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Tris(1,10-phenanthroline-κ^2N,N')-cobalt(III) tris(trifluoromethanesulfonate) dihydrate

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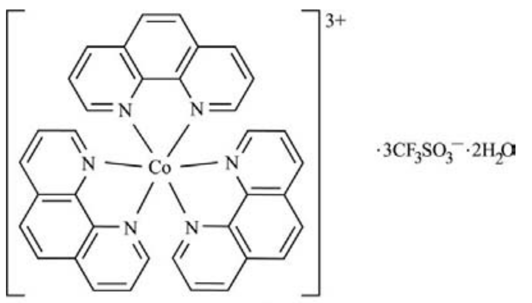
The title compound, $[Co(C_{12}H_8N_2)_3](CF_3SO_3)_3\cdot 2H_2O$, crystallizes to form infinite chains of complex cations that are connected through offset face-to-face and edge-to-face interactions between their phenanthroline ligands. The chains are themselves interconnected through weak offset face-to-face ligand interactions. The three trifluoromethanesulfonate anions of the asymmetric unit are connected with one another through the two water molecules by hydrogen bonds. One of the trifluoromethanesulfonate anions is described by a disorder over three positions, with occupancies of 0.35, 0.35 and 0.3 in the refined model.

Comment

The tris(1,10-phenanthroline)cobalt(III) complex, $[Co(phen)_3]^{3+}$, was first synthesized by Pfeiffer & Werdelmann (1950). It has been used in conjunction with the tris(1,10-phenanthroline)-cobalt(II) complex as a redox couple in dye-sensitized solar cells (Nusbaumer, 2004), serving as an alternative to the prolific I^-/I_3^- couple (Grätzel, 2005). Cobalt complexes with various ligands have been used with trifluoromethanesulfonate counter-ions (Wen *et al.*, 2000; Nusbaumer, 2004); the title compound, (I), is an example of such a complex.



(I)

Compound (I) crystallizes as a racemic triclinic structure with two water molecules per complex cation. Powder X-ray diffraction confirms that the synthesis of (I) yields a stoichiometric compound with only one crystal structure.

The asymmetric unit contains one $[Co(phen)_3]^{3+}$ cation, three trifluoromethanesulfonate anions and two solvent water molecules. The three trifluoromethanesulfonate ions interact with the two water molecules to form a chain, bridged by hydrogen bonds (Fig. 1 and Table 1). The complex cations are not isolated by the anions and water molecules, but rather they interact with one another in motifs that have been described in the literature (Russell *et al.*, 2001). The structure contains four different pairs of cations with a significant van der Waals interaction between ligands (Figs. 2*a*–*d*).

In general, two types of motifs are distinguished, depending on whether the planes of the interacting ligands are parallel (face-to-face) or perpendicular (edge-to-face) to one another. Offset face-to-face (OFF) interactions are clearly present in the motifs shown in Figs. 2(*b*) and 2(*c*), and an edge-to-face (EF) interaction can be recognized in Fig. 2(*b*). However, the motifs presented in Figs. 2(*a*) and 2(*d*) have limited OFF or EF characteristics. This is supported by additional geometric parameters given in Table 2. It should be noted that Russell *et al.* (2001) limited their characterization of OFF ligand interactions to those complex pairs that fulfilled certain geometric criteria. In our context, where all motifs are centrosymmetric, these translate to a plane-to-plane distance in the range

