metal-organic papers

Diaquabis(1,10-phenanthroline-κ^2N,N')cobalt(II) dihydrogenphosphate nitrate dihydrate

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The structure of the title compound, $[Co(C_{12}H_8N_2)_2(H_2O)_2](H_2PO_4)(NO_3)\cdot 2H_2O$, is built up from layers of complex $[Co(C_{12}H_8N_2)_2(H_2O)_2]^{2+}$ cations and phosphate units parallel to (010), delimiting a-axis tunnels in which the nitrate anions and the water molecules are located. The molecular structure is stabilized by intermolecular hydrogen bonds and weak π–π stacking interactions.

Comment

Organic–inorganic hybrid metal phosphates have been greatly developed, due to their potential application in the fields of catalysis, adsorption, and optical and electromagnetic functional materials (Ferey, 2001; Cui *et al.*, 2004).

(I)
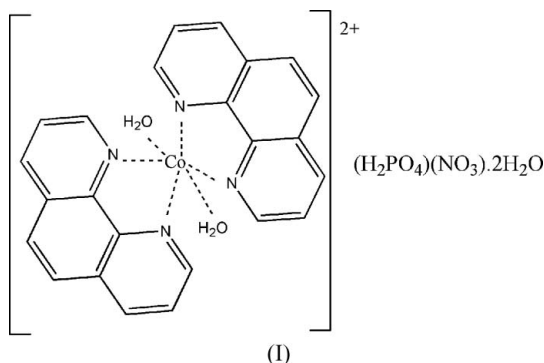
The title compound, (I), is made up of complex $[Co(C_{12}H_8N_2)_2(H_2O)_2]^{2+}$ cations, nitrate and dihydrogenphosphate anions and two water molecules (Fig. 1). The $[Co(C_{12}H_8N_2)_2(H_2O)_2]^{2+}$ cation and phosphate units form layers parallel to (010), thus delimiting a-axis tunnels in which the nitrate anions and the water molecules are located.

The metal ion exhibits a distorted octahedral environment, with the four N atoms from two bidentate phenanthroline (phen) ligands and two O atoms of aqua ligands in *cis* positions. Atoms O1, N1, N3 and N4 constitute the equatorial plane of the octahedron, the mean deviation being 0.148 (1) Å and the Co atom being 0.075 (1) Å out of this plane.

The Co—N and Co—O bond lengths of 2.134 (3)–2.181 (3) and 2.049 (3)–2.114 (3) Å, respectively, agree with those reported for similar compounds (Abdelhak *et al.*, 2004; Fan *et al.*, 2005).

Within the crystal structure, there are strong intermolecular O—H···O hydrogen bonds between coordinated water molecules and phosphate anions (Fig. 2). There is also a significant π–π stacking interaction between the N3/C13–C17 ring and its symmetry equivalent [symmetry code $(1 - x, 1 - x, 1 - z)$],
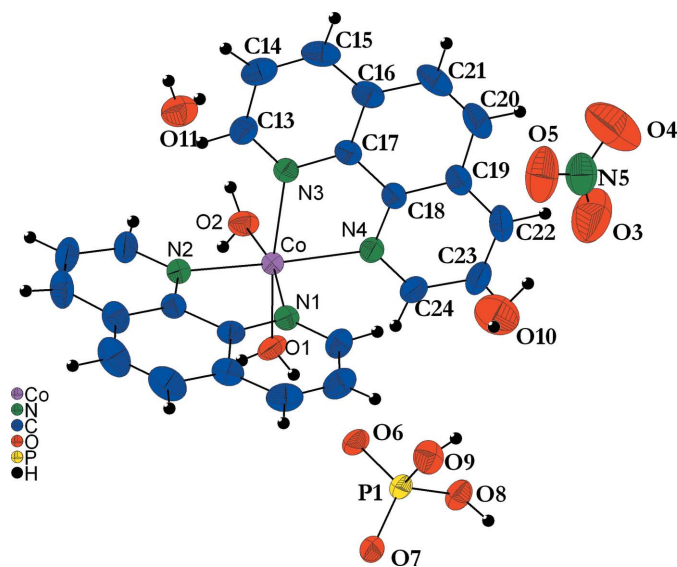
Figure 1
The asymmetric unit of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radii.
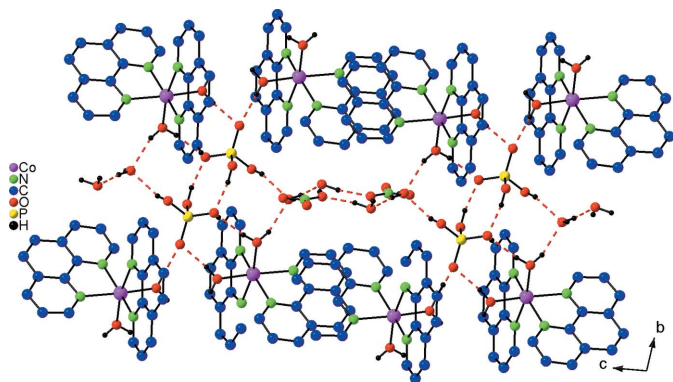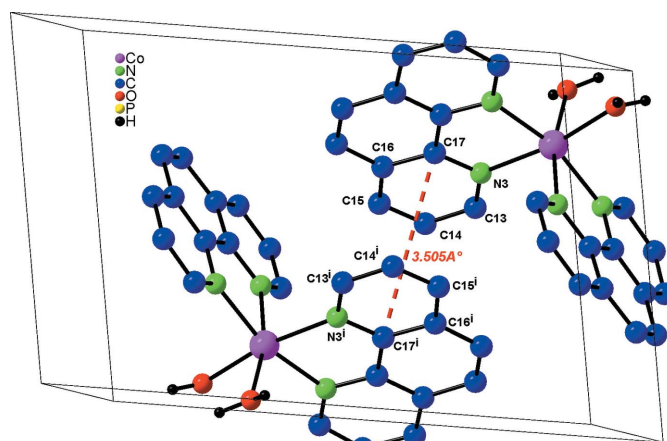

