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Tetraaquabis(4,4′-bipyridine)cobalt(II) 2-aminonaphthalene-1-sulfonate hexahydrate

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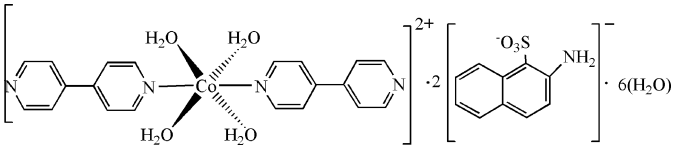
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.039; wR factor = 0.109; data-to-parameter ratio = 13.6.

The title compound, $[Co(C_{10}H_8N_2)_2(H_2O)_4](C_{10}H_8NO_3S)_2\cdot 6H_2O$, contains a tetraaquabis(4,4′-bipyridine)cobalt(II) cation, two ANS^- anions (HANS = 2-aminonaphthalene-1-sulfonic acid) and six solvent water molecules. The Co^{II} atom lies on an inversion centre and is coordinated octahedrally by two mutually *trans* 4,4′-bipyridine molecules bound in a monodentate fashion and by four water molecules in the equatorial plane. The cations and water molecules are arranged into infinite two-dimensional layers by an extensive network of hydrogen bonds. The ANS^- anions are trapped between these layers *via* N—H···O interactions between the amino groups and the solvent and coordinated water molecules. Adjacent layers are stacked *via* weak π–π interactions between 4,4′-bipyridine molecules [nearest centroid-to-centroid distance 3.662 (0) Å].

Related literature

For details of the role of water molecules in self-assembly processes, see Tajkhorshid *et al.* (2002). For investigations of water-based clusters assembled by hydrogen bonds, see: Yoshizawa *et al.* (2005); Sreenivasulu & Vittal (2004).



Experimental

Crystal data

$[Co(C_{10}H_8N_2)_2(H_2O)_4]\cdot(C_{10}H_8NO_3S)_2\cdot 6H_2O$
M_r = 995.93
Monoclinic, $P2_1/c$
a = 12.4737 (14) Å
b = 18.358 (2) Å
c = 10.9196 (13) Å
β = 114.148 (1)°
V = 2281.7 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.54 mm^{-1}
T = 293 (2) K
0.32 × 0.28 × 0.22 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.840, T_{max} = 0.887
12190 measured reflections
4021 independent reflections
3270 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.109
S = 1.05
4021 reflections
295 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O6	0.85	1.87	2.700 (3)	166
O1—H1B···O7	0.85	2.03	2.821 (3)	155
O2—H2A···N2^{i}	0.85	1.91	2.756 (3)	174
O2—H2B···O4^{ii}	0.85	1.96	2.803 (2)	173
O2—H2B···S1^{ii}	0.85	2.93	3.6985 (18)	152
N3—H3A···O5	0.86	1.98	2.660 (4)	135
N3—H3B···O4^{iii}	0.86	2.15	2.980 (3)	162
O6—H6A···O5	0.85	2.35	2.784 (3)	112
O6—H6B···O3^{iv}	0.85	1.85	2.684 (3)	167
O6—H6B···S1^{iv}	0.85	3.03	3.768 (2)	147
O7—H7A···O8	0.85	2.04	2.881 (5)	172
O7—H7B···O5^{iii}	0.85	2.21	2.953 (4)	145
O8—H8A···O6	0.85	2.27	2.949 (4)	137
O8—H8B···O7^{v}	0.85	2.41	2.980 (4)	125

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL* and *DIAMOND* (Brandenburg & Berndt, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2334).

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supplementary materials

Acta Cryst. (2007). E**63**, m2413 [**doi:10.1107/S1600536807040913**]

Tetraaquabis(4,4'-bipyridine)cobalt(II) 2-aminonaphthalene-1-sulfonate hexahydrate

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Comment

The asymmetric unit of the title complex (Fig. 1) contains half of a Co^{II} center, one monodentate 4,4'-bipyridine ligand, one free ANS^{-} anion, two coordinated water (O1 and O2) and three lattice water molecules (O6, O7 and O8). The Co^{II} atom, which lies on an inversion center, is six-coordinated to four oxygen atoms from four coordinated water molecules and two nitrogen atoms from two 4,4'-bipyridine ligands, exhibiting a nearly ideal octahedral coordination geometry. The isolated cations are connected to three lattice water molecules by extensive O—H···O hydrogen bonds interactions to generate a two-dimensional Co^{II}–H_2O layer (Fig. 2 and Table 1). And these adjacent two-dimensional layers are further stacked together by weak π–π interactions between interlayer 4,4'-bipy, exhibiting three-dimensional interdigitated supramoleuclar architectures. The nearest centroid-to-centroid distance is 3.662 (0) Å. Free ANS anions are tightly encapsulated in the channels of the three-dimensional packing structure *via* N—H···O interactions between amino groups and the lattice as well as coordinated water molecules (Fig. 3 and Table 2).

