

Hexaaquacobalt(II) 3-ammonionaphthalene-1,5-disulfonate tetrahydrate

Dane J. Genter,^a Philip J. Squattrito,^{a*} Kristin Kirschbaum^b and A. Alan Pinkerton^b

^aDepartment of Chemistry, Central Michigan University, Mount Pleasant, MI 48859, USA, and ^bDepartment of Chemistry, University of Toledo, Toledo, OH 43606, USA
Correspondence e-mail: p.squattrito@cmich.edu

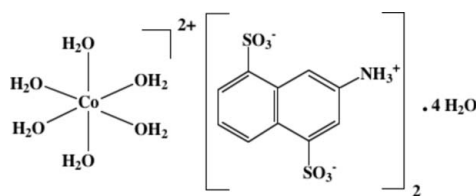
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Key indicators: single-crystal X-ray study; $T = 140$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; H-atom completeness 89%; disorder in solvent or counterion; R factor = 0.035; wR factor = 0.098; data-to-parameter ratio = 23.4.

The title compound, $[\text{Co}(\text{H}_2\text{O})_6][\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2] \cdot 4\text{H}_2\text{O}$, is part of an isostructural family that includes the nickel(II) and zinc(II) analogues. The salts contain centrosymmetric hexaaquacobalt cations and protonated ammonionaphthalene-disulfonate anions arranged in alternating layers. The anions stack so that the charged groups face the cationic layers, maximizing electrostatic interactions. The non-coordinated water molecules are located in the cation layers. An extensive network of strong near-linear $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds involving the ammonio group, water molecules and sulfonate O atoms further anchors the packing. One of the uncoordinated water molecules is disordered over at least two sites (modelled over two positions with almost equal site occupancies).

Related literature

The title compound is isostructural with its nickel(II) (Gunderman, Kabell *et al.*, 1997) and zinc(II) (Genter *et al.*, 2007) analogues. For background, see: Cote & Shimizu (2003); Cai (2004); Gunderman & Squattrito (1995); Morris *et al.* (2003); Downer *et al.* (2006); Gunderman, Dubey & Squattrito (1997); Leonard *et al.* (1999). For related literature, see: Chen *et al.* (2002).



Experimental

Crystal data

$[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_8\text{NO}_6\text{S}_2) \cdot 4\text{H}_2\text{O}$
 $M_r = 843.68$
 Triclinic, $P\bar{1}$
 $a = 5.4549$ (1) Å
 $b = 12.7528$ (3) Å
 $c = 12.9382$ (3) Å
 $\alpha = 114.646$ (1)°
 $\beta = 101.477$ (1)°
 $\gamma = 90.919$ (1)°
 $V = 796.73$ (3) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.90$ mm⁻¹
 $T = 140$ (2) K
 $0.25 \times 0.22 \times 0.10$ mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
 $T_{\min} = 0.765$, $T_{\max} = 0.910$
 11827 measured reflections
 6574 independent reflections
 6288 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.098$
 $S = 1.07$
 6574 reflections
 281 parameters
 8 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.10$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.83$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O9	2.0667 (10)	Co1—O8	2.1175 (10)
Co1—O7	2.0946 (9)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O7—H9···O1 ⁱ	0.818 (16)	1.832 (16)	2.6404 (13)	169 (2)
O7—H10···O5 ⁱⁱ	0.800 (15)	1.867 (16)	2.6501 (13)	166 (2)
O8—H11···O1 ⁱⁱⁱ	0.830 (16)	1.915 (16)	2.7435 (13)	177 (2)
O8—H12···O2	0.819 (16)	1.977 (17)	2.7589 (14)	159 (2)
O9—H13···O7 ^{iv}	0.826 (16)	1.993 (17)	2.8092 (14)	170 (2)
O9—H14···O4 ⁱⁱ	0.818 (16)	1.865 (17)	2.6713 (14)	168 (3)
N1—H6···O6 ^{iv}	0.88 (2)	1.95 (2)	2.7993 (15)	162 (2)
N1—H7···O3 ^v	0.82 (2)	2.01 (2)	2.8124 (15)	168 (2)
N1—H8···O11A	0.79 (2)	2.12 (2)	2.863 (7)	159 (2)
O10—H15···O6 ⁱⁱ	0.925 (18)	1.97 (2)	2.8816 (19)	167 (3)
O10—H16···O8	0.924 (18)	2.25 (3)	3.036 (2)	143 (3)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2483).