Figure 2
The crystal packing, viewed down the a axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

with an interplanar distance of 3.505 Å. These generate two-dimensional layers parallel to (010) (Fig. 3).

Strong hydrogen bonds between the $H_2PO_4^-$ units, nitrate anions and uncoordinated water molecules connect the two-dimensional layers, building up a three-dimensional framework in which the nitrate anions and the water molecules are located.

Experimental

The title compound, (I), was prepared as good quality dark-red single crystals from a mixture of cobalt(II) nitrate hexahydrate (0.3 g), 1,10-phenanthroline monohydrate (0.4 g) and phosphoric acid (3 ml) dissolved in water (20 ml). The resulting mixture was heated to boiling point and stirred for 1 h. A brown precipitate formed

Figure 3
A view of part of a sheet of molecules of the title compound, linked by π–π stacking interactions between the neighbouring phen ligands. H atoms of phen ligands have been omitted for clarity. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]

immediately. After a few days, single crystals were obtained by slow evaporation of an aqueous solution at room temperature.

Crystal data

$[Co(C_{12}H_8N_2)_2(H_2O)_2](H_2PO_4)$- $(NO_3)\cdot 2H_2O$	$\gamma = 93.49\ (5)°$
$M_r = 650.40$	$V = 1359.6\ (11)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.245\ (4)$ Å	$D_x = 1.589$ Mg m^{-3}
$b = 10.487\ (6)$ Å	Mo $K\alpha$ radiation
$c = 14.357\ (6)$ Å	$\mu = 0.76$ mm^{-1}
$\alpha = 97.72\ (4)°$	$T = 298\ (2)$ K
$\beta = 98.49\ (4)°$	Prism, red
	$0.6 \times 0.6 \times 0.4$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	5693 independent reflections
$\omega/2\theta$ scans	3889 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.031$
	$\theta_{max} = 27.0°$
$T_{min} = 0.640$, $T_{max} = 0.738$	2 standard reflections
5917 measured reflections	frequency: 120 min
	intensity decay: 5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 0.2914P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.003$
5693 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
405 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—HW1···O6	0.82 (2)	1.87 (2)	2.673 (3)	168 (4)
O1—HW2···O6^i	0.83 (2)	1.84 (2)	2.659 (4)	170 (4)
O2—HW3···O7^i	0.83 (2)	1.95 (2)	2.772 (4)	171 (4)
O2—HW4···O11	0.82 (2)	1.99 (2)	2.784 (4)	161 (3)
O8—H25···O7^{ii}	0.82	1.82	2.632 (3)	173
O9—H26···O11^{iii}	0.82	1.97	2.747 (4)	157
O11—HW5···O10	0.84 (4)	1.92 (5)	2.739 (5)	168 (6)
O11—HW6···O4^{iv}	0.82 (2)	2.30 (3)	3.026 (6)	148 (5)

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O11—HW6$\cdots$O3^{iv}	0.82 (2)	2.41 (3)	3.188 (6)	160 (5)
O10—HW7$\cdots$O3	0.85 (2)	2.11 (2)	2.938 (6)	168 (4)
O10—HW7$\cdots$O5	0.85 (2)	2.65 (4)	3.278 (7)	132 (4)
O10—HW8$\cdots$O5^{v}	0.83 (2)	2.08 (2)	2.894 (6)	172 (5)

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

All H atoms attached to C atoms or to hydroxyl groups were treated as riding on their parent atoms, with C—H = 0.93 Å [U_{iso}(H) = 1.2U_{eq}(C)] and O—H = 0.82 Å [U_{iso}(H) = 1.5U_{eq}(C)]. The water H atoms were refined using the restraints O—H = 0.82 (1) Å, H$\cdots$H = 1.39 (1) Å and U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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