Experimental

The title complex was synthesized by dissolving $Co(CH_3COO)_2 4H_2O$ (99.6 mg, 0.4 mmol), 4,4'-bipyridine (38.4 mg, 0.2 mmol), HANS (89.3 mg, 0.4 mmol), NaOH (24 mg, 0.6 mmol), and H_2O (15 ml) in a 23 ml Teflon lined autoclave under autogenous pressure at 140°C for 2 days. The mixture was slowly cooled to room temperature at a rate of 5 K h^{-1}, pale-red block-shaped crystals suitable for X-ray analysis were obtained in 33% yield. Analysis calculated for $C_{40}H_{52}CoN_6O_{16}S_2$: C 48.24, H 5.26, N 8.44%; found: C 48.20, H 5.38, N 8.62%.

Refinement

H atoms were initially located in difference maps, but were subsequently introduced in calculated positions and treated as riding, with C—H = 0.93, O—H = 0.85 and N—H = 0.86 Å. All H atoms were allocated displacement parameters related to those of their parent atoms [U_{iso}(H) = 1.2U_{eq}(C, N), or 1.5U_{eq}(O)].

Figures

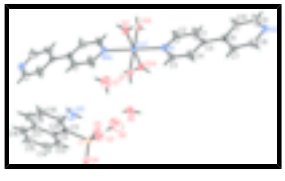
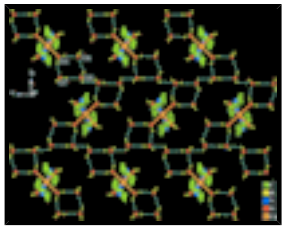
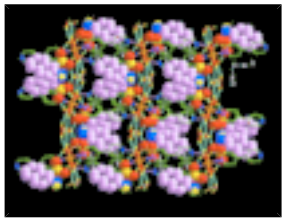
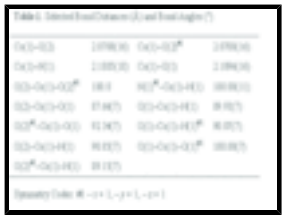
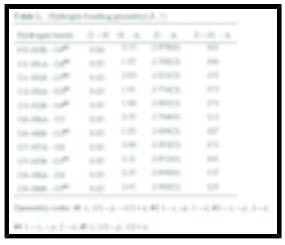


Fig. 1. The structure of the title compound with thermal ellipsoids drawn at the 30% probability level.
Fig. 2. The two dimensional layer structure formed by O—H···O hydrogen bonds (dashed lines) between the complex molecules and the water solvates.
Fig. 3. Packing diagram for the title complex.









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Crystal data

$[Co(C_{10}H_8N_2)_2(H_2O)_4](C_{10}H_8NO_3S)_2·6H_2O$	F_{000} = 1042
M_r = 995.93	D_x = 1.450 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 3808 reflections
a = 12.4737 (14) Å	θ = 2.3–25.1º
b = 18.358 (2) Å	μ = 0.54 mm^{-1}
c = 10.9196 (13) Å	T = 293 (2) K
β = 114.148 (1)º	Block, pale red
V = 2281.7 (5) Å^3	0.32 × 0.28 × 0.22 mm
Z = 2	

Data collection

Bruker APEXII CCD area-detector diffractometer	4021 independent reflections
Radiation source: fine-focus sealed tube	3270 reflections with $I > 2\sigma(I)$

Monochromator: graphite
T = 293(2) K
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.840, T_{max} = 0.887
12190 measured reflections
R_{int} = 0.019
θ_{max} = 25.0º
θ_{min} = 2.1º
h = −14→12
k = −19→21
l = −12→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.109
S = 1.05
4021 reflections
295 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 1.0964P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: none

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.5000	0.03414 (14)
S1	0.68106 (5)	0.61872 (4)	−0.02091 (6)	0.04513 (18)
O1	0.44371 (14)	0.57897 (9)	0.34621 (16)	0.0459 (4)
H1A	0.4393	0.5695	0.2681	0.069*
H1B	0.4480	0.6239	0.3668	0.069*
O2	0.48301 (14)	0.57884 (10)	0.62652 (17)	0.0498 (4)
H2A	0.4184	0.5872	0.6326	0.075*
H2B	0.5442	0.5939	0.6919	0.075*
O3	0.7056 (2)	0.54311 (11)	0.0094 (2)	0.0897 (8)
O4	0.67303 (18)	0.63600 (12)	−0.15273 (18)	0.0664 (6)
O5	0.57611 (19)	0.64226 (16)	−0.0080 (3)	0.0948 (8)

