Diaquabis(4-fluorobenzoato-κO)-bis(nicotinamide-κN)cobalt(II)

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The title compound, $[Co(C_7H_4FO_2)_2(C_6H_6N_2O)_2(H_2O)_2]$, is a three-dimensional hydrogen-bonded supramolecular complex. The Co^{II} ion resides on a centre of symmetry and is in an octahedral coordination environment comprising two pyridyl N atoms, two carboxylate O atoms and two O atoms from water molecules. Intermolecular N—H···O and O—H···O hydrogen bonds produce $R_3^2(6)$, $R_2^2(12)$ and $R_2^2(16)$ rings, which lead to two-dimensional chains. An extensive three-dimensional network of C—H···F, N—H···O and O—H···O hydrogen bonds and π–π interactions are responsible for crystal stabilization.

Comment

Metal–organic supramolecular complexes with various fascinating topologies have been studied widely for their versatile chemical and physical properties and for their 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 constructing

(I)
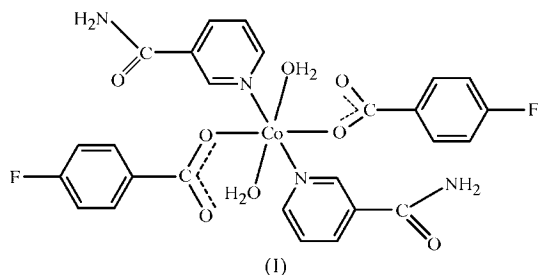
these functional materials. In the development of supramolecular chemistry, hydrogen-bonding and π–π interactions acting as two main driving forces play an important role in self-assembling multidimensional metal–organic supramolecular frameworks or networks (Graham & Pike, 2000; Mitzi et al., 1995). Some interesting coordination polymers

assembled with 4,4'-bipyridine (bipy) have been reported, showing various structural motifs, including two-dimensional layers (Carlucci et al., 1997; Tong et al., 1998) and three-dimensional nets (Lu et al., 1998; Hagrman et al., 1998; Kondo et al., 1999; Greve et al., 2003; Zhang et al., 1999). We report here the structure of the title compound, (I), in which hydrogen-bond interactions lead to a three-dimensional supramolecular network.

The molecular structure, with the atomic labelling scheme, is presented in Fig. 1. Compound (I) crystallizes in the space group $P2_1/n$ with $Z' = \frac{1}{2}$. The Co^{II} ion is located on a symmetry centre and is coordinated by two O atoms from two equivalent carboxylate groups and two O atoms from two water molecules, which form the equatorial plane, and by two N atoms from as many 4,4'-bpy ligands at the axial positions (Table 1). The coordination geometry around the Co^{II} ion can be described as a slightly distorted octahedron. The distortion arises from the N1—Co1—N1^i axis, which is not perfectly perpendicular to the coordination plane (O2/O4/O2^i/O4^i/Co1). Carboxylate atom O3 is pendant, with a longer Co1···O3 distance [3.347 (2) Å] and larger Co1—O2—C7 angle consistent with the absence of bonding between Co1 and O3. The carboxylate group is not coplanar with the attached benzene ring, the dihedral angle between the planes being 8.7 (3)°. The pyridine and benzene rings are planar, the maximum deviations from the least-squares planes being 0.0042 (15) Å for atom C3 and 0.0056 (16) Å for atom C8.

Molecules are linked by intermolecular hydrogen bonding, and we employ graph-set notation (Bernstein et al., 1995) to describe the resulting patterns. Molecules of (I) are linked into sheets by a combination of O—H···O, N—H···O, C—H···O and C—H···F hydrogen bonds (Table 2). Thus, C5—H5···O2, O4—H4A···O3 and C1—H1···O2^i hydrogen bonds produce an $S(5)S(6)S(5)$ motif (Fig. 1). Ring atom C5 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, via H5, to atom F1^v, so forming a $C(11)[R_2^2(22)]$ chain of rings running
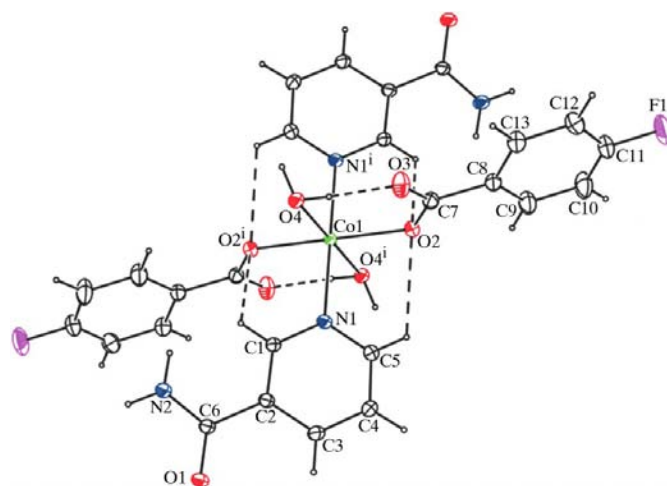

