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trans-Diaquabis(nicotinamide-κN)-bis(salicylato-κO)cobalt(II)

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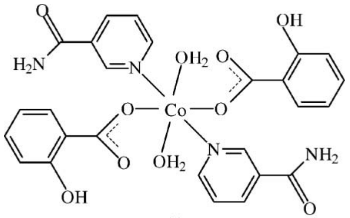
The title compound, $[Co(C_7H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$, forms a three-dimensional hydrogen-bonded supramolecular structure. The Co^{II} ion is in an octahedral coordination environment comprising two pyridyl N atoms, two carboxylate O atoms and two O atoms from water molecules. Intermolecular N—H···O and O—H···O hydrogen bonds produce $R_2^2(8)$, $R_2^2(12)$ and $R_2^2(14)$ rings, which lead to two-dimensional chains. An extensive three-dimensional supramolecular network of C—H···O, N—H···O and O—H···O hydrogen bonds and C—H···π interactions is responsible for crystal structure stabilization. This study is an example of the construction of a supramolecular assembly based on hydrogen bonds in mixed-ligand metal complexes.

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 for constructing these functional materials. In the development of supramolecular chemistry, hydrogen-bonding and π–π interactions, acting as the two main driving forces, play an important role in the self-assembly of 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; Şahin *et al.*, 2007). We report here the structure of the title complex, (I), in which hydrogen-bond interactions lead to a three-dimensional supramolecular network.

The molecular structure of (I) and the atom-labelling scheme are shown in Fig. 1. The Co^{II} ion is coordinated by two O atoms from two identical carboxylate groups, two O atoms from two water molecules and two pyridyl N atoms. The geometry around the Co^{II} ion (Table 1) is that of a slightly distorted octahedron. The distortion arises from the N1—Co1—N2 axis, which is not perfectly perpendicular to the coordination plane (O1/O2/O3/O4/Co1). The significant difference between the Co—O bond distances in the equatorial plane and the Co—N bond distances in the axial positions has also been observed in another cobalt complex (Şahin *et al.*, 2007).



(I)

The molecules of (I) are linked by intermolecular hydrogen bonding, and we employ graph-set notation (Bernstein *et al.*, 1995) to describe the patterns of hydrogen bonding. Molecules of (I) are linked into sheets by a combination of C—H···O, O—H···O and N—H···O hydrogen bonds (Table 2). Within the selected asymmetric unit, intramolecular O—H···O hydrogen bonds define $S_2^1(10)$ and $S(6)$ motifs (Fig. 1). Water atom O1 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* atoms H1*A* and H1*B*, to atom O5 at ($x+1$, y, z) and O10 at ($x+1$, y, z), respectively, so forming a $C(6)C(8)[R_2^2(12)]$ chain of rings running parallel to the [100] direction. Similarly,