N1	0.31765 (16)	0.46586 (11)	0.44211 (19)	0.0387 (4)
N2	−0.27372 (18)	0.40516 (14)	0.3473 (2)	0.0551 (6)
N3	0.6869 (3)	0.73128 (17)	0.1974 (3)	0.0915 (10)
H3A	0.6234	0.7088	0.1481	0.110*
H3B	0.6862	0.7629	0.2551	0.110*
C1	0.1718 (2)	0.39321 (19)	0.4720 (4)	0.0805 (11)
H1	0.1558	0.3521	0.5115	0.097*
C2	0.2858 (2)	0.40909 (18)	0.4935 (4)	0.0777 (11)
H2	0.3444	0.3777	0.5479	0.093*
C3	0.2301 (2)	0.50586 (18)	0.3617 (3)	0.0679 (9)
H3	0.2479	0.5451	0.3193	0.081*
C4	0.1139 (2)	0.49405 (18)	0.3355 (3)	0.0661 (9)
H4	0.0567	0.5251	0.2777	0.079*
C5	0.08187 (19)	0.43739 (13)	0.3932 (2)	0.0378 (5)
C6	−0.04222 (19)	0.42505 (13)	0.3733 (2)	0.0388 (5)
C7	−0.1325 (2)	0.4684 (2)	0.2911 (3)	0.0686 (9)
H7	−0.1181	0.5056	0.2421	0.082*
C8	−0.2450 (2)	0.4563 (2)	0.2816 (3)	0.0740 (10)
H8	−0.3046	0.4865	0.2250	0.089*
C9	−0.1865 (3)	0.36315 (18)	0.4241 (4)	0.0726 (9)
H9	−0.2035	0.3259	0.4711	0.087*
C10	−0.0719 (2)	0.37078 (16)	0.4394 (4)	0.0661 (9)
H10	−0.0146	0.3389	0.4948	0.079*
C11	0.8024 (2)	0.66754 (12)	0.0958 (2)	0.0384 (5)
C12	0.9161 (2)	0.65456 (12)	0.0952 (2)	0.0389 (5)
C13	0.9385 (2)	0.60407 (14)	0.0116 (3)	0.0482 (6)
H13	0.8773	0.5756	−0.0468	0.058*
C14	1.0489 (3)	0.59610 (18)	0.0148 (3)	0.0685 (9)
H14	1.0611	0.5625	−0.0421	0.082*
C15	1.1428 (3)	0.6372 (2)	0.1010 (4)	0.0785 (11)
H15	1.2172	0.6313	0.1020	0.094*
C16	1.1250 (3)	0.6855 (2)	0.1833 (4)	0.0723 (10)
H16	1.1880	0.7130	0.2413	0.087*
C17	1.0133 (2)	0.69561 (15)	0.1836 (3)	0.0525 (7)
C18	0.9945 (3)	0.74661 (16)	0.2700 (3)	0.0676 (9)
H18	1.0575	0.7742	0.3277	0.081*
C19	0.8892 (3)	0.75618 (16)	0.2710 (3)	0.0695 (9)
H19	0.8811	0.7897	0.3304	0.083*
C20	0.7885 (3)	0.71681 (15)	0.1840 (3)	0.0544 (7)
O6	0.4298 (2)	0.57428 (12)	0.0930 (2)	0.0804 (7)
H6A	0.4992	0.5625	0.1042	0.121*
H6B	0.3781	0.5419	0.0552	0.121*
O7	0.4464 (2)	0.73225 (13)	0.3298 (3)	0.0924 (8)
H7A	0.4282	0.7334	0.2458	0.139*
H7B	0.5077	0.7554	0.3798	0.139*
O8	0.3637 (3)	0.72911 (17)	0.0418 (3)	0.1175 (11)
H8A	0.3643	0.6869	0.0100	0.176*
H8B	0.4063	0.7611	0.0272	0.176*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0231 (2)	0.0467 (3)	0.0319 (2)	−0.00243 (18)	0.01052 (17)	−0.00211 (18)
S1	0.0398 (3)	0.0500 (4)	0.0410 (3)	−0.0111 (3)	0.0118 (3)	0.0024 (3)
O1	0.0433 (10)	0.0538 (10)	0.0381 (9)	−0.0024 (8)	0.0142 (8)	0.0024 (7)
