

Tetraaqua(1,10-phenanthroline- κ^2N,N')cobalt(II) dinitrate: a hydrogen-bonded supramolecular network

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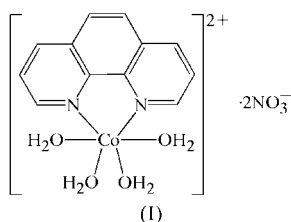
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The structure of the title compound, $[\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{NO}_3)_2$, consists of tetraaqua(1,10-phenanthroline)cobalt(II) cations and nitrate anions. The Co atom is located on a twofold rotation axis and is coordinated by the two N atoms of a 1,10-phenanthroline ligand and four O atoms of water molecules. The cations and anions are linked by hydrogen-bond interactions into a three-dimensional supramolecular network.

Comment

Metal-organic supramolecular complexes with various fascinating topologies have been studied widely for their versatile chemical and physical properties and potential applications as functional materials (Janiak, 2003; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003). Self-assembly based on molecular building blocks has become an effective approach to construct these functional materials. In the development of supramolecular chemistry, hydrogen-bonding and π - π interactions acting as two main driving forces play an important role in self-assembling multi-dimensional metal-organic supramolecular frameworks or networks (Graham & Pike, 2000; Mitzi *et al.*, 1995). We report here the structure of $[\text{Co}(\text{phen})(\text{H}_2\text{O})_4](\text{NO}_3)_2$ (phen is 1,10-phenanthroline), (I), in which hydrogen-bond interactions lead to a three-dimensional supramolecular network.



Compound (I) (Fig. 1) consists of $[\text{Co}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$ cations and nitrate anions. The Co atom, lying on a twofold

rotation axis, is six-coordinated by the two N atoms of a chelating phen ligand and four O atoms of water molecules in an octahedral geometry. The twofold rotation axis passes through the phen ligand. Therefore, the asymmetric unit of (I) contains half of the Co atom and half of the phen ligand accompanied by two water molecules and one nitrate anion. In the complex cation, two water molecules and two N atoms are located in the equatorial plane, and the other two water molecules occupy the axial positions. Bond lengths and angles are in normal ranges (Wang *et al.*, 2005; Yang *et al.*, 2003). Each of the coordinated water molecules donates its two H atoms to two neighboring nitrate anions, while each nitrate ion accepts four hydrogen bonds from four neighboring coordinated water molecules (Table 1). The equatorial water molecule (O2) is hydrogen bonded to the O5 atom of two centrosymmetrically related nitrates at $(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, so generating a centrosymmetric $R_2^2(8)$ motif (Bernstein *et al.*, 1995). The axial water molecule acts as a hydrogen-bond donor to atom O3 of the nitrate group at (x, y, z) and atom O4 of another nitrate group at $(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$. In this way, a $C_4^4(12)$ helical chain is formed along the 2_1

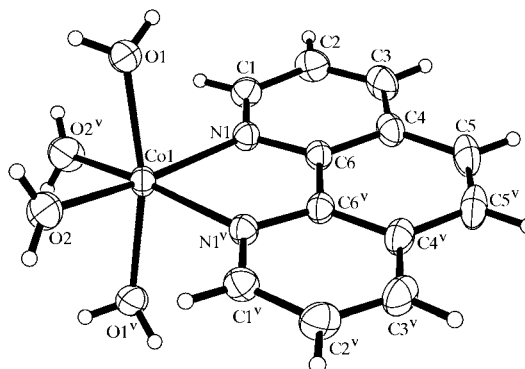


Figure 1

The structure of the complex cation in (I), showing the atomic numbering scheme. The nitrate anions are not shown. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (v) $-x + 1, y, -z + \frac{1}{2}$.]

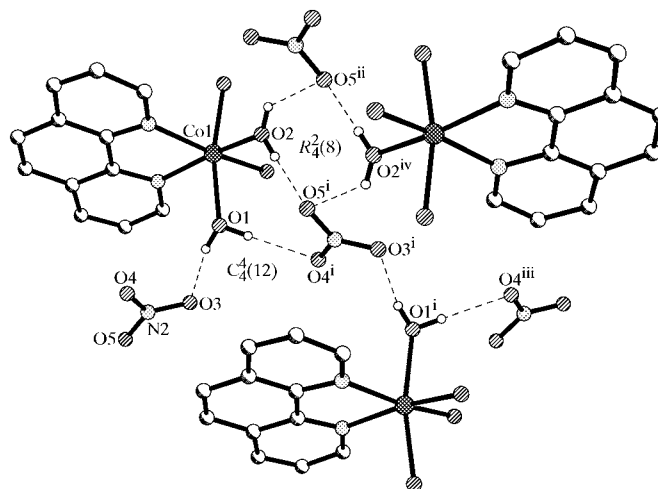


Figure 2

Two types of hydrogen-bonding motifs in (I). [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z + 1$.]

