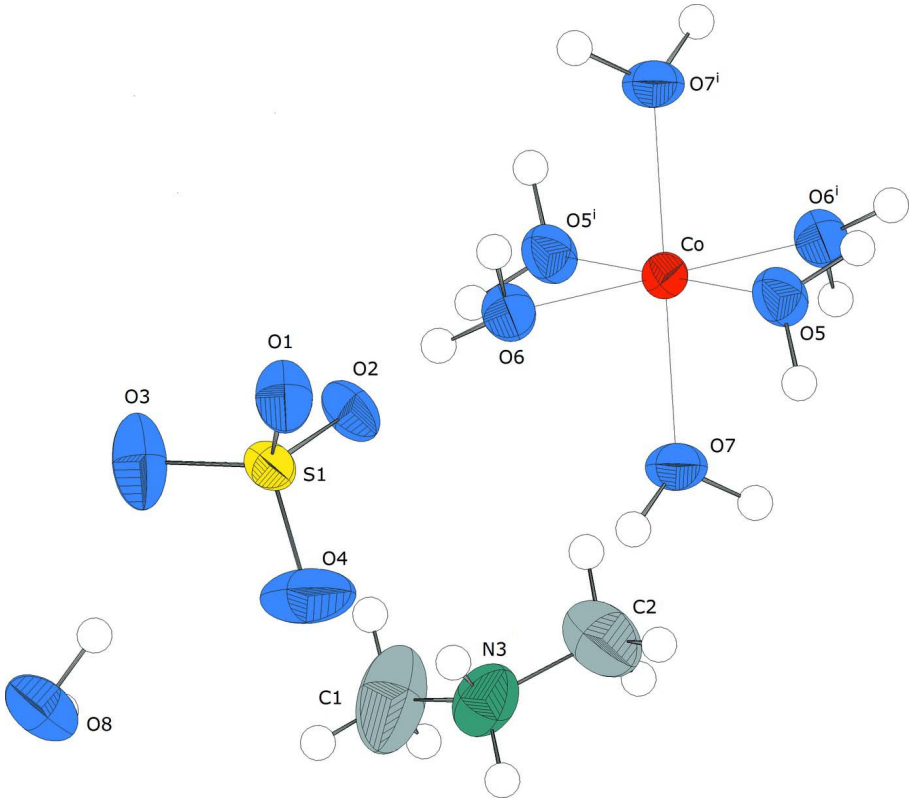

Figure 1

The molecular entities in the structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) -*x*, -*y* + 1, -*z* - 1.]

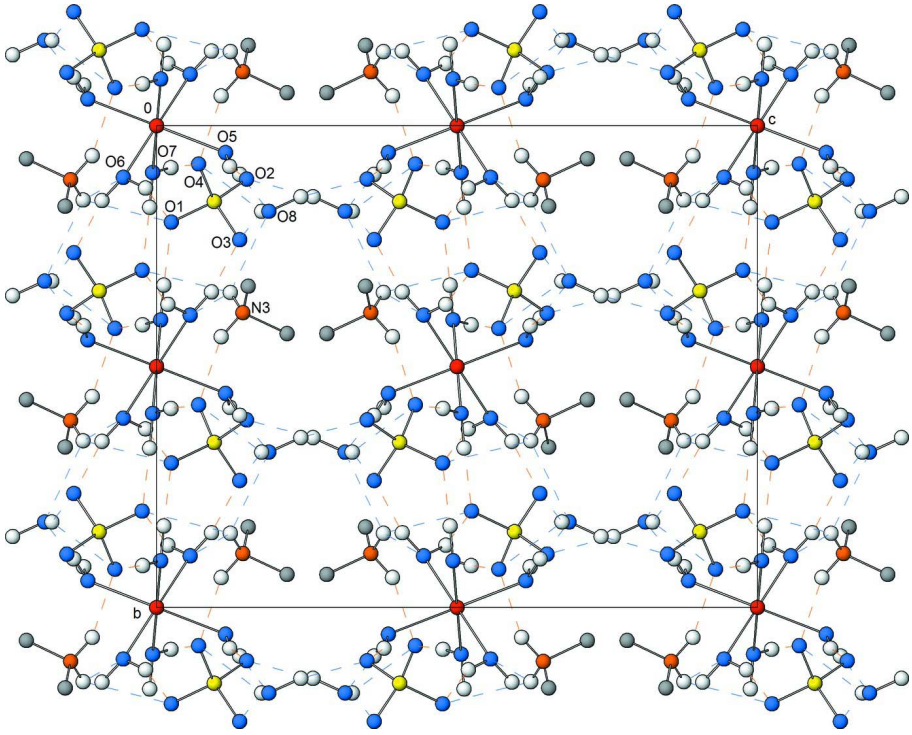

Figure 2

(100)-projection of the crystal structure of the title compound. Colour scheme: S (yellow), Co (red), O (blue), N (orange), C (grey), H (colourless), H···O bonds up to 1.8 Å are given as red dashed lines, and from 1.85 to 2.7 Å as light-blue dashed lines.