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supplementary materials

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Hexaaquacobalt(II) 3-ammonionaphthalene-1,5-disulfonate tetrahydrate

D. J. Genther, P. J. Squattrito, K. Kirschbaum and A. A. Pinkerton

Comment

Metal sulfonate salts have been actively studied in recent years as part of the growing field of mixed inorganic-organic structures of interest in crystal engineering. Key results have been summarized in two recent reviews (Cote & Shimizu, 2003; Cai, 2004).

We have characterized a variety of naphthalenesulfonate salts of main group and transition metals (Gunderman & Squattrito, 1995; Gunderman, Kabell *et al.*, 1997; Morris *et al.*, 2003; Downer *et al.*, 2006) with the goal of discerning structural trends as functions of metal cation and substitution of the sulfonate group. As part of our continuing interest in this chemistry, we have synthesized a series of salts of 3-aminonaphthalene-1,5-sulfonate with divalent transition metals.

The result is a family of isostructural salts of formula $[M(\text{H}_2\text{O})_6](\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2)_2 \cdot 4\text{H}_2\text{O}$ where $M = \text{Co}, \text{Ni} \& \text{Zn}$. The title cobalt compound consists of hexaaquacobalt(II) cations, 3-ammonionaphthalene-1,5-disulfonate anions, and water molecules of crystallization (Fig. 1). Owing to the protonation of the amine group, each anion carries a single negative charge and the salt has the same 1:2 stoichiometry as would be observed with a monosulfonate anion. The cations reside on centers of inversion and display very regular octahedral geometry with maximum deviation from ideal 90° bond angles of just under 5° . This feature is very similar to what is found in other cobalt sulfonates (Gunderman, Dubey & Squattrito, 1997; Leonard *et al.*, 1999).

The crystal packing (Fig. 2) is typical for transition metal arene- and naphthalenesulfonates (Chen *et al.*, 2002; Gunderman, Dubey & Squattrito, 1997), consisting of alternating layers of hexaaquametal cations and sulfonate anions parallel to the *ac* plane, with the anions positioned so that the charged groups (*i.e.*, NH_3^+ and SO_3^-) line the surface of the layer. The anions are positioned so that all the rings are parallel with contacts between adjacent rings of *ca* 3.7 Å. Neighboring rows of anions running along the *a* axis have the ammonio groups inverted. The water molecules of crystallization are located in between the cations in close association with the charged groups and coordinated water molecules so as to participate in hydrogen bonding interactions. One of the two crystallographically independent water molecules is disordered over at least two positions.

The layers are held together by a series of strong O—H \cdots O and N—H \cdots O hydrogen bonds involving water and ammonio donors and sulfonate and water acceptors (Table 2).

Experimental

The title compound was prepared by direct reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and disodium 3-aminonaphthalene-1,5-disulfonate (1:2 stoichiometry) in aqueous solution. Following approximately one hour of heating, during which most of the reactants dissolved, the resulting solution was gravity filtered and set out in open air. Upon evaporation of the water, many small reddish, needles of (I) were recovered.

Refinement

The O11 atom, corresponding to one water of crystallization, was found to be disordered and was refined on split positions *ca* 0.5 Å apart with occupancy factors constrained to sum to 1. Final occupancies were roughly 53% (O11A) and 47% (O11B). The B site has a significantly prolate displacement ellipsoid, but further splitting of the position could not be successfully modeled. The H atoms attached to the disordered water molecule could not be located. All other H atoms were located in difference maps and positionally refined either freely or with distance restraints of O—H = 0.82 (2) Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N},\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Figures

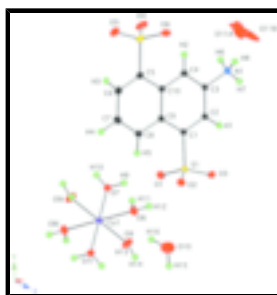


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms. Symmetry-equivalent water molecules (marked 'i') are included to show the full coordination sphere of the cobalt cation. [symmetry operation (i): $-x, -y, -z$]

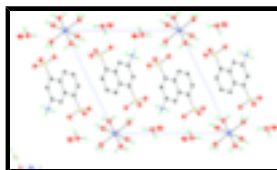


Fig. 2. The packing of (I), viewed down the *a* axis, showing layers connected by O—H...O and N—H...O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted.

