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μ-Peroxo-bis[acetonitrilebis(ethylenediamine)-cobalt(III)] tetratriflate

Sarah E. McMullen and Karl S. Hagen*

Department of Chemistry, Emory University, 1515 Pierce Dr., Atlanta, GA 30322, USA

Correspondence e-mail: khagen@emory.edu

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Key indicators

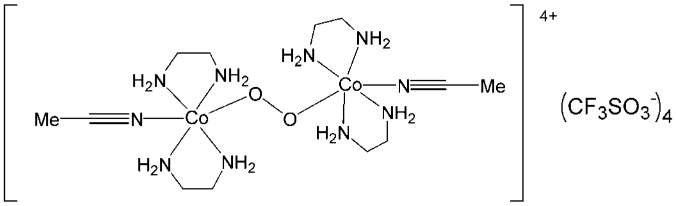
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.100
Data-to-parameter ratio = 13.3

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

The crystals of the title compound, $\{[Co(en)_2(MeCN)]_2(\mu\text{-}O_2)\}(CF_3SO_3)_4$ or $[Co_2(O_2)(C_2H_3N)_2(C_2H_8N_2)_4](CF_3O_3S)_4$, are built of binuclear tetracations and trifluoromethanesulfonate anions. The cation occupies a special position on the inversion center; the separation between the Co atoms, which have a slightly distorted octahedral coordination, is 4.4966 (7) Å, with Co—N(MeCN), Co—O, and average Co—N(en) distances of 1.938 (2), 1.8736 (17), and 1.950 Å, respectively. Both acetonitriles are *trans* to the O—O bridge, the O—O distance being 1.496 (3) Å. The $[Co(en)_2]$ moieties have $\delta\delta$ and the inversion-related $\lambda\lambda$ conformations.

Comment

The crystal structure of the title compound, (I), is built of centrosymmetric μ_2-peroxo tetracationic dicobalt(III) complexes and trifluoromethanesulfonate anions. It is noteworthy that poorly coordinating trifluoromethanesulfonate anions do not form direct bonds to Co atoms, which prefer to complete their coordination environment with the solvent acetonitrile molecules (Fig. 1). The nearly regular octahedral Co atoms each have two ethylenediamine ligands in the $\delta\delta$ conformation for Co1 and the centrosymmetrically related $\lambda\lambda$ for Co1*A* [Co—N(en): 1.941 (2), 1.947 (2), 1.950 (2), and 1.963 (2) Å]. The acetonitrile ligands are *trans* to the O—O bridge, with a Co—N(MeCN) distance of 1.938 (2) Å. In accordance with the crystallographic symmetry, the Co—O—O—Co geometry is *trans* planar, with Co1—O1 and O1—O1*A* distances of 1.8736 (17) and 1.496 (3) Å, respectively. The O1—O1*A* distance is consistent with a peroxo rather than a superoxo bridge. The average for the O—O bond over 29 μ_2-peroxo-dicobalt complexes, retrieved from the October 2001 Release of the Cambridge Structural Database (Allen & Kennard, 1993), is 1.46 (3) Å, whereas the O—O bond lengths in five μ_2-superoxo-dicobalt complexes average 1.33 (2) Å.



(I)

All of the NH groups are involved in either intracationic hydrogen bonds with the peroxide O atoms or interionic hydrogen bonds with the O atoms of trifluoromethane-

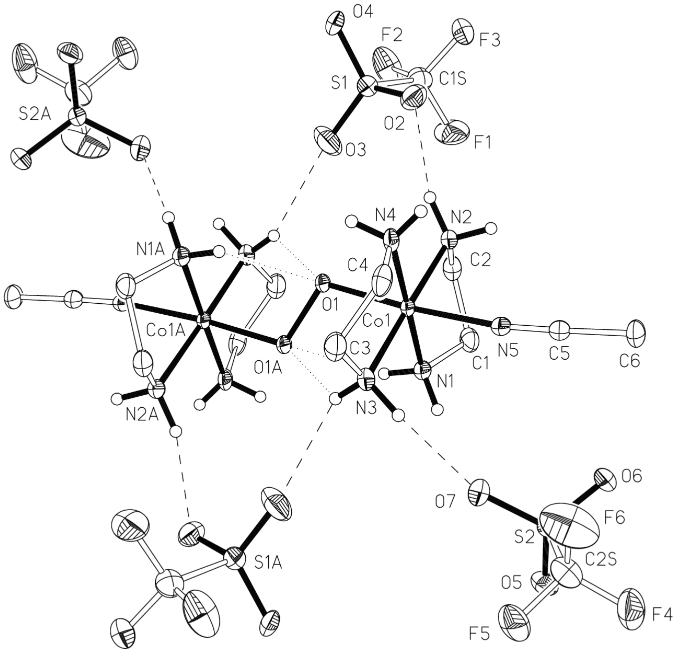


Figure 1

View of the title structure with 50% probability displacement ellipsoids, showing the extensive hydrogen bonding involving the trifluoromethanesulfonate anions. Methylene H atoms have been excluded for clarity.