Figure 1
View of one molecule of (I), showing the atom-numbering scheme. Hydrogen bonds are indicated by dashed lines. Displacement ellipsoids are drawn at the 30% probability level. [Symmety code: (i) $-x$, $-y + 1$, $-z + 1$.]

parallel to the [100] direction and centrosymmetric $R_2^2(22)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer) (Fig. 2). Fig. 3 shows the way in which the amino group, aqua ligand and carboxylate atom O1 enter into intermolecular hydrogen-bonding interactions. As a result, zigzag tapes are formed through O4—H4B···O1^{iv}, N2^{iii}—H2B^{iii}···O1^{iv}, N2^{iii}—H2A^{iii}···O4 and N2—H2B···O1^{iii} interactions (symmetry codes as in Table 2), which define $R_3^2(6)$ and $R_2^2(12)$ ring patterns. Furthermore, water atom O4 in the reference molecule at (x, y, z) acts as hydrogen-bond donor, via H4B, to atom O1^{iv}, so forming a $C(8)[R_2^2(16)]$ chain of rings running parallel to the [010] direction and centrosymmetric $R_2^2(16)$ rings centred at $(0, n, \frac{1}{2})$ (n = zero or integer). Propagation of three hydrogen bonds thus forms a complex chain of rings, containing $R_3^2(6)R_2^2(12)R_2^2(16)$ sequences of three edge-fused rings.

In the extended structure of (I), shown in Fig. 4, an intermolecular π–π contact occurs between the two symmetry-related pyridine rings of neighbouring molecules. Ring A is oriented in such a way that the perpendicular distance from A to A^{vi} is 3.588 Å [symmetry code: (vi) $-x$, $-y + 2$, $-z + 1$]. The distance between the ring centroids is 3.7612 (12) Å. The π–π

Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric $R_2^2(22)$ dimer. Dashed lines indicate hydrogen bonds. H atoms not involved in these interactions have been omitted for clarity.

Figure 3
Part of the crystal structure of (I), showing the formation of an edge-fused chain of $R_3^2(6)$, $R_2^2(12)$ and $R_2^2(16)$ rings. H atoms not involved in these interactions have been omitted for clarity. (Symmetry codes as in Table 2.)
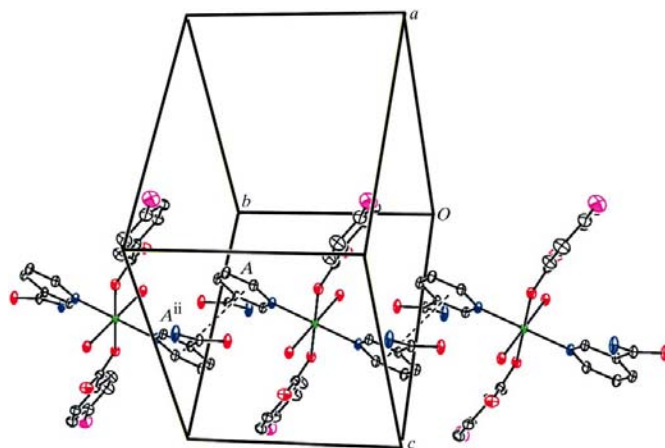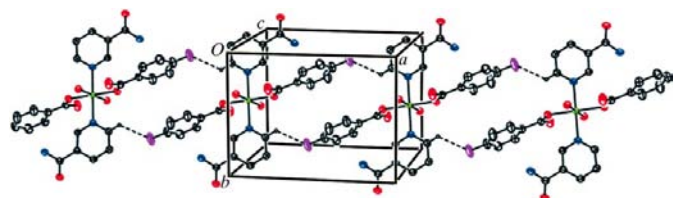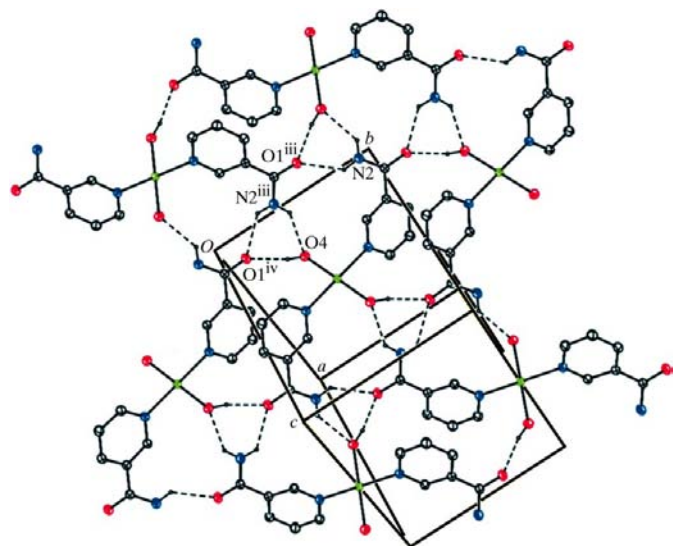

Figure 4
Part of the crystal structure of (I), showing the formation of a chain along [010] generated by π–π interactions. For the sake of clarity, H atoms have been omitted. [Symmetry code: (vi) $-x$, $-y + 2$, $-z + 1$.]

interaction produces a chain running parallel to the [010] direction.