hexaaquacobalt(II) 3-ammonionaphthalene-1,5-disulfonate tetrahydrate

Crystal data

$[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_8\text{NO}_6\text{S}_2)_2 \cdot 4\text{H}_2\text{O}$

$M_r = 843.68$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 5.45490(10)\ \text{\AA}$

$b = 12.7528(3)\ \text{\AA}$

$c = 12.9382(3)\ \text{\AA}$

$\alpha = 114.646(1)^\circ$

$\beta = 101.477(1)^\circ$

$\gamma = 90.919(1)^\circ$

$V = 796.73(3)\ \text{\AA}^3$

$Z = 1$

$F_{000} = 437$

$D_x = 1.758\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6586 reflections

$\theta = 3.0\text{--}34.4^\circ$

$\mu = 0.90\ \text{mm}^{-1}$

$T = 140(2)\ \text{K}$

Triangular prism, red

$0.25 \times 0.22 \times 0.10\ \text{mm}$

Data collection

Bruker SMART 6000 CCD area-detector

6574 independent reflections

diffractometer
 Radiation source: fine-focus sealed tube 6288 reflections with $I > 2\sigma(I)$
 Monochromator: graphite $R_{\text{int}} = 0.016$
 $T = 140(2)$ K $\theta_{\text{max}} = 35.6^\circ$
 ω scans $\theta_{\text{min}} = 1.8^\circ$
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004) $h = -8 \rightarrow 8$
 $T_{\text{min}} = 0.765$, $T_{\text{max}} = 0.910$ $k = -20 \rightarrow 20$
 11827 measured reflections $l = -20 \rightarrow 21$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.035$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.098$ $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.5867P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.07$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 6574 reflections $\Delta\rho_{\text{max}} = 1.10 \text{ e } \text{\AA}^{-3}$
 281 parameters $\Delta\rho_{\text{min}} = -0.82 \text{ e } \text{\AA}^{-3}$
 8 restraints Extinction correction: none
 Primary atom site location: structure-invariant direct methods

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.0000	0.0000	0.0000	0.01194 (5)	
O7	-0.26578 (18)	-0.12241 (8)	-0.00331 (8)	0.01604 (16)	
H9	-0.347 (4)	-0.1672 (18)	-0.0681 (15)	0.024*	
H10	-0.224 (4)	-0.1529 (19)	0.0394 (18)	0.024*	
O8	-0.05274 (19)	0.10605 (9)	0.16887 (9)	0.01862 (17)	
H11	-0.168 (4)	0.1482 (18)	0.178 (2)	0.028*	
H12	0.070 (4)	0.1440 (19)	0.2203 (18)	0.028*	
O9	0.30321 (19)	-0.05179 (10)	0.08400 (10)	0.02177 (19)	

