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Tetraaquabis(2-methyl-1*H*-imidazole-κN^3)cobalt(II) naphthalene-1,5-disulfonate

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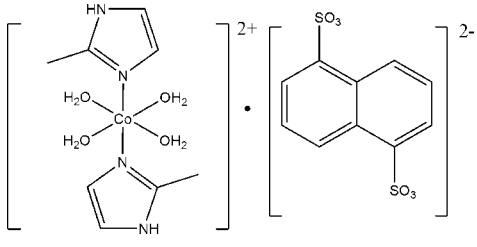
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.028; wR factor = 0.073; data-to-parameter ratio = 15.4.

In the title complex, $[Co(C_4H_6N_2)_2(H_2O)_4](C_{10}H_6O_6S_2)$, the cation and anion both reside on crystallographic inversion centers, such that the asymmetric unit comprises one half cation and one half anion. The central Co^{II} ion is coordinated by four water molecules and two 2-methylimidazole ligands, resulting in a *trans*-octahedral coordination geometry. The existence of strong N—H···O and O—H···O hydrogen-bonding interactions gives rise to a three-dimensional structure.

Related literature

For general background to ferroelectric metal-organic frameworks, see: Wu *et al.* (2011); Ye *et al.* (2006); Zhang *et al.* (2008, 2010); Fu *et al.* (2009).



Experimental

Crystal data

$[Co(C_4H_6N_2)_2(H_2O)_4](C_{10}H_6O_6S_2)$
M_r = 581.48
Monoclinic, $P2_1/n$
a = 8.0260 (16) Å
b = 12.923 (3) Å
c = 11.658 (2) Å
β = 99.27 (3)°
V = 1193.5 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.96 mm^{-1}
T = 293 K
0.3 × 0.3 × 0.2 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.489, T_{max} = 1.000
12041 measured reflections
2729 independent reflections
2558 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.073
S = 1.09
2729 reflections
177 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H4···O5^{i}	0.85 (1)	1.97 (1)	2.815 (2)	174 (3)
O2—H5···O4^{ii}	0.84 (1)	1.88 (1)	2.7149 (19)	171 (3)
O1—H6···O5^{ii}	0.84 (1)	2.21 (1)	3.026 (2)	167 (3)
O1—H7···O3^{iii}	0.84 (1)	1.92 (1)	2.7661 (18)	179 (2)
N1—H1*B*···O4	0.86	2.06	2.906 (2)	170

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2459).

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supplementary materials

Acta Cryst. (2011). E**67**, m1686 [**doi:10.1107/S160053681104548X**]

Tetraaquabis(2-methyl-1*H*-imidazole-κN^3)cobalt(II) naphthalene-1,5-disulfonate

Y. Jin

Comment

In recent years, simple molecular-ionic compounds containing inorganic cations and organic anions have attracted great interest owing to the tunability of their special structural features and their potential ferroelectrics property. Ferroelectric materials that exhibit reversible electric polarization in response to an external electric field have found many applications such as nonvolatile memory storage, electronics and optics. The freezing of a certain functional group at low temperature forces significant orientational motions of the guest molecules and thus induces the formation of the ferroelectric phase. (Fu *et al.*, 2009; Zhang *et al.*, 2010; Zhang *et al.*, 2008;Ye *et al.*, 2006).

The asymmetric unit of the title compound is shown in Fig1, which consists of one $(C_{10}H_6O_6S_2)^{2-}$ anion and one $2C_4H_6N_2.4H2O.Co(II)$ molecule-based cation.The title complex crystallizes in monoclinic P 21/n space group, the whole compound shall be stable thanks to the numerous hydrogen bonds formed in molecules, such as the N—H···O and the O—H···O bonds. The length of N—H···O is 2.06 Å, while the length of O—H···O hydrogen bonds ranges from 1.878 to 2.205 Å. Further details about the hydrogen bonds are listed in Table 1.

Experimental

$Co(CH_3COO^-)_2.4H_2O$ (4.96 g, 20 mmol) mixed with K_2CO_3 (2.76, 20 mmol) were dissolved into 15 ml distilled water under stirring for 5 minutes, and turbid liquid was filtered,and then $CoCO_3$ was obtained in about 90% yield. $CoCO_3$(1.19, 10 mmol) were dissolved into solution containing 2.88 g 1,5-naphthalene disulfonic acid under stirring for 5 minutes, and then 2-methylimidazole (3.28 g, 40 mmol) were added to the solution.At last, the solution was filtered, then tansparent solution was located in a quiet and clean place, block pink crystals suitable for X-ray diffraction were obtained in about 78% yield after two days and filtered and washed with distilled water.