Bis(dimethylammonium) hexaaquacobalt(II) bis(sulfate) dihydrate

Crystal data

$(C_2H_8N)_2[Co(H_2O)_6](SO_4)_2·2H_2O$
M_r = 487.37
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 8.975 (5) Å
b = 13.268 (5) Å
c = 16.528 (5) Å
V = 1968.2 (15) Å^3
Z = 4
$F(000)$ = 1028
D_x = 1.645 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.0–20.8°
μ = 1.16 mm^{-1}
T = 295 K
Parallelepiped, light blue
0.30 × 0.27 × 0.24 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.903, T_{max} = 1.000
3383 measured reflections
1733 independent reflections
936 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
θ_{max} = 25.0°, θ_{min} = 2.5°
h = 0→10
k = 0→15
l = −19→19
3 standard reflections every 100 reflections
intensity decay: 1.5%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.111$
$S = 0.98$
1733 reflections
148 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0022 (6)

Special details

Experimental. A suitable single-crystal was carefully selected under a polarizing microscope and mounted in a glass capillary.

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}
Co	0.0000	0.5000	0.5000	0.0278 (3)
S1	0.44510 (13)	0.65726 (9)	0.59555 (8)	0.0319 (3)
O1	0.3702 (4)	0.6999 (2)	0.5243 (2)	0.0466 (10)
O2	0.3355 (4)	0.6107 (3)	0.6497 (2)	0.0419 (9)
O3	0.5255 (5)	0.7366 (3)	0.6378 (2)	0.0634 (12)
O4	0.5493 (5)	0.5793 (3)	0.5696 (3)	0.0791 (15)
O5	−0.0505 (5)	0.4446 (3)	0.3854 (2)	0.0422 (10)
H51	−0.136 (7)	0.422 (4)	0.380 (3)	0.040 (18)*
H52	0.010 (8)	0.403 (5)	0.365 (5)	0.11 (3)*
O6	0.1413 (5)	0.6068 (3)	0.4439 (3)	0.0391 (10)
H61	0.103 (8)	0.653 (5)	0.415 (4)	0.09 (3)*
H62	0.198 (6)	0.620 (4)	0.470 (3)	0.03 (2)*
O7	0.1808 (5)	0.4036 (3)	0.5066 (3)	0.0444 (10)
H71	0.251 (7)	0.412 (4)	0.484 (3)	0.037 (19)*
H72	0.172 (5)	0.350 (3)	0.512 (3)	0.021 (16)*
O8	0.1675 (5)	0.3224 (4)	0.3135 (3)	0.0558 (13)
H81	0.245 (7)	0.326 (5)	0.322 (4)	0.06 (2)*
H82	0.174 (8)	0.348 (5)	0.268 (4)	0.09 (3)*
N3	0.0327 (6)	0.1120 (3)	0.3563 (3)	0.0567 (14)
H3A	0.1016	0.1541	0.3769	0.068*
H3B	0.0187	0.0622	0.3925	0.068*

C1	0.0909 (10)	0.0689 (5)	0.2833 (4)	0.094 (3)
H1A	0.1825	0.0344	0.2950	0.141*
H1B	0.1092	0.1214	0.2446	0.141*
H1C	0.0201	0.0219	0.2615	0.141*
C2	−0.1060 (7)	0.1669 (5)	0.3473 (4)	0.074 (2)
H2A	−0.1450	0.1833	0.3998	0.111*
H2B	−0.1767	0.1260	0.3187	0.111*
H2C	−0.0883	0.2279	0.3175	0.111*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0269 (5)	0.0257 (4)	0.0309 (4)	0.0003 (5)	−0.0026 (5)	−0.0010 (5)
S1	0.0249 (6)	0.0340 (6)	0.0368 (7)	−0.0010 (6)	−0.0005 (6)	0.0065 (6)
O1	0.055 (2)	0.042 (2)	0.044 (2)	−0.0080 (19)	−0.0180 (18)	0.0107 (17)
O2	0.0289 (19)	0.052 (2)	0.045 (2)	−0.0104 (17)	0.0059 (17)	0.0093 (18)
O3	0.084 (3)	0.060 (2)	0.047 (2)	−0.034 (3)	−0.023 (2)	0.0151 (19)
O4	0.063 (3)	0.067 (3)	0.108 (4)	0.026 (2)	0.042 (3)	0.032 (3)
O5	0.034 (2)	0.053 (2)	0.040 (2)	−0.004 (2)	−0.002 (2)	−0.0102 (19)
O6	0.035 (2)	0.039 (2)	0.043 (2)	−0.004 (2)	−0.007 (2)	0.007 (2)
O7	0.035 (2)	0.036 (3)	0.062 (3)	0.007 (2)	0.012 (2)	0.010 (2)
O8	0.035 (3)	0.093 (4)	0.039 (3)	−0.004 (3)	−0.001 (2)	−0.009 (3)
N3	0.069 (4)	0.047 (3)	0.054 (3)	0.005 (3)	−0.018 (3)	−0.004 (2)
C1	0.135 (8)	0.056 (4)	0.090 (6)	0.016 (5)	0.054 (5)	0.009 (4)
C2	0.057 (4)	0.084 (5)	0.080 (5)	0.005 (4)	0.007 (4)	0.016 (4)