supplementary materials

H13	0.435 (4)	-0.064 (2)	0.061 (2)	0.033*	
H14	0.283 (5)	-0.088 (2)	0.121 (2)	0.033*	
S1	0.53450 (5)	0.32370 (2)	0.32171 (2)	0.01216 (6)	
O1	0.57766 (18)	0.25223 (8)	0.20469 (8)	0.01694 (16)	
O2	0.30255 (18)	0.28088 (8)	0.33761 (9)	0.01758 (16)	
O3	0.75299 (19)	0.33977 (8)	0.41332 (9)	0.01965 (18)	
S2	0.02330 (6)	0.76432 (3)	0.20505 (3)	0.01597 (6)	
O4	0.2482 (2)	0.80285 (11)	0.18029 (11)	0.0254 (2)	
O5	-0.2059 (2)	0.75551 (10)	0.12117 (10)	0.0231 (2)	
O6	0.0067 (2)	0.83554 (9)	0.32609 (9)	0.02269 (19)	
N1	0.8711 (2)	0.75479 (10)	0.47987 (10)	0.01682 (18)	
H6	0.947 (4)	0.7786 (19)	0.4385 (19)	0.020*	
H7	0.971 (4)	0.7319 (19)	0.5194 (19)	0.020*	
H8	0.816 (4)	0.808 (2)	0.523 (2)	0.020*	
C1	0.4958 (2)	0.46391 (9)	0.32593 (10)	0.01224 (17)	
C2	0.6852 (2)	0.55077 (10)	0.39846 (10)	0.01341 (18)	
H1	0.825 (4)	0.5357 (18)	0.4432 (18)	0.016*	
C3	0.6687 (2)	0.66256 (10)	0.40344 (10)	0.01317 (18)	
C4	0.4698 (2)	0.68835 (10)	0.33892 (10)	0.01455 (19)	
H2	0.455 (4)	0.7608 (18)	0.3429 (18)	0.017*	
C5	0.0561 (2)	0.62243 (10)	0.19476 (10)	0.01454 (19)	
C6	-0.1328 (2)	0.53561 (11)	0.12103 (11)	0.0175 (2)	
H3	-0.262 (4)	0.5579 (19)	0.0848 (19)	0.021*	
C7	-0.1188 (2)	0.42229 (11)	0.11258 (12)	0.0181 (2)	
H4	-0.263 (4)	0.3552 (19)	0.0557 (19)	0.022*	
C8	0.0825 (2)	0.39777 (10)	0.17861 (11)	0.01547 (19)	
H5	0.086 (4)	0.3219 (19)	0.1696 (19)	0.019*	
C9	0.2820 (2)	0.48519 (10)	0.25561 (10)	0.01230 (17)	
C10	0.2705 (2)	0.60020 (10)	0.26370 (10)	0.01281 (17)	
O10	-0.2264 (4)	0.04228 (14)	0.34619 (16)	0.0478 (4)	
H15	-0.173 (7)	-0.028 (2)	0.342 (3)	0.072*	
H16	-0.244 (7)	0.043 (3)	0.274 (2)	0.072*	
O11A	0.5969 (16)	0.9484 (5)	0.5775 (6)	0.087 (3)	0.526 (16)
O11B	0.6756 (17)	0.9458 (5)	0.5908 (11)	0.109 (4)	0.474 (16)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01256 (9)	0.01138 (9)	0.01237 (10)	0.00226 (7)	0.00272 (7)	0.00557 (8)
O7	0.0172 (4)	0.0157 (4)	0.0156 (4)	-0.0004 (3)	0.0007 (3)	0.0084 (3)
O8	0.0165 (4)	0.0186 (4)	0.0162 (4)	0.0040 (3)	0.0024 (3)	0.0036 (3)
O9	0.0180 (4)	0.0309 (5)	0.0297 (5)	0.0095 (4)	0.0095 (4)	0.0236 (4)
S1	0.01264 (11)	0.00967 (11)	0.01284 (12)	0.00055 (8)	0.00019 (8)	0.00475 (9)
O1	0.0182 (4)	0.0134 (4)	0.0163 (4)	0.0037 (3)	0.0043 (3)	0.0034 (3)
O2	0.0171 (4)	0.0168 (4)	0.0192 (4)	-0.0025 (3)	0.0030 (3)	0.0087 (3)
O3	0.0184 (4)	0.0162 (4)	0.0214 (4)	-0.0005 (3)	-0.0059 (3)	0.0100 (4)
S2	0.01772 (13)	0.01645 (13)	0.01914 (13)	0.00369 (9)	0.00455 (10)	0.01259 (11)
O4	0.0209 (4)	0.0322 (5)	0.0375 (6)	0.0037 (4)	0.0091 (4)	0.0275 (5)

O5	0.0209 (4)	0.0261 (5)	0.0286 (5)	0.0057 (4)	0.0015 (4)	0.0194 (4)
O6	0.0349 (5)	0.0148 (4)	0.0217 (5)	0.0050 (4)	0.0090 (4)	0.0098 (4)
N1	0.0210 (5)	0.0127 (4)	0.0141 (4)	-0.0036 (3)	-0.0023 (3)	0.0061 (4)
C1	0.0135 (4)	0.0102 (4)	0.0121 (4)	0.0010 (3)	0.0017 (3)	0.0045 (4)
C2	0.0147 (4)	0.0112 (4)	0.0128 (4)	-0.0004 (3)	-0.0001 (3)	0.0053 (4)
C3	0.0157 (4)	0.0106 (4)	0.0113 (4)	-0.0016 (3)	0.0002 (3)	0.0041 (4)
C4	0.0178 (5)	0.0117 (4)	0.0141 (5)	0.0005 (3)	0.0014 (4)	0.0064 (4)
C5	0.0154 (4)	0.0146 (5)	0.0150 (5)	0.0030 (4)	0.0023 (4)	0.0082 (4)
C6	0.0161 (5)	0.0184 (5)	0.0180 (5)	0.0017 (4)	-0.0003 (4)	0.0097 (4)
C7	0.0158 (5)	0.0168 (5)	0.0190 (5)	-0.0006 (4)	-0.0015 (4)	0.0075 (4)
C8	0.0153 (5)	0.0124 (4)	0.0164 (5)	0.0005 (3)	-0.0001 (4)	0.0057 (4)
C9	0.0128 (4)	0.0110 (4)	0.0122 (4)	0.0013 (3)	0.0015 (3)	0.0047 (4)
C10	0.0146 (4)	0.0118 (4)	0.0120 (4)	0.0015 (3)	0.0016 (3)	0.0057 (4)
O10	0.0634 (11)	0.0327 (7)	0.0484 (9)	0.0123 (7)	0.0125 (8)	0.0185 (7)
O11A	0.098 (4)	0.043 (2)	0.062 (3)	0.033 (3)	-0.037 (3)	-0.010 (2)
O11B	0.079 (4)	0.0177 (17)	0.199 (9)	-0.010 (2)	0.106 (5)	-0.015 (3)