Refinement

H atoms bound to carbon and nitrogen were placed at idealized positions [C—H = 0.93–0.96 Å and N—H = 0.86 Å] and allowed to ride on their parent atoms with U_{iso} fixed at 1.2 U_{eq}(C,*N*). The hydrogen atoms from water molecules were added from a difference map, and the length of O—H bonds was fixed to 0.84Å with a deviation of 0.01 Å.

Figures

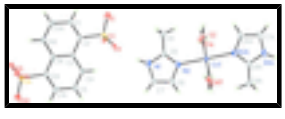

Fig. 1. Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 30% probability level.

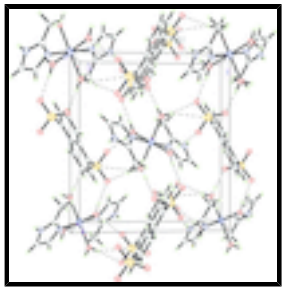

Fig. 2. Crystal structure of the title compound with view along the *a* axis. Intermolecular interactions are shown as dashed lines.

Tetraaquabis(2-methyl-1*H*-imidazole-κN^3)cobalt(II) naphthalene-1,5-disulfonate

Crystal data

$[Co(C_4H_6N_2)_2(H_2O)_4](C_{10}H_6O_6S_2)$	$F(000) = 602$
$M_r = 581.48$	$D_x = 1.618$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 3450 reflections
$a = 8.0260$ (16) Å	$\theta = 6.2–55.3°$
$b = 12.923$ (3) Å	$\mu = 0.96$ mm^{-1}
$c = 11.658$ (2) Å	$T = 293$ K
$\beta = 99.27$ (3)°	Block, pink
$V = 1193.5$ (4) Å^3	0.3 × 0.3 × 0.2 mm
$Z = 2$	

Data collection

Rigaku Mercury CCD diffractometer	2729 independent reflections
Radiation source: fine-focus sealed tube	2558 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.031$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$h = -10\rightarrow10$
$T_{min} = 0.489$, $T_{max} = 1.000$	$k = -16\rightarrow16$
12041 measured reflections	$l = -15\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.073$	$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 0.6244P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
2729 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}

177 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
4 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0260 (17)

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 $F^2 > \sigma(F^2)$ 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}
C1	1.0422 (2)	0.82564 (13)	0.59914 (16)	0.0329 (4)
H1A	1.0320	0.7642	0.6389	0.039*
C2	0.91065 (19)	0.89391 (12)	0.58123 (13)	0.0237 (3)
C3	0.92275 (18)	0.98928 (11)	0.52102 (14)	0.0221 (3)
C4	0.7893 (2)	1.06210 (13)	0.50084 (16)	0.0304 (4)
H4C	0.6886	1.0486	0.5278	0.036*
C5	0.8068 (2)	1.15174 (14)	0.44245 (18)	0.0376 (4)
H5C	0.7178	1.1986	0.4299	0.045*
C6	0.1443 (2)	1.11040 (14)	0.80184 (15)	0.0351 (4)
H6B	0.0598	1.1600	0.7984	0.042*
C7	0.2652 (3)	1.10886 (16)	0.73404 (17)	0.0411 (4)
H7B	0.2799	1.1559	0.6761	0.049*
C8	0.2985 (2)	0.97570 (14)	0.85354 (17)	0.0349 (4)
C9	0.3757 (3)	0.88003 (18)	0.9091 (2)	0.0561 (6)
H9A	0.3124	0.8573	0.9677	0.084*
H9B	0.4901	0.8940	0.9442	0.084*
H9C	0.3746	0.8269	0.8515	0.084*
Co1	0.0000	1.0000	1.0000	0.02367 (11)
H4	0.217 (4)	0.8773 (10)	1.141 (2)	0.074 (9)*
H5	0.233 (3)	0.9781 (17)	1.1808 (15)	0.058 (8)*
H6	0.118 (3)	1.169 (2)	1.1307 (16)	0.072 (9)*
H7	0.006 (2)	1.2076 (11)	1.0401 (18)	0.039 (6)*
N1	0.3618 (2)	1.02391 (14)	0.76803 (14)	0.0405 (4)
H1B	0.4490	1.0044	0.7394	0.049*
N2	0.16477 (19)	1.02694 (11)	0.87765 (13)	0.0310 (3)
O1	0.05471 (19)	1.15356 (9)	1.06915 (12)	0.0378 (3)
O2	0.20133 (17)	0.94019 (10)	1.12236 (12)	0.0356 (3)
O3	0.60123 (15)	0.83245 (10)	0.52393 (11)	0.0341 (3)