O2	0.0274 (8)	0.0727 (12)	0.0491 (10)	−0.0074 (8)	0.0156 (7)	−0.0223 (9)
O3	0.0922 (17)	0.0486 (12)	0.0858 (16)	−0.0270 (12)	−0.0068 (13)	0.0134 (11)
O4	0.0602 (12)	0.0839 (14)	0.0397 (10)	−0.0284 (11)	0.0045 (9)	0.0050 (9)
O5	0.0512 (13)	0.140 (2)	0.0998 (18)	−0.0185 (14)	0.0372 (13)	−0.0230 (17)
N1	0.0286 (10)	0.0476 (12)	0.0395 (10)	−0.0019 (9)	0.0137 (8)	−0.0020 (9)
N2	0.0327 (12)	0.0803 (16)	0.0553 (13)	−0.0074 (11)	0.0210 (10)	−0.0121 (12)
N3	0.088 (2)	0.096 (2)	0.108 (2)	0.0034 (17)	0.0578 (19)	−0.0365 (19)
C1	0.0311 (14)	0.081 (2)	0.118 (3)	0.0009 (14)	0.0194 (16)	0.052 (2)
C2	0.0289 (14)	0.073 (2)	0.119 (3)	0.0047 (14)	0.0177 (16)	0.042 (2)
C3	0.0308 (14)	0.094 (2)	0.0695 (19)	−0.0048 (14)	0.0112 (13)	0.0424 (17)
C4	0.0277 (13)	0.088 (2)	0.0715 (19)	0.0032 (13)	0.0088 (13)	0.0391 (17)
C5	0.0274 (11)	0.0475 (13)	0.0384 (12)	−0.0032 (10)	0.0134 (10)	−0.0062 (10)
C6	0.0286 (11)	0.0496 (14)	0.0386 (12)	−0.0023 (10)	0.0141 (10)	−0.0088 (10)
C7	0.0346 (14)	0.116 (3)	0.0572 (17)	0.0102 (16)	0.0207 (13)	0.0350 (18)
C8	0.0301 (14)	0.134 (3)	0.0538 (17)	0.0148 (17)	0.0131 (13)	0.0266 (19)
C9	0.0471 (17)	0.0645 (19)	0.119 (3)	−0.0043 (15)	0.0465 (19)	0.0164 (19)
C10	0.0398 (15)	0.0577 (17)	0.106 (2)	0.0045 (13)	0.0355 (16)	0.0215 (17)
C11	0.0403 (13)	0.0358 (12)	0.0348 (12)	−0.0024 (10)	0.0110 (10)	0.0018 (10)
C12	0.0398 (13)	0.0364 (12)	0.0350 (12)	−0.0005 (10)	0.0095 (10)	0.0108 (10)
C13	0.0502 (15)	0.0450 (14)	0.0478 (14)	0.0072 (12)	0.0186 (12)	0.0082 (11)
C14	0.072 (2)	0.072 (2)	0.073 (2)	0.0298 (18)	0.0413 (18)	0.0262 (17)
C15	0.0443 (18)	0.097 (3)	0.096 (3)	0.0162 (18)	0.0308 (19)	0.047 (2)
C16	0.0393 (16)	0.081 (2)	0.079 (2)	−0.0086 (15)	0.0064 (15)	0.0287 (19)
C17	0.0467 (16)	0.0482 (15)	0.0477 (14)	−0.0069 (12)	0.0043 (12)	0.0140 (12)
C18	0.073 (2)	0.0526 (18)	0.0506 (16)	−0.0213 (15)	−0.0014 (15)	−0.0064 (14)
C19	0.093 (3)	0.0526 (18)	0.0548 (17)	−0.0071 (17)	0.0224 (17)	−0.0175 (14)
C20	0.0661 (18)	0.0461 (15)	0.0519 (15)	0.0029 (13)	0.0252 (14)	−0.0023 (12)
O6	0.1082 (18)	0.0777 (15)	0.0730 (14)	−0.0410 (13)	0.0551 (14)	−0.0252 (12)
O7	0.1018 (19)	0.0765 (16)	0.1005 (19)	−0.0156 (14)	0.0430 (16)	−0.0103 (14)
O8	0.127 (3)	0.102 (2)	0.161 (3)	0.0241 (18)	0.098 (2)	0.018 (2)