These intermolecular interactions, namely an extensive network of hydrogen bonds and π–π stacking, are responsible for constructing an infinite three-dimensional lattice in the crystal structure of (I).

Experimental

p-Halobenzoic acid sodium salts were prepared according to the following equation: $2p\text{-FBA} + 2\text{NaHCO}_3 \rightarrow 2\text{Na}(p\text{-FBA}) + 2\text{CO}_2 + 2\text{H}_2\text{O}$ (p-FBA is p-fluorobenzoic acid). The Co^{II}–p-FBA salt was then synthesized from the Na(p-FBA) salt by the substitution reaction $2\text{Na}(p\text{-FBA}) + \text{CoSO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{Co}(p\text{-FBA})_2 \cdot n\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$. The compounds Co($p$-FBA)$_2 \cdot nH_2$O were obtained in aqueous media. For the synthesis of the mixed-ligand complexes, a solution of N,N'-diethylnicotinamide (2 mmol) in distilled water (30 ml) was added dropwise with stirring to a solution of Co(p-FBA)$_2 \cdot n$H$_2$O (1 mmol) in hot distilled water (50 ml). The solutions were heated to 323 K in a temperature-controlled bath, stirred for 4 h, cooled to room temperature and then allowed to stand for 10–12 days for crystallization. The crystals which formed were filtered off, washed with cold water and acetone, and dried in vacuo. The mixed-ligand complexes were prepared according to the following equation: Co(p-FBA)$_2 \cdot n$H$_2$O + 2NA $\rightarrow$ [Co(p-FBA)$_2$(NA)$_2$(H$_2$O)$_2$] (NA is nicotinamide). Analysis found: C 50.57, H 3.89, N 9.10%; calculated for C$_{26}$H$_{24}$CoF$_2$N$_4$O$_8$: C 50.73, H 4.01, N 9.37%.

Crystal data

[Co(C$_7$H$_4$FO$_2$)$_2$(C$_6$H$_6$N$_2$O)$_2$(H$_2$O)$_2$]	V = 1327.4 (2) Å^3
M_r = 617.42	Z = 2
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 11.9883 (10) Å	μ = 0.72 mm^{-1}
b = 8.9128 (5) Å	T = 296 K
c = 12.4236 (15) Å	0.62 × 0.48 × 0.41 mm
β = 90.499 (8)°	

Data collection

Stoe IPDSII diffractometer	8334 measured reflections
Absorption correction: integration	3148 independent reflections
(X-RED32; Stoe & Cie, 2002)	2717 reflections with $I > 2\sigma(I)$
T_{min} = 0.707, T_{max} = 0.795	R_{int} = 0.077

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.121$
$S = 1.06$
3148 reflections
196 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—Co1	2.1662 (14)	O4—Co1	2.1294 (14)
O2—Co1	2.0650 (13)		
C7—O2—Co1	128.14 (12)	O4—Co1—N1	89.07 (5)
O2—Co1—O4	90.97 (6)	O2—Co1—N1^i	89.28 (6)
O2—Co1—O4^i	89.03 (6)	O4—Co1—N1^i	90.93 (5)
O2—Co1—N1	90.72 (6)		

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$O2^i	0.93	2.50	3.036 (2)	117
N2—H2$A\cdots$O4^{ii}	0.86	2.27	2.969 (2)	139
N2—H2$B\cdots$O1^{iii}	0.86	2.22	2.883 (2)	134
O4—H4$A\cdots$O3	0.850 (17)	1.728 (18)	2.571 (2)	171 (3)
O4—H4$B\cdots$O1^{iv}	0.848 (16)	1.940 (17)	2.7741 (18)	167 (3)
C5—H5$\cdots$F1^v	0.93	2.57	3.185 (3)	125
C5—H5$\cdots$O2	0.93	2.56	3.098 (2)	117

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

H atoms bonded to C and N atoms were included in their expected positions and allowed to ride, with C—H and N—H distances restrained to 0.93 and 0.86 Å, respectively; H atoms were assigned a U_{iso}(H) value of 1.2U_{eq} of the parent atom. Water H atoms were located in difference maps and refined subject to a DFIX restraint of O—H = 0.83 (2) Å.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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