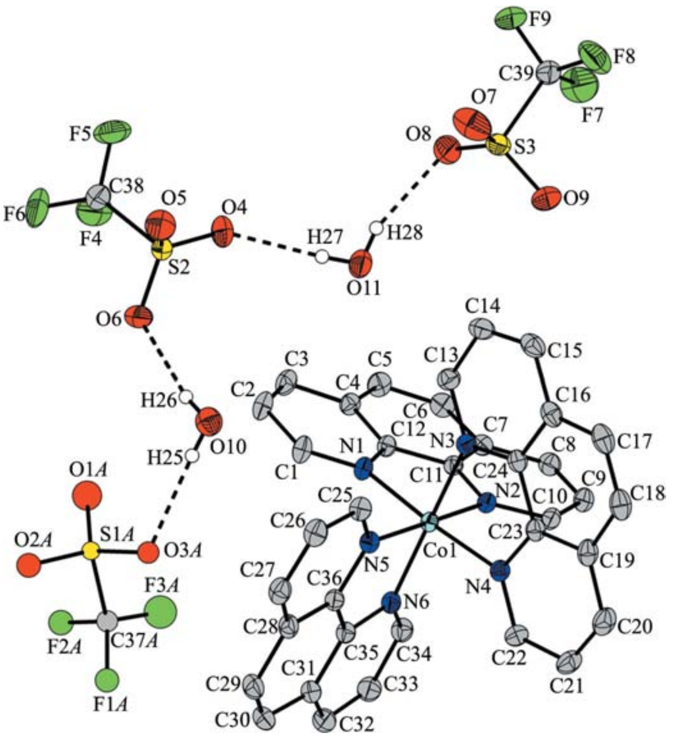


Figure 1
The asymmetric unit of the crystal structure of (I) at 140 K, showing the atomic labeling and 50% probability displacement ellipsoids. Aromatic H atoms and two sites of the disordered anion have been omitted for clarity. Dashed lines represent hydrogen bonds.

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3.2–3.6 Å and a shortest C···C distance between a C atom equivalent to C11 (assuming D_3 symmetry for the complex cation) and any C atom of the second phenanthroline ligand not exceeding 4.0 Å (Russell *et al.*, 2001). As motifs (*a*) and (*d*) do not comply with these requirements, they will be considered to be weak interactions compared with (*b*) and (*c*).

Further characterization of these motifs was carried out by calculating the energy contributions arising from van der Waals (vdW) and Coulombic interactions, considering either a complete pair of complex cations or only a pair of ligands forming an OFF or EF motif. This was achieved using the methodology of Russell *et al.* (2001). The atomic charge distribution of a complex cation was approximated on the basis of the charge distribution of an $[Fe(phen)_3]^{2+}$ cation (Russell *et al.*, 2001), multiplying each partial charge by 1.5 to achieve the correct total charge. Although this procedure does not take into account details such as electronegativity in distributing the additional charge, other approaches (such as adding an equal fractional charge to each atom) only result in minor quantitative deviations. The obtained values for the interactions (Table 3) show that only OFF interaction motifs (*b*) and (*c*) contribute significantly to a favorable attractive energy. The total intermolecular energy is positive in all cases, however, owing to the high total charge of the complex cations.

It is interesting to note that motif (*a*), in which the distance between Co atoms is shortest, has the least favorable interaction energy. The close proximity of the cations leads to a strong Coulombic repulsion and only a weak van der Waals attraction between ligands, since their close approach causes them to avoid one another.

The packing of the complex cations can be described as infinite chains along [111] that are formed through the strong interaction motifs (*b*) and (*c*), as shown in Fig. 2(*e*). These chains are interconnected in two directions by the weaker interaction motifs (*a*) and (*d*), and form a three-dimensional network similar to a distorted diamond structure. The voids and channels of this network are then filled with the short chains of anions and water molecules. The two ordered trifluoromethanesulfonate anions are located in channels (rings), whereas the disordered trifluoromethanesulfonate anion points into a void (cage). This might provide enough freedom to allow a rocking motion of the anion, resulting in the observed disorder. Such anionic and solvent disorder is a common phenomenon found in crystals containing $[M(phen)_3]^{n+}$ complex cations (Anderson, 1973; Baker *et al.*, 1975; Boys *et al.*, 1984; Deacon *et al.*, 1979; Freire *et al.*, 1998; Goodwin *et al.*, 1984; Koh *et al.*, 1994; Luck *et al.*, 2000).

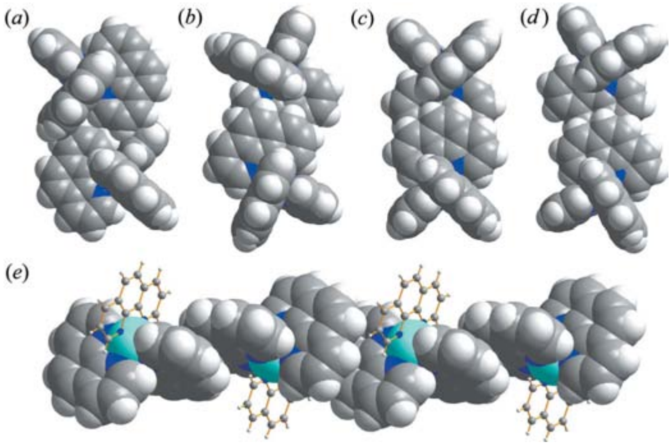

Figure 2
(*a*)–(*d*) Supramolecular motifs formed by pairs of complex cations in the order of increasing Co···Co distance. The view is perpendicular to the phenanthroline ligand planes participating in an OFF interaction (see *Comment*). (*e*) Chains formed from an alternating succession of motifs (*b*) and (*c*). The third ligand is shown as a ball-and-stick model for clarity.