Geometric parameters (Å, °)

Co1—O2^{i}	2.0708 (16)	C6—C7	1.371 (4)
Co1—O2	2.0708 (16)	C7—C8	1.382 (4)
Co1—O1^{i}	2.1096 (16)	C7—H7	0.9300
Co1—O1	2.1096 (16)	C8—H8	0.9300
Co1—N1^{i}	2.1885 (18)	C9—C10	1.377 (4)
Co1—N1	2.1885 (18)	C9—H9	0.9300
S1—O3	1.431 (2)	C10—H10	0.9300
S1—O4	1.4369 (19)	C11—C20	1.383 (3)

S1—O5	1.439 (2)	C11—C12	1.441 (3)
S1—C11	1.772 (2)	C12—C13	1.406 (4)
O1—H1A	0.8499	C12—C17	1.419 (3)
O1—H1B	0.8500	C13—C14	1.372 (4)
O2—H2A	0.8501	C13—H13	0.9300
O2—H2B	0.8500	C14—C15	1.387 (5)
N1—C3	1.311 (3)	C14—H14	0.9300
N1—C2	1.320 (3)	C15—C16	1.345 (5)
N2—C9	1.317 (4)	C15—H15	0.9300
N2—C8	1.318 (4)	C16—C17	1.406 (4)
N3—C20	1.360 (4)	C16—H16	0.9300
N3—H3A	0.8600	C17—C18	1.416 (4)
N3—H3B	0.8600	C18—C19	1.329 (5)
C1—C5	1.367 (4)	C18—H18	0.9300
C1—C2	1.374 (4)	C19—C20	1.424 (4)
C1—H1	0.9300	C19—H19	0.9300
C2—H2	0.9300	O6—H6A	0.8505
C3—C4	1.375 (4)	O6—H6B	0.8502
C3—H3	0.9300	O7—H7A	0.8501
C4—C5	1.358 (4)	O7—H7B	0.8500
C4—H4	0.9300	O8—H8A	0.8501
C5—C6	1.490 (3)	O8—H8B	0.8501
C6—C10	1.368 (4)		
$O2^{i}$—Co1—O2	180.0	C10—C6—C7	116.2 (2)
$O2^{i}$—Co1—$O1^{i}$	87.66 (7)	C10—C6—C5	121.6 (2)
O2—Co1—$O1^{i}$	92.34 (7)	C7—C6—C5	122.2 (2)
$O2^{i}$—Co1—O1	92.34 (7)	C6—C7—C8	119.6 (3)
O2—Co1—O1	87.66 (7)	C6—C7—H7	120.2
$O1^{i}$—Co1—O1	180.0	C8—C7—H7	120.2
$O2^{i}$—Co1—$N1^{i}$	90.85 (7)	N2—C8—C7	124.6 (3)
O2—Co1—$N1^{i}$	89.15 (7)	N2—C8—H8	117.7
$O1^{i}$—Co1—$N1^{i}$	89.93 (7)	C7—C8—H8	117.7
O1—Co1—$N1^{i}$	90.07 (7)	N2—C9—C10	124.3 (3)
$O2^{i}$—Co1—N1	89.15 (7)	N2—C9—H9	117.9
O2—Co1—N1	90.85 (7)	C10—C9—H9	117.9
$O1^{i}$—Co1—N1	90.07 (7)	C6—C10—C9	120.2 (3)
O1—Co1—N1	89.93 (7)	C6—C10—H10	119.9
$N1^{i}$—Co1—N1	180.00 (11)	C9—C10—H10	119.9
O3—S1—O4	111.52 (15)	C20—C11—C12	121.0 (2)
O3—S1—O5	112.69 (17)	C20—C11—S1	121.2 (2)
O4—S1—O5	109.78 (15)	C12—C11—S1	117.77 (17)
O3—S1—C11	106.57 (12)	C13—C12—C17	116.8 (2)
O4—S1—C11	107.32 (11)	C13—C12—C11	124.6 (2)
O5—S1—C11	108.73 (13)	C17—C12—C11	118.6 (2)
Co1—O1—H1A	121.5	C14—C13—C12	121.2 (3)
Co1—O1—H1B	119.4	C14—C13—H13	119.4

H1A—O1—H1B	115.7	C12—C13—H13	119.4
Co1—O2—H2A	122.6	C13—C14—C15	121.3 (3)
Co1—O2—H2B	119.1	C13—C14—H14	119.4
H2A—O2—H2B	115.5	C15—C14—H14	119.4
C3—N1—C2	114.4 (2)	C16—C15—C14	119.2 (3)
C3—N1—Co1	121.05 (17)	C16—C15—H15	120.4
C2—N1—Co1	124.17 (17)	C14—C15—H15	120.4
C9—N2—C8	115.3 (2)	C15—C16—C17	121.5 (3)
C20—N3—H3A	120.0	C15—C16—H16	119.2
C20—N3—H3B	120.0	C17—C16—H16	119.2
H3A—N3—H3B	120.0	C16—C17—C18	121.5 (3)
C5—C1—C2	120.5 (3)	C16—C17—C12	120.0 (3)
C5—C1—H1	119.8	C18—C17—C12	118.4 (3)
C2—C1—H1	119.8	C19—C18—C17	121.8 (3)
N1—C2—C1	124.4 (3)	C19—C18—H18	119.1
N1—C2—H2	117.8	C17—C18—H18	119.1
C1—C2—H2	117.8	C18—C19—C20	122.2 (3)
N1—C3—C4	124.7 (2)	C18—C19—H19	118.9
N1—C3—H3	117.6	C20—C19—H19	118.9
C4—C3—H3	117.6	N3—C20—C11	126.2 (3)
C5—C4—C3	120.6 (2)	N3—C20—C19	115.8 (3)
C5—C4—H4	119.7	C11—C20—C19	118.0 (3)
C3—C4—H4	119.7	H6A—O6—H6B	114.7
C4—C5—C1	115.2 (2)	H7A—O7—H7B	116.9
C4—C5—C6	122.3 (2)	H8A—O8—H8B	116.3
C1—C5—C6	122.5 (2)		
$O2^{i}$—Co1—N1—C3	−106.1 (2)	N2—C9—C10—C6	0.5 (6)
O2—Co1—N1—C3	73.9 (2)	O3—S1—C11—C20	−119.3 (2)
$O1^{i}$—Co1—N1—C3	166.3 (2)	O4—S1—C11—C20	121.1 (2)
O1—Co1—N1—C3	−13.7 (2)	O5—S1—C11—C20	2.4 (3)
$N1^{i}$—Co1—N1—C3	94 (100)	O3—S1—C11—C12	61.1 (2)
$O2^{i}$—Co1—N1—C2	81.0 (3)	O4—S1—C11—C12	−58.5 (2)
O2—Co1—N1—C2	−99.0 (3)	O5—S1—C11—C12	−177.19 (19)
$O1^{i}$—Co1—N1—C2	−6.7 (3)	C20—C11—C12—C13	178.2 (2)
O1—Co1—N1—C2	173.3 (3)	S1—C11—C12—C13	−2.2 (3)
$N1^{i}$—Co1—N1—C2	−79 (100)	C20—C11—C12—C17	−2.5 (3)
C3—N1—C2—C1	−2.9 (5)	S1—C11—C12—C17	177.12 (17)
Co1—N1—C2—C1	170.4 (3)	C17—C12—C13—C14	−1.0 (3)
C5—C1—C2—N1	−0.1 (6)	C11—C12—C13—C14	178.4 (2)
C2—N1—C3—C4	3.3 (5)	C12—C13—C14—C15	0.4 (4)
Co1—N1—C3—C4	−170.3 (3)	C13—C14—C15—C16	0.2 (5)
N1—C3—C4—C5	−0.6 (6)	C14—C15—C16—C17	−0.2 (5)
C3—C4—C5—C1	−2.5 (5)	C15—C16—C17—C18	−179.9 (3)
C3—C4—C5—C6	176.6 (3)	C15—C16—C17—C12	−0.4 (4)
C2—C1—C5—C4	2.8 (5)	C13—C12—C17—C16	0.9 (3)
C2—C1—C5—C6	−176.3 (3)	C11—C12—C17—C16	−178.5 (2)
C4—C5—C6—C10	−175.4 (3)	C13—C12—C17—C18	−179.5 (2)