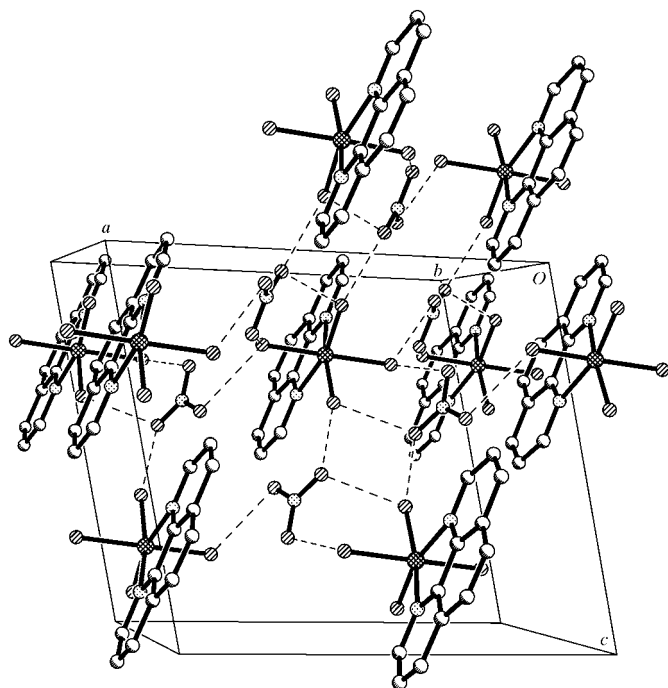


Figure 3
View of the three-dimensional supramolecular structure in (I).

screw axis in the [010] direction (Fig. 2). As a result, each complex cation is hydrogen bonded to six nitrate anions, which in turn link together eight cations (Fig. 3). The effect of the two hydrogen-bond motifs is to link the complex cations and nitrate anions into a three-dimensional network. The structure is further stabilized by weak π - π stacking interactions between two adjacent phen rings in an offset arrangement. The distance between the centroids of the six-membered C1-C4/C6/N1 ring and its equivalent at $(1-x, 1-y, -z)$ is 3.73 (1) Å and the average interplanar spacing is 3.431 Å.

The phen ligand has strong chelating ability. Co^{II} -phen complexes can be formed with a Co^{II} to phen ratio of 1:1, 1:2 or 1:3. We have previously reported the structure of a 1:2 complex, $[\text{Co}(\text{phen})_2(\text{NO}_3)]\text{NO}_3 \cdot 4\text{H}_2\text{O}$ (Li *et al.*, 2006), in which a layer-like structure was observed, consisting of hydrogen-bonded water-nitrate anionic sheets and π - π -interaction-linked $[\text{Co}(\text{phen})_2(\text{NO}_3)]^+$ cationic sheets. Thus, the hydrogen-bonding interactions between water molecules and nitrates, and π - π interactions between phen ligands, are crucial to the structural architecture. We intend to examine further how anions influence supramolecular structures in the Co^{II} -phen system by varying the ratio of Co^{II} to phen when the anions have different geometry and hydrogen-bonding ability.

Experimental

An aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60 mg, 0.1 mmol) and an ethanol solution of phen (40 mg, 0.1 mmol) were mixed and stirred for 30 min. The resulting solution was then left for aerial evaporation at room temperature. Dark-red crystals of (I), suitable in size for single-crystal X-ray diffraction, appeared after three weeks (yield 38%).

Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{NO}_3)_2$
 $M_r = 435.22$
 Monoclinic, $C2/c$
 $a = 13.9136$ (16) Å
 $b = 10.4852$ (12) Å
 $c = 12.3991$ (14) Å
 $\beta = 102.165$ (2)°
 $V = 1768.2$ (3) Å³

$Z = 4$
 $D_x = 1.635$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.03$ mm⁻¹
 $T = 293$ (2) K
 Block, dark red
 $0.30 \times 0.25 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.746$, $T_{\text{max}} = 0.887$

4991 measured reflections
 1752 independent reflections
 1618 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 26.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.075$
 $S = 1.05$
 1752 reflections
 135 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.9246P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1-H1A \cdots O3	0.84 (2)	2.08 (2)	2.891 (2)	163 (3)
O1-H1B \cdots O4 ⁱ	0.83 (2)	2.05 (2)	2.884 (2)	175 (2)
O2-H2A \cdots O5 ⁱ	0.83 (2)	1.91 (2)	2.736 (2)	179 (3)
O2-H2B \cdots O5 ⁱⁱ	0.80 (2)	2.27 (3)	2.867 (2)	132 (2)

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

H atoms of the phen ring system were positioned geometrically and refined as riding, with C-H distances of 0.93 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. H atoms of water molecules were located in a difference map and refined with restraints of O-H = 0.85 (2) Å and H \cdots H = 1.33 (2) Å, and with $U_{\text{iso}}(\text{H})$ values set at $1.5U_{\text{eq}}(\text{O})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3059). Services for accessing these data are described at the back of the journal.

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