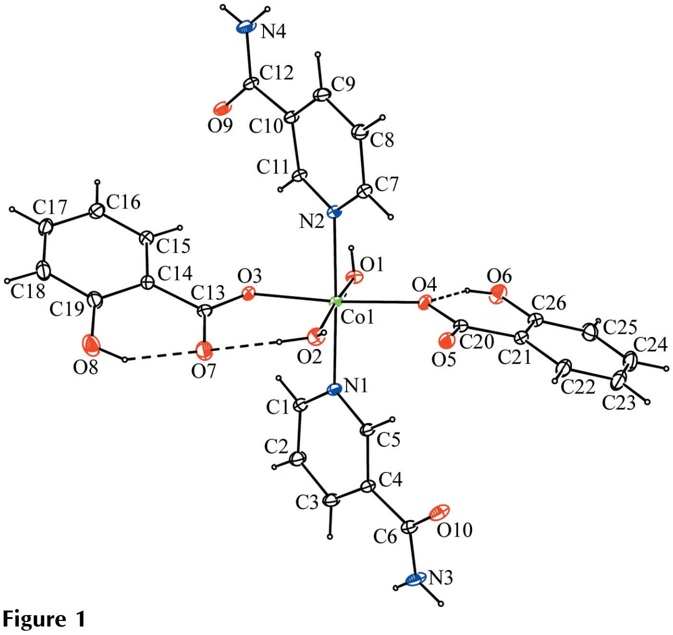


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

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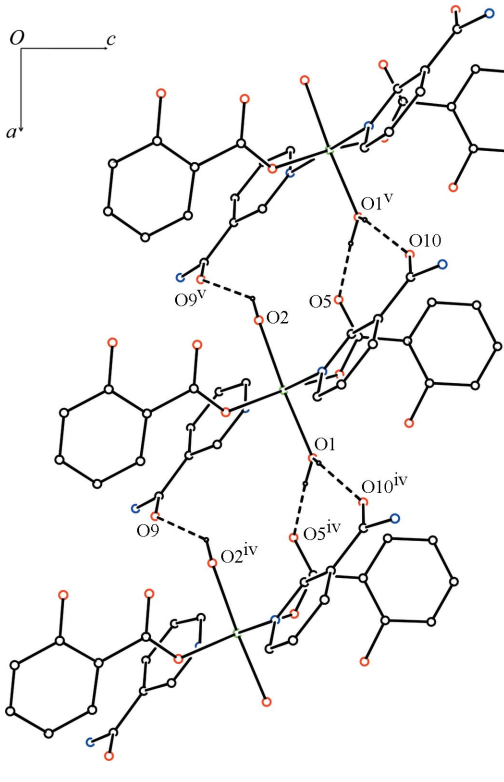

Figure 2
Part of the crystal structure of (I), showing the formation of $R_2^2(12)$ and $R_2^2(14)$ rings. Hydrogen bonds are indicated by dashed lines. H atoms not involved in these interactions have been omitted for clarity. (Symmetry codes as in Table 2.)

water atom O2 in the reference molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H2*B*, to atom O9 in the molecule at (x − 1, y, z), so forming a $C(8)$ chain running parallel to the [$\bar{1}$00] direction. The combination of $C(6)$ and $C(8)$ chains generates a chain of edge-fused $R_2^2(14)$ rings running parallel to the [100] direction (Fig. 2). Amino atom N4 in the reference molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H4*A*, to atom O10 in the molecule at (x + 1, y, z − 1), so forming a $C(12)$ chain running parallel to the [10$\bar{1}$] direction (Fig. 3). Amino atom N3 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H3*A*, to atom O9 in the molecule at (x − 1, y, z + 1), so forming a $C(12)$ chain running parallel to the [$\bar{1}$01] direction. The combination of $C(12)$ chains generates a chain of edge-fused $R_2^2(8)$ rings running parallel to the [10$\bar{1}$] direction (Fig. 3).

Fig. 4 shows the way in which amino atom N4, hydroxyl atom O6, atom C18 and carboxylate atom O5 enter into intermolecular hydrogen-bonding interactions. As a result, amino atom N4 in the reference molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H4*B*, to atom O6 in the molecule at (x, y, z − 1), so forming a $C(12)$ chain running parallel to the [00$\bar{1}$] direction. At the same time, atom C18 in the reference molecule at (x, y, z) acts as hydrogen-bond donor, *via* atom H18, to atom O5 in the molecule at ($-x$, $y - \frac{1}{2}$, $-z$), so forming a $C(10)$ chain running parallel to the [0$\bar{1}$0] direction. The combination of $C(10)$ and $C(12)$ chains generates a chain of edge-fused $R_4^4(40)$ rings parallel to the *bc* plane (Fig. 4).

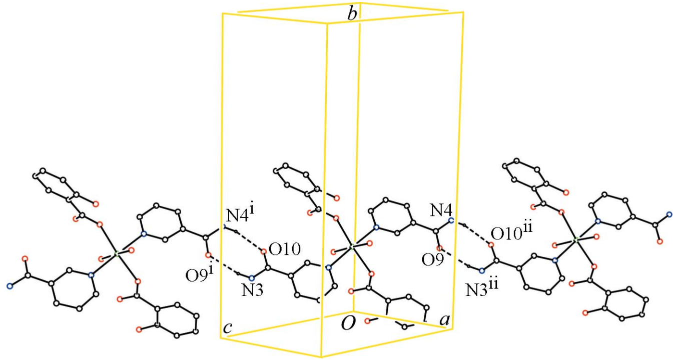

Figure 3
Part of the crystal structure of (I), showing the formation of an $R_2^2(8)$ dimer. Hydrogen bonds are indicated by dashed lines. H atoms not involved in these interactions have been omitted for clarity. (Symmetry codes as in Table 2.)