C1—C5—C6—C10	3.7 (4)	C11—C12—C17—C18	1.1 (3)
C4—C5—C6—C7	2.7 (4)	C16—C17—C18—C19	−179.8 (3)
C1—C5—C6—C7	−178.2 (3)	C12—C17—C18—C19	0.7 (4)
C10—C6—C7—C8	1.3 (5)	C17—C18—C19—C20	−1.0 (5)
C5—C6—C7—C8	−176.9 (3)	C12—C11—C20—N3	−177.1 (3)
C9—N2—C8—C7	−1.3 (5)	S1—C11—C20—N3	3.3 (4)
C6—C7—C8—N2	0.2 (6)	C12—C11—C20—C19	2.1 (4)
C8—N2—C9—C10	0.9 (5)	S1—C11—C20—C19	−177.4 (2)
C7—C6—C10—C9	−1.6 (5)	C18—C19—C20—N3	179.0 (3)
C5—C6—C10—C9	176.6 (3)	C18—C19—C20—C11	−0.4 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···O6	0.85	1.87	2.700 (3)	166
O1—H1B···O7	0.85	2.03	2.821 (3)	155
O2—H2A···N2^{ii}	0.85	1.91	2.756 (3)	174
O2—H2B···O4^{iii}	0.85	1.96	2.803 (2)	173
O2—H2B···S1^{iii}	0.85	2.93	3.6985 (18)	152
N3—H3A···O5	0.86	1.98	2.660 (4)	135
N3—H3B···O4^{iv}	0.86	2.15	2.980 (3)	162
O6—H6A···O5	0.85	2.35	2.784 (3)	112
O6—H6B···O3^{v}	0.85	1.85	2.684 (3)	167
O6—H6B···S1^{v}	0.85	3.03	3.768 (2)	147
O7—H7A···O8	0.85	2.04	2.881 (5)	172
O7—H7B···O5^{iv}	0.85	2.21	2.953 (4)	145
O8—H8A···O6	0.85	2.27	2.949 (4)	137
O8—H8B···O7^{vi}	0.85	2.41	2.980 (4)	125