Geometric parameters (Å, °)

Co1—O9 ⁱ	2.0667 (10)	N1—H6	0.88 (2)
Co1—O9	2.0667 (10)	N1—H7	0.82 (2)
Co1—O7 ⁱ	2.0946 (9)	N1—H8	0.79 (2)
Co1—O7	2.0946 (9)	C1—C2	1.3735 (16)
Co1—O8 ⁱ	2.1175 (10)	C1—C9	1.4334 (16)
Co1—O8	2.1175 (10)	C2—C3	1.4052 (16)
O7—H9	0.818 (16)	C2—H1	0.94 (2)
O7—H10	0.800 (15)	C3—C4	1.3644 (16)
O8—H11	0.830 (16)	C4—C10	1.4214 (16)
O8—H12	0.819 (16)	C4—H2	0.91 (2)
O9—H13	0.826 (16)	C5—C6	1.3747 (18)
O9—H14	0.818 (16)	C5—C10	1.4317 (16)
S1—O3	1.4474 (10)	C6—C7	1.4076 (18)
S1—O2	1.4548 (10)	C6—H3	0.88 (2)
S1—O1	1.4752 (10)	C7—C8	1.3762 (17)
S1—C1	1.7833 (11)	C7—H4	1.06 (2)
S2—O5	1.4515 (11)	C8—C9	1.4224 (16)
S2—O4	1.4553 (11)	C8—H5	0.93 (2)
S2—O6	1.4691 (11)	C9—C10	1.4296 (16)
S2—C5	1.7730 (12)	O10—H15	0.925 (18)
N1—C3	1.4610 (16)	O10—H16	0.924 (18)
O9 ⁱ —Co1—O9	180.0	C3—N1—H7	110.2 (15)
O9 ⁱ —Co1—O7 ⁱ	94.83 (4)	H6—N1—H7	111 (2)
O9—Co1—O7 ⁱ	85.17 (4)	C3—N1—H8	110.2 (16)
O9 ⁱ —Co1—O7	85.17 (4)	H6—N1—H8	108 (2)
O9—Co1—O7	94.83 (4)	H7—N1—H8	108 (2)
O7 ⁱ —Co1—O7	180.0	C2—C1—C9	121.31 (10)
O9 ⁱ —Co1—O8 ⁱ	86.09 (4)	C2—C1—S1	116.45 (8)