Experimental

Compound (I) was synthesized according to a method described by Nusbaumer (2004). To cobalt(II) chloride hexahydrate (236 mg) in water (10 ml) was added 1,10-phenanthroline hydrate (596 mg) in methanol (2 ml), and the mixture was stirred at room temperature for 30 min. Bromine (0.1 ml) in water (8 ml) was added dropwise, whereupon a red–brown powder precipitated. The temperature was elevated to 318–323 K to complete the oxidation. Immediately after the oxidation step, the counter-ions were exchanged by adding silver trifluoromethanesulfonate (0.567 mg) in methanol (2.5 ml). The Ag halide precipitate was filtered off, leaving an orange solution. Evaporation under reduced pressure led to large orange crystals.

Crystal data

$[Co(C_{12}H_8N_2)_3](CF_3O_3S)_3\cdot 2H_2O$	$\gamma = 91.878\ (1)^\circ$
$M_r = 1082.78$	$V = 2069.2\ (1)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 12.4096\ (4)$ Å	Mo $K\alpha$ radiation
$b = 13.0039\ (4)$ Å	$\mu = 0.68$ mm^{-1}
$c = 13.4669\ (4)$ Å	$T = 140\ (2)$ K
$\alpha = 92.764\ (1)^\circ$	0.28 × 0.20 × 0.15 mm
$\beta = 107.367\ (1)^\circ$	

Data collection

Bruker SMART 6000 diffractometer	36176 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	14813 independent reflections
$T_{min} = 0.77$, $T_{max} = 0.90$	13149 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	21 restraints
$wR(F^2) = 0.107$	All H-atom parameters refined
$S = 1.05$	$\Delta\rho_{max} = 0.75$ e Å^{-3}
14813 reflections	$\Delta\rho_{min} = -0.63$ e Å^{-3}
758 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O10—H26···O6	0.77 (3)	2.15 (3)	2.913 (2)	170 (3)
O10—H25···O3*A*	0.75 (3)	2.14 (3)	2.891 (7)	177 (3)
O10—H25···O3*B*	0.75 (3)	2.38 (3)	3.126 (7)	178 (3)
O10—H25···O3*C*	0.75 (3)	2.08 (3)	2.817 (6)	170 (3)
O11—H27···O4	0.77 (3)	2.07 (3)	2.841 (2)	175 (3)
O11—H28···O8	0.78 (3)	2.12 (3)	2.870 (2)	162 (3)

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Table 2
Additional geometrical parameters (Å) for possible OFF motifs.

Motif	Co···Co	Interplanar distance[i]	C···C[ii]
(*a*)	9.1	3.1	6.4 (C36···C25^{iii})
(*b*)	9.7	3.4	4.0 (C11···C6^{iv})
(*c*)	10.0	3.5	3.9 (C36···C30^{v})
(*d*)	11.1	3.0	4.2 (C24···C17^{vi})

Notes: (i) the distance between the two ligand planes in the OFF motif; (ii) the shortest distance between a C atom equivalent to C11 (assuming D_3 symmetry) and any C atom of the second phenanthroline ligand of the OFF motif. Symmetry codes: (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y+1, -z+2$; (v) $-x, -y, -z+1$; (vi) $-x, -y+1, -z+2$.

Table 3
Calculated energy contributions (kcal mol^{-1}) for all motifs.

Motif	Total	vdW	Coulombic	Primary motif	Total[i]	vdW[i]	Coulombic[i]
(*a*)	12.4	−8.6	21.0	OFF	−0.2	−1.3	1.1
(*b*)	3.0	−16.5	19.5	OFF	−6.5	−9.4	2.9
				EF	−0.3	−2.8	2.5
(*c*)	5.0	−14.2	19.2	OFF	−6.8	−9.5	2.7
(*d*)	8.9	−6.9	15.8	OFF	−0.9	−4.7	3.8

Notes: (i) the calculated energy considering only the two phenanthroline ligands that characterize a primary motif. Note that the EF motif exists twice per cation pair.

All atoms except those of the disordered trifluoromethanesulfonate anion were refined anisotropically. The final model describes the disorder by considering three different orientations of the disordered trifluoromethanesulfonate anion (referred to as *A*, *B* and *C*). Restraints were used in order to equalize the C—S bond lengths (of *A*, *B* and *C*) and the C—F, S—O and C···O distances (separately for *A* and *B*). Occupancies were constrained to add to unity and were fixed after convergence to 35 (*A*), 30 (*B*) and 35% (*C*). All H-atom parameters were refined, giving C—H distances in the range 0.88 (3)–0.96 (2) Å.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3194). Services for accessing these data are described at the back of the journal.

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