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

Fig. 1

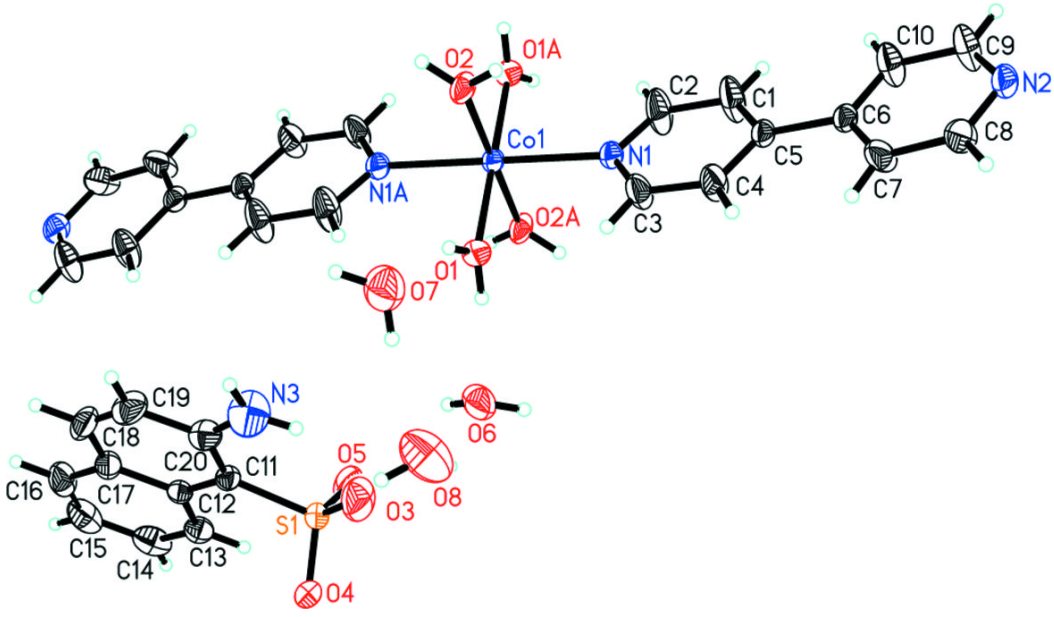
O2
O1A
Co1
N1A
N1
C2
C1
C6
C10
C9
N2
C8
C5
C4
C7
C3
O2A
O1
O7
C19
N3
C18
C20
C11
C16
C17
C12
S1
C15
C14
C13
O5
O6
O8
O3
O4