Geometric parameters (Å, º)

Co—O7^{i}	2.069 (4)	O7—H71	0.74 (6)
Co—O7	2.069 (4)	O7—H72	0.72 (4)
Co—O5^{i}	2.081 (4)	O8—H81	0.71 (6)
Co—O5	2.081 (4)	O8—H82	0.83 (6)
Co—O6	2.116 (4)	N3—C1	1.434 (7)
Co—O6^{i}	2.116 (4)	N3—C2	1.450 (7)
S1—O3	1.454 (4)	N3—H3A	0.9000
S1—O4	1.459 (4)	N3—H3B	0.9000
S1—O2	1.467 (3)	C1—H1A	0.9600
S1—O1	1.470 (3)	C1—H1B	0.9600
O5—H51	0.82 (6)	C1—H1C	0.9600
O5—H52	0.84 (7)	C2—H2A	0.9600
O6—H61	0.85 (7)	C2—H2B	0.9600
O6—H62	0.69 (5)	C2—H2C	0.9600
O7^{i}—Co—O7	180.0 (3)	Co—O6—H62	109 (4)
O7^{i}—Co—O5^{i}	90.04 (18)	H61—O6—H62	119 (6)
O7—Co—O5^{i}	89.96 (18)	Co—O7—H71	123 (4)
O7^{i}—Co—O5	89.96 (18)	Co—O7—H72	122 (4)
O7—Co—O5	90.04 (18)	H71—O7—H72	109 (6)

O5^{i}—Co—O5	180.000 (1)	H81—O8—H82	95 (7)
O7^{i}—Co—O6	91.87 (19)	C1—N3—C2	115.3 (5)
O7—Co—O6	88.13 (19)	C1—N3—H3A	108.5
O5^{i}—Co—O6	91.80 (18)	C2—N3—H3A	108.5
O5—Co—O6	88.20 (18)	C1—N3—H3B	108.5
O7^{i}—Co—O6^{i}	88.13 (19)	C2—N3—H3B	108.5
O7—Co—O6^{i}	91.87 (19)	H3A—N3—H3B	107.5
O5^{i}—Co—O6^{i}	88.20 (18)	N3—C1—H1A	109.5
O5—Co—O6^{i}	91.80 (18)	N3—C1—H1B	109.5
O6—Co—O6^{i}	180.0	H1A—C1—H1B	109.5
O3—S1—O4	109.6 (3)	N3—C1—H1C	109.5
O3—S1—O2	110.1 (2)	H1A—C1—H1C	109.5
O4—S1—O2	108.1 (2)	H1B—C1—H1C	109.5
O3—S1—O1	109.5 (2)	N3—C2—H2A	109.5
O4—S1—O1	109.3 (3)	N3—C2—H2B	109.5
O2—S1—O1	110.2 (2)	H2A—C2—H2B	109.5
Co—O5—H51	116 (4)	N3—C2—H2C	109.5
Co—O5—H52	117 (5)	H2A—C2—H2C	109.5
H51—O5—H52	108 (6)	H2B—C2—H2C	109.5
Co—O6—H61	119 (5)		

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H51···O2^{i}	0.82 (6)	1.91 (6)	2.724 (6)	169 (5)
O5—H52···O8	0.84 (7)	1.97 (8)	2.806 (7)	171 (7)
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N3—H3*B*···O4^{vi}	0.90	2.00	2.823 (6)	152

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*−1/2, −*y*+3/2, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+1/2, *y*−1/2, *z*; (v) −*x*+1/2, −*y*+1, *z*−1/2; (vi) *x*−1/2, −*y*+1/2, −*z*+1.