O4	0.66384 (16)	0.94058 (10)	0.69426 (11)	0.0378 (3)
O5	0.76184 (17)	0.76414 (10)	0.70195 (12)	0.0396 (3)
S1	0.72008 (5)	0.85486 (3)	0.62836 (3)	0.02460 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0290 (8)	0.0262 (8)	0.0442 (10)	0.0024 (7)	0.0079 (7)	0.0075 (7)
C2	0.0199 (7)	0.0238 (7)	0.0278 (8)	−0.0024 (6)	0.0052 (6)	−0.0018 (6)
C3	0.0178 (7)	0.0225 (7)	0.0259 (7)	−0.0013 (5)	0.0031 (6)	−0.0029 (6)
C4	0.0197 (7)	0.0304 (8)	0.0426 (9)	0.0035 (6)	0.0097 (7)	0.0026 (7)
C5	0.0253 (8)	0.0317 (9)	0.0572 (12)	0.0098 (7)	0.0111 (8)	0.0098 (8)
C6	0.0412 (10)	0.0322 (9)	0.0334 (9)	−0.0028 (7)	0.0111 (8)	0.0004 (7)
C7	0.0494 (11)	0.0433 (11)	0.0333 (9)	−0.0123 (9)	0.0142 (8)	−0.0024 (8)
C8	0.0334 (9)	0.0347 (9)	0.0394 (10)	−0.0020 (7)	0.0148 (8)	−0.0073 (7)
C9	0.0531 (13)	0.0455 (12)	0.0764 (16)	0.0166 (10)	0.0304 (12)	0.0034 (11)
Co1	0.02407 (17)	0.02192 (17)	0.02595 (17)	0.00133 (11)	0.00684 (12)	0.00013 (11)
N1	0.0364 (9)	0.0496 (9)	0.0405 (9)	−0.0068 (7)	0.0215 (7)	−0.0112 (7)
N2	0.0325 (8)	0.0285 (7)	0.0346 (8)	−0.0008 (6)	0.0134 (6)	−0.0015 (6)
O1	0.0499 (8)	0.0237 (6)	0.0364 (7)	0.0016 (5)	−0.0035 (6)	−0.0006 (5)
O2	0.0363 (7)	0.0313 (7)	0.0365 (7)	0.0043 (5)	−0.0022 (5)	−0.0040 (5)
O3	0.0273 (6)	0.0388 (7)	0.0354 (7)	−0.0091 (5)	0.0028 (5)	−0.0059 (5)
O4	0.0373 (7)	0.0389 (7)	0.0416 (7)	−0.0062 (5)	0.0197 (6)	−0.0141 (6)
O5	0.0402 (7)	0.0370 (7)	0.0431 (7)	−0.0047 (6)	0.0115 (6)	0.0119 (6)
S1	0.0228 (2)	0.0253 (2)	0.0269 (2)	−0.00531 (14)	0.00757 (15)	−0.00294 (14)

Geometric parameters (Å, °)

C1—C2	1.366 (2)	C8—C9	1.484 (3)
C1—C5^{i}	1.406 (2)	C9—H9A	0.9600
C1—H1A	0.9300	C9—H9B	0.9600
C2—C3	1.429 (2)	C9—H9C	0.9600
C2—S1	1.7795 (16)	Co1—O2^{ii}	2.1215 (14)
C3—C4	1.417 (2)	Co1—O2	2.1215 (14)
C3—C3^{i}	1.432 (3)	Co1—N2	2.1242 (15)
C4—C5	1.362 (2)	Co1—N2^{ii}	2.1242 (15)
C4—H4C	0.9300	Co1—O1^{ii}	2.1603 (13)
C5—C1^{i}	1.406 (2)	Co1—O1	2.1603 (13)
C5—H5C	0.9300	N1—H1B	0.8600
C6—C7	1.347 (3)	O1—H6	0.837 (10)
C6—N2	1.387 (2)	O1—H7	0.843 (9)
C6—H6B	0.9300	O2—H4	0.845 (10)
C7—N1	1.365 (3)	O2—H5	0.844 (10)
C7—H7B	0.9300	O3—S1	1.4498 (13)
C8—N2	1.329 (2)	O4—S1	1.4605 (12)
C8—N1	1.343 (2)	O5—S1	1.4596 (13)
C2—C1—C5^{i}	120.04 (16)	O2—Co1—N2	91.27 (6)