Fig. 2

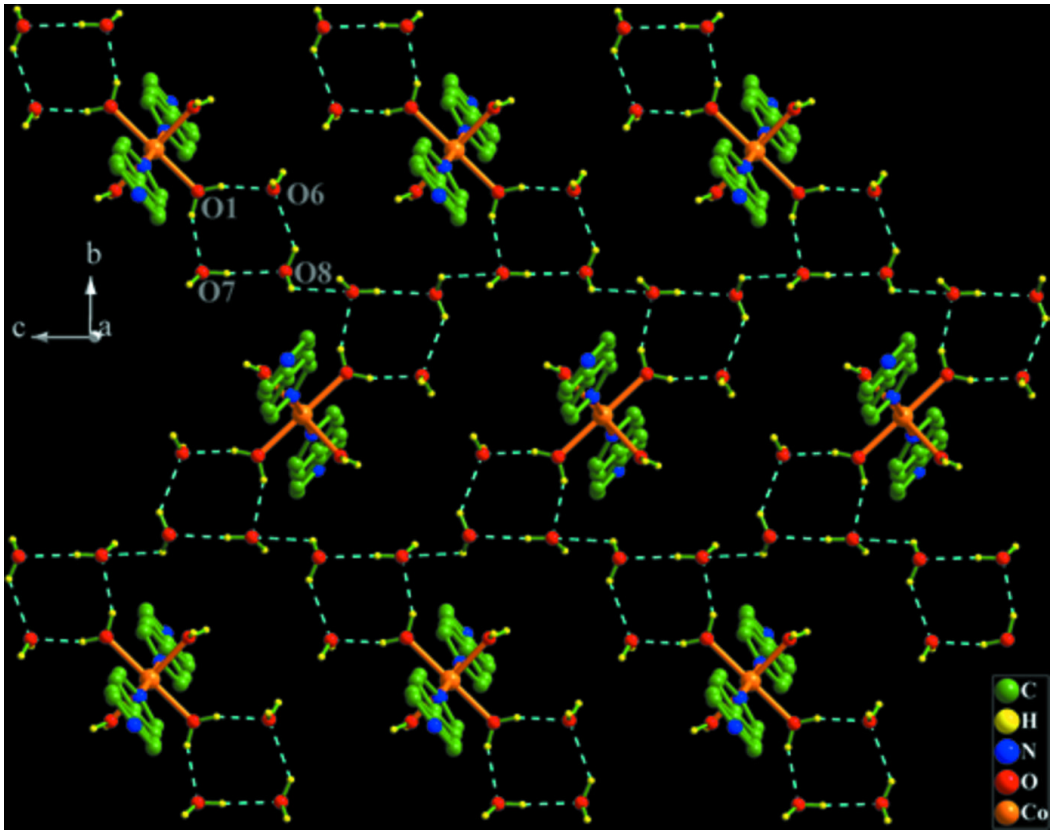

Fig. 3

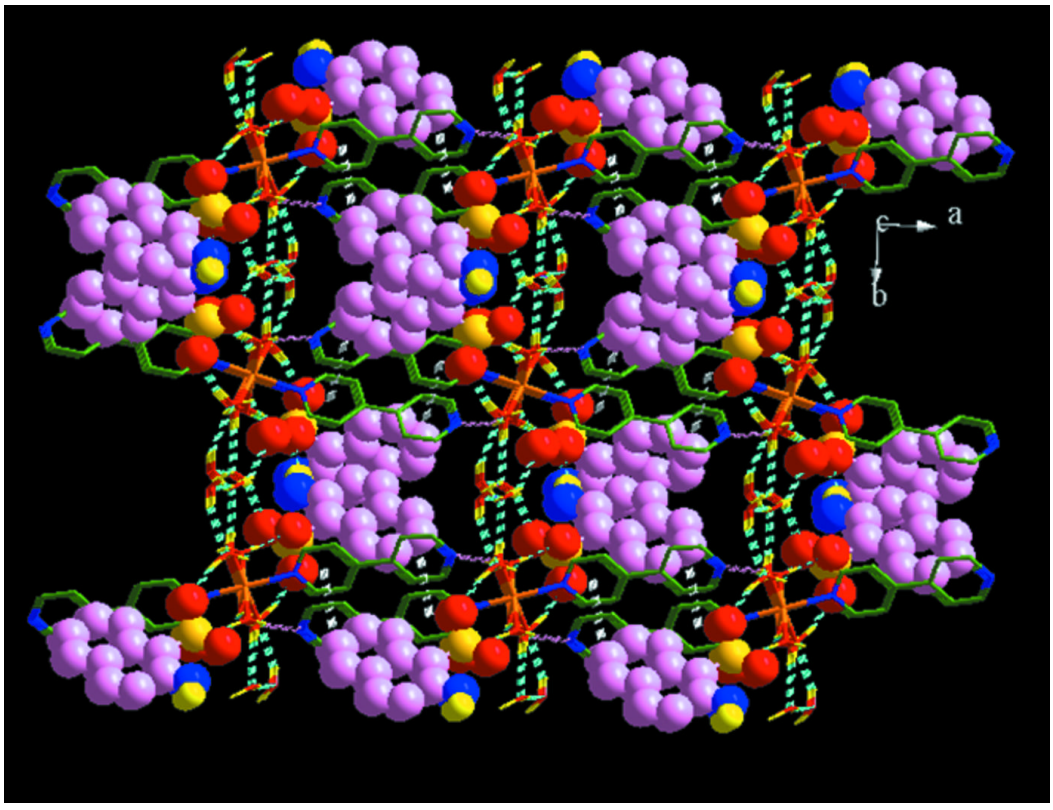

Fig. 4

Table 1. Selected Bond Distances (Å) and Bond Angles (°)

Co(1)–O(2)	2.0708(16)	Co(1)–O(2)$^{\#1}$	2.0708(16)
Co(1)–N(1)	2.1885(18)	Co(1)–O(1)	2.1096(16)
O(2)–Co(1)–O(2)$^{\#1}$	180.0	N(1)$^{\#1}$–Co(1)–N(1)	180.00(11)
O(2)–Co(1)–O(1)	87.66(7)	O(1)–Co(1)–N(1)	89.93(7)
O(2)$^{\#1}$–Co(1)–O(1)	92.34(7)	O(1)–Co(1)–N(1)$^{\#1}$	90.07(7)
O(2)–Co(1)–N(1)	90.85(7)	O(1)–Co(1)–O(1)$^{\#1}$	180.00(7)
O(2)$^{\#1}$–Co(1)–N(1)	89.15(7)		

Symmetry Codes: #1 $-x+1, -y+1, -z+1$

Fig. 5

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

Hydrogen bonds	D – H	H ··· A	D ··· A	D – H ··· A
N3–H3B···O4$^{\#1}$	0.86	2.15	2.979(4)	162
O1–H1A···O6$^{\#2}$	0.85	1.87	2.700(3)	166
O1–H1B···O7$^{\#2}$	0.85	2.03	2.821(3)	155
O2–H2A···N2$^{\#3}$	0.85	1.91	2.756(3)	173
O2–H2B···O4$^{\#4}$	0.85	1.96	2.803(3)	173
O6–H6A···O5	0.85	2.35	2.784(4)	112
O6–H6B···O3$^{\#2}$	0.85	1.85	2.684(3)	167
O7–H7A···O8	0.85	2.04	2.882(5)	172
O7–H7B···O5$^{\#1}$	0.85	2.21	2.953(4)	145
O8–H8A···O6	0.85	2.27	2.949(4)	137
O8–H8B···O7$^{\#5}$	0.85	2.41	2.980(5)	125

Symmetry codes: #1 $x, 1/2-y, -1/2+z$; #2 $1-x, -y, 1-z$; #3 $-x, -y, 2-z$; #4 $1-x, -y, 2-z$; #5 $x, 1/2-y, 1/2+z$.