supplementary materials

O9—Co1—O8 ⁱ	93.91 (4)	C9—C1—S1	122.22 (8)
O7 ⁱ —Co1—O8 ⁱ	85.98 (4)	C1—C2—C3	119.16 (10)
O7—Co1—O8 ⁱ	94.02 (4)	C1—C2—H1	120.6 (13)
O9 ⁱ —Co1—O8	93.91 (4)	C3—C2—H1	120.2 (13)
O9—Co1—O8	86.09 (4)	C4—C3—C2	122.30 (10)
O7 ⁱ —Co1—O8	94.02 (4)	C4—C3—N1	118.50 (10)
O7—Co1—O8	85.98 (4)	C2—C3—N1	119.20 (10)
O8 ⁱ —Co1—O8	180.0	C3—C4—C10	119.66 (10)
Co1—O7—H9	115.7 (16)	C3—C4—H2	123.1 (13)
Co1—O7—H10	117.1 (16)	C10—C4—H2	117.2 (13)
H9—O7—H10	113 (2)	C6—C5—C10	121.30 (11)
Co1—O8—H11	121.2 (17)	C6—C5—S2	118.00 (9)
Co1—O8—H12	118.7 (17)	C10—C5—S2	120.67 (9)
H11—O8—H12	106 (2)	C5—C6—C7	120.07 (11)
Co1—O9—H13	122.3 (17)	C5—C6—H3	115.2 (14)
Co1—O9—H14	120.9 (18)	C7—C6—H3	124.6 (14)
H13—O9—H14	112 (2)	C8—C7—C6	120.39 (11)
O3—S1—O2	114.09 (6)	C8—C7—H4	119.2 (12)
O3—S1—O1	112.03 (6)	C6—C7—H4	120.4 (12)
O2—S1—O1	111.47 (6)	C7—C8—C9	121.18 (11)
O3—S1—C1	105.87 (5)	C7—C8—H5	117.7 (13)
O2—S1—C1	107.54 (6)	C9—C8—H5	121.1 (13)
O1—S1—C1	105.17 (5)	C8—C9—C10	118.76 (10)
O5—S2—O4	113.34 (6)	C8—C9—C1	123.26 (10)
O5—S2—O6	112.50 (7)	C10—C9—C1	117.97 (10)
O4—S2—O6	111.14 (7)	C4—C10—C9	119.59 (10)
O5—S2—C5	106.52 (6)	C4—C10—C5	122.13 (10)
O4—S2—C5	107.20 (6)	C9—C10—C5	118.29 (10)
O6—S2—C5	105.57 (6)	H15—O10—H16	109 (3)
C3—N1—H6	110.3 (14)		
O3—S1—C1—C2	8.14 (11)	S2—C5—C6—C7	-178.09 (10)
O2—S1—C1—C2	130.48 (9)	C5—C6—C7—C8	0.6 (2)
O1—S1—C1—C2	-110.61 (10)	C6—C7—C8—C9	-0.8 (2)
O3—S1—C1—C9	-173.34 (10)	C7—C8—C9—C10	0.05 (18)
O2—S1—C1—C9	-51.01 (11)	C7—C8—C9—C1	-179.85 (12)
O1—S1—C1—C9	67.90 (10)	C2—C1—C9—C8	179.47 (12)
C9—C1—C2—C3	-0.10 (17)	S1—C1—C9—C8	1.02 (16)
S1—C1—C2—C3	178.43 (9)	C2—C1—C9—C10	-0.43 (17)
C1—C2—C3—C4	0.27 (18)	S1—C1—C9—C10	-178.88 (9)
C1—C2—C3—N1	-179.52 (11)	C3—C4—C10—C9	-0.65 (18)
C2—C3—C4—C10	0.11 (18)	C3—C4—C10—C5	179.42 (11)
N1—C3—C4—C10	179.90 (11)	C8—C9—C10—C4	-179.11 (11)
O5—S2—C5—C6	-3.92 (12)	C1—C9—C10—C4	0.80 (17)
O4—S2—C5—C6	-125.54 (11)	C8—C9—C10—C5	0.82 (17)
O6—S2—C5—C6	115.89 (11)	C1—C9—C10—C5	-179.27 (10)
O5—S2—C5—C10	177.64 (10)	C6—C5—C10—C4	178.90 (12)
O4—S2—C5—C10	56.02 (11)	S2—C5—C10—C4	-2.71 (16)

O6—S2—C5—C10	-62.55 (11)	C6—C5—C10—C9	-1.03 (18)
C10—C5—C6—C7	0.34 (19)	S2—C5—C10—C9	177.36 (9)

Symmetry codes: (i) $-x, -y, -z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O7—H9 \cdots O1 ⁱ	0.818 (16)	1.832 (16)	2.6404 (13)	169 (2)
O7—H10 \cdots O5 ⁱⁱ	0.800 (15)	1.867 (16)	2.6501 (13)	166 (2)
O8—H11 \cdots O1 ⁱⁱⁱ	0.830 (16)	1.915 (16)	2.7435 (13)	177 (2)
O8—H12 \cdots O2	0.819 (16)	1.977 (17)	2.7589 (14)	159 (2)
O9—H13 \cdots O7 ^{iv}	0.826 (16)	1.993 (17)	2.8092 (14)	170 (2)
O9—H14 \cdots O4 ⁱⁱ	0.818 (16)	1.865 (17)	2.6713 (14)	168 (3)
N1—H6 \cdots O6 ^{iv}	0.88 (2)	1.95 (2)	2.7993 (15)	162 (2)
N1—H7 \cdots O3 ^v	0.82 (2)	2.01 (2)	2.8124 (15)	168 (2)
N1—H8 \cdots O11A	0.79 (2)	2.12 (2)	2.863 (7)	159 (2)
O10—H15 \cdots O6 ⁱⁱ	0.925 (18)	1.97 (2)	2.8816 (19)	167 (3)
O10—H16 \cdots O8	0.924 (18)	2.25 (3)	3.036 (2)	143 (3)