C2—C1—H1A	120.0	O2^{ii}—Co1—N2^{ii}	91.27 (6)
C5^{i}—C1—H1A	120.0	O2—Co1—N2^{ii}	88.73 (6)
C1—C2—C3	121.33 (14)	N2—Co1—N2^{ii}	180.000 (1)
C1—C2—S1	116.83 (12)	O2^{ii}—Co1—O1^{ii}	89.81 (5)
C3—C2—S1	121.73 (11)	O2—Co1—O1^{ii}	90.19 (5)
C4—C3—C2	123.03 (14)	N2—Co1—O1^{ii}	90.63 (6)
C4—C3—C3^{i}	119.19 (17)	N2^{ii}—Co1—O1^{ii}	89.37 (6)
C2—C3—C3^{i}	117.78 (17)	O2^{ii}—Co1—O1	90.19 (5)
C5—C4—C3	120.77 (15)	O2—Co1—O1	89.81 (5)
C5—C4—H4C	119.6	N2—Co1—O1	89.37 (6)
C3—C4—H4C	119.6	N2^{ii}—Co1—O1	90.63 (6)
C4—C5—C1^{i}	120.88 (16)	O1^{ii}—Co1—O1	180.0
C4—C5—H5C	119.6	C8—N1—C7	108.86 (16)
C1^{i}—C5—H5C	119.6	C8—N1—H1B	125.6
C7—C6—N2	109.89 (17)	C7—N1—H1B	125.6
C7—C6—H6B	125.1	C8—N2—C6	105.61 (15)
N2—C6—H6B	125.1	C8—N2—Co1	132.19 (13)
C6—C7—N1	105.70 (17)	C6—N2—Co1	122.19 (12)
C6—C7—H7B	127.2	Co1—O1—H6	127.2 (19)
N1—C7—H7B	127.2	Co1—O1—H7	124.0 (15)
N2—C8—N1	109.93 (17)	H6—O1—H7	109 (2)
N2—C8—C9	128.11 (18)	Co1—O2—H4	126 (2)
N1—C8—C9	121.95 (18)	Co1—O2—H5	115.3 (18)
C8—C9—H9A	109.5	H4—O2—H5	110 (3)
C8—C9—H9B	109.5	O3—S1—O5	113.01 (8)
H9A—C9—H9B	109.5	O3—S1—O4	112.08 (8)
C8—C9—H9C	109.5	O5—S1—O4	111.17 (8)
H9A—C9—H9C	109.5	O3—S1—C2	106.22 (8)
H9B—C9—H9C	109.5	O5—S1—C2	106.38 (8)
O2^{ii}—Co1—O2	180.0	O4—S1—C2	107.53 (7)
O2^{ii}—Co1—N2	88.73 (6)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H4···O5^{iii}	0.85 (1)	1.97 (1)	2.815 (2)	174 (3)
O2—H5···O4^{iv}	0.84 (1)	1.88 (1)	2.7149 (19)	171 (3)
O1—H6···O5^{iv}	0.84 (1)	2.21 (1)	3.026 (2)	167 (3)
O1—H7···O3^{v}	0.84 (1)	1.92 (1)	2.7661 (18)	179 (2)
N1—H1B···O4	0.86	2.06	2.906 (2)	170

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

Fig. 1

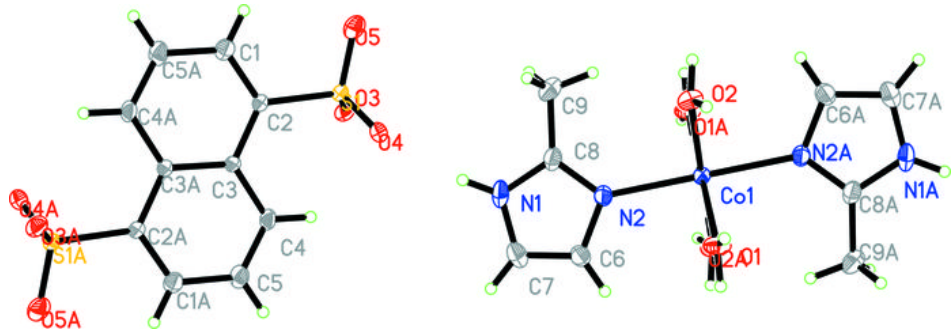
C1
C5A
O5
O3
C4A
C2
O4
C3A
C3
O4A
O3A
S1A
C2A
C4
C5
C1A
O5A
C9
O2
O1A
C6A
C7A
C8
N2A
N1A
N1
Co1
C8A
N2
C6
O2A
O1
C9A
C7

Fig. 2