sulfonate anions (see Table 1). All three O atoms of one of the two independent trifluoromethanesulfonates (S1), but only two of the O atoms of the other trifluoromethanesulfonate (S2), are involved in the hydrogen-bonding system which links the cations and anions into stacks stretching along the *b* axis (Fig. 2). The stacks are connected through hydrogen bonds involving the remaining O atom on the S2 trifluoromethanesulfonate (O6).

Experimental

The title compound was isolated as brown plates from an air-oxidized (approximately one month exposure) solution containing $Co(OTf)_2\cdot 4MeCN$ (0.5 mmol), ethylenediamine (0.4 mmol), benzoic acid (0.6 mmol), H_2O (0.2 mmol), and triethylamine (0.8 mmol).

Crystal data

$[Co_2(O_2)(C_2H_3N)_2(C_2H_8N_2)_4]$-$(CF_3O_3S)_4$
$M_r = 1068.64$
Monoclinic, $P2_1/n$
$a = 13.164$ (1) Å
$b = 8.3883$ (7) Å
$c = 17.939$ (2) Å
$\beta = 97.869$ (2)°
$V = 1962.2$ (3) Å^3
$Z = 2$

$D_x = 1.809$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6714 reflections
$\theta = 2.3$–32.2°
$\mu = 1.18$ mm^{-1}
$T = 100$ (2) K
Plate, brown
0.35 × 0.13 × 0.04 mm

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.661$, $T_{max} = 0.954$
17919 measured reflections

4487 independent reflections
3403 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -10 \rightarrow 10$
$l = -23 \rightarrow 23$

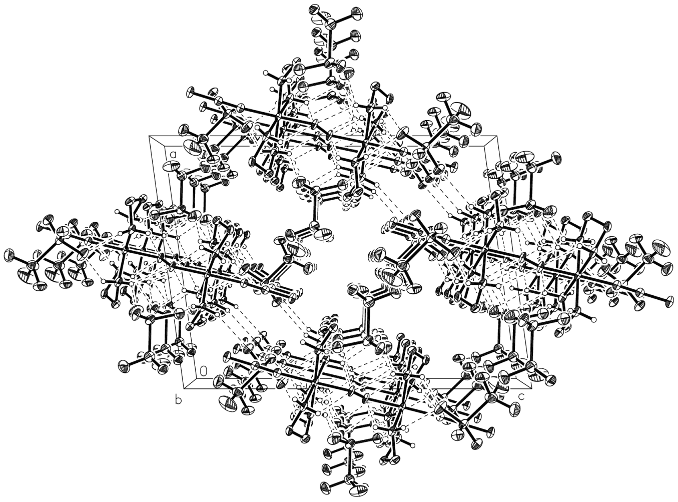


Figure 2

The stacks of cations and anions in the title structure viewed down the *b* axis. Methylene H atoms have been excluded for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.100$
$S = 1.04$
4487 reflections
338 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.49$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O7	0.89 (3)	2.33 (3)	3.162 (3)	157 (2)
N1—H1D···O1^{i}	0.87 (3)	2.22 (3)	2.832 (3)	128 (3)
N1—H1D···O4^{ii}	0.87 (3)	2.49 (3)	3.130 (3)	131 (3)
N2—H2C···O2	0.92 (3)	2.04 (3)	2.937 (3)	164 (3)
N2—H2D···O6^{iii}	0.87 (3)	2.38 (3)	3.150 (3)	147 (3)
N3—H3C···O1^{i}	0.84 (3)	2.29 (3)	2.840 (3)	123 (3)
N3—H3C···O3^{i}	0.84 (3)	2.29 (3)	2.908 (3)	130 (3)
N3—H3D···O7	0.93 (3)	2.35 (3)	3.127 (3)	141 (2)
N4—H4C···O5^{iv}	0.77 (3)	2.30 (3)	3.032 (3)	160 (3)
N4—H4D···O4^{v}	0.83 (3)	2.22 (3)	2.947 (3)	147 (3)

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

All H atoms were placed in geometrically calculated positions and included in subsequent refinement in an isotropic approximation (the refined bond-length ranges for N—H and C—H bonds are 0.77–0.93 and 0.87–1.01 Å, respectively). There is a large peak (1.493 e Å^{-3}) between S1 and O3 of a trifluoromethanesulfonate anion. This could not be attributed to any reasonable disorder model.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART* and *SAINT*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); 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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