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

Fig. 1

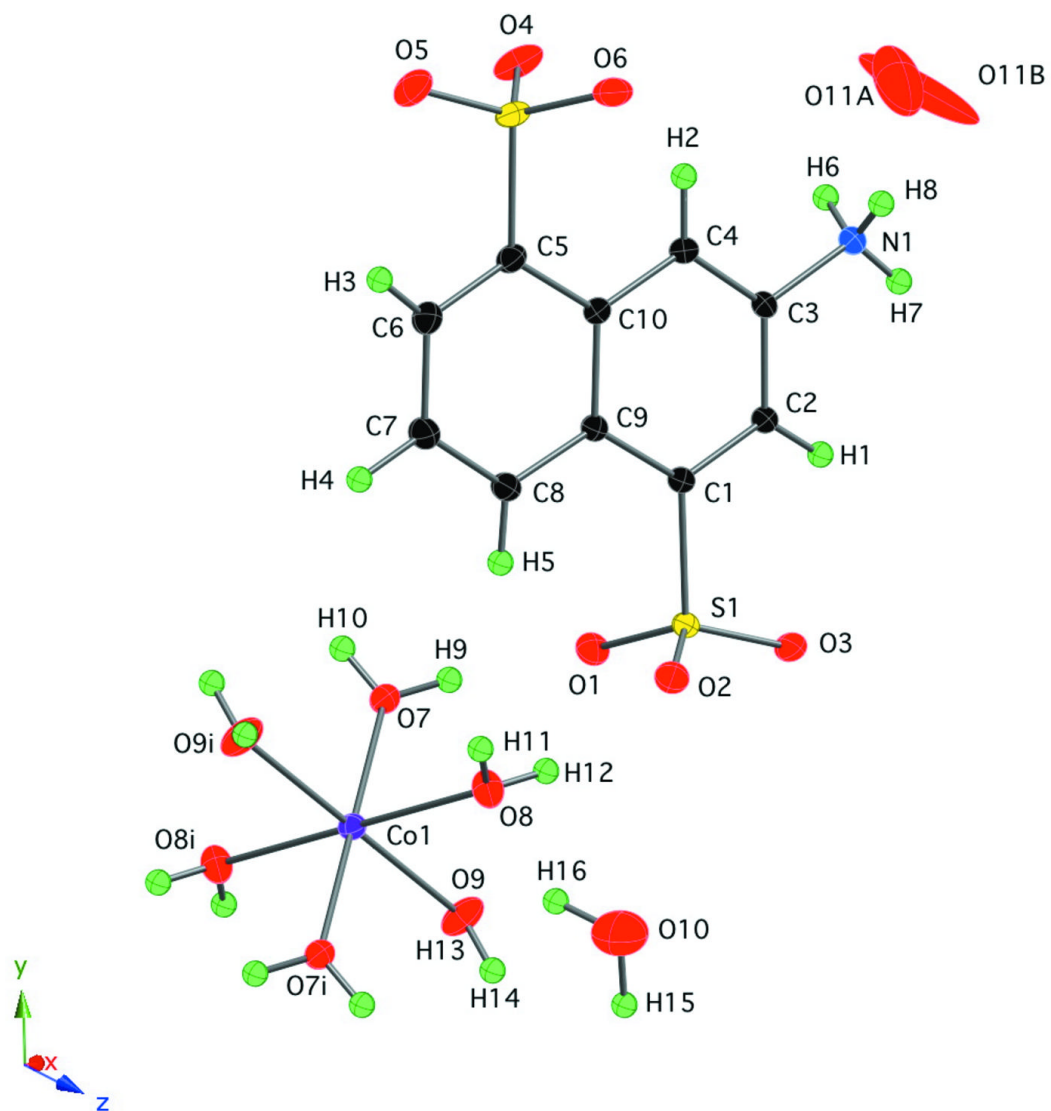


Fig. 2