Compound (I) also contains two intermolecular C—H$\cdots\pi$ interactions. In the first, atom C9 in the molecule at (x, y, z) acts as hydrogen-bond donor to the C21–C26 benzene ring in the molecule at (x, y, z − 1), so forming a chain running parallel to the [00$\bar{1}$] direction. In the second, atom C3 in the molecule at (x, y, z) acts as hydrogen-bond donor to the C14–C19 benzene ring in the molecule at (x, y, z + 1), so forming a chain running parallel to the [001] direction. Details of these interactions are given in Table 2. The combination of C—H$\cdots\pi$ interactions defines an $R_2^2(20)$ ring pattern (Fig. 5).

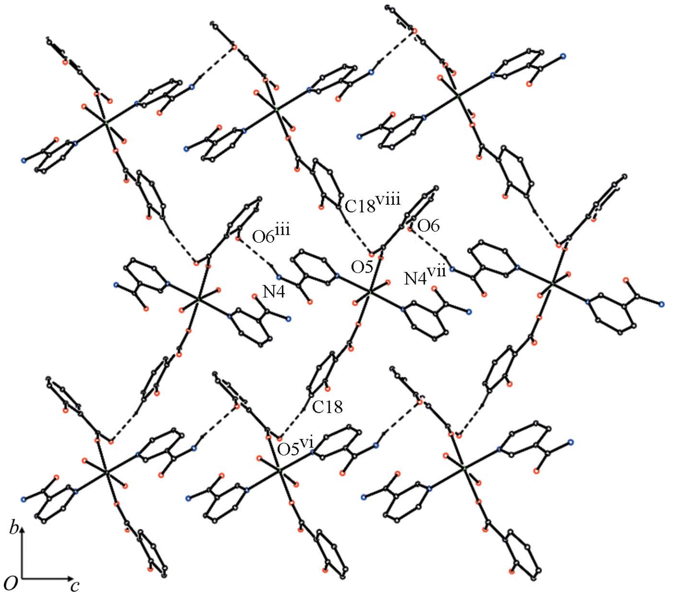

Figure 4
Part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_4^4(40)$ rings. Hydrogen bonds are indicated by dashed lines. For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (iii) x, y, z − 1; (vi) $-x$, $y - \frac{1}{2}$, $-z$; (vii) x, y, z + 1; (viii) $-x$, $y + \frac{1}{2}$, $-z$.]

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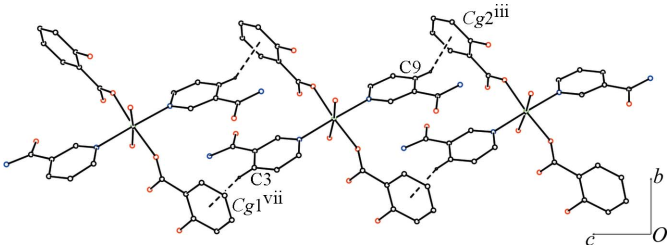

Figure 5
Part of the crystal structure of (I), showing the formation of a chain along [001] generated by the C—H$\cdots\pi$ interactions (dashed lines; see Table 2). For the sake of clarity, H atoms not involved in the motif shown have been omitted. [Symmetry codes: (iii) $x, y, z - 1$; (vii) $x, y, z + 1$.]

Table 1
Selected geometric parameters (Å, °).

N1—Co1	2.157 (3)	O2—Co1	2.121 (3)
N2—Co1	2.147 (3)	O3—Co1	2.079 (3)
O1—Co1	2.112 (3)	O4—Co1	2.076 (3)
C13—O3—Co1	130.1 (3)	O1—Co1—O2	174.40 (12)
C20—O4—Co1	134.1 (3)	N2—Co1—N1	178.26 (12)
O4—Co1—O3	174.58 (11)		

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

*Cg*1 and *Cg*2 are the centroids of the C14–C19 and C21–C26 benzene rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$A\cdots$O9^{i}	0.86	2.11	2.955 (4)	167
N4—H4$A\cdots$O10^{ii}	0.86	2.09	2.916 (5)	162
N4—H4$B\cdots$O6^{iii}	0.86	2.48	3.210 (6)	144
O6—H6$\cdots$O4	0.82	1.80	2.521 (4)	146
O8—H8$A\cdots$O7	0.82	1.83	2.553 (5)	147
O1—H1$A\cdots$O5^{iv}	0.83 (5)	1.86 (5)	2.684 (4)	172 (5)
O1—H1$B\cdots$O10^{iv}	0.81 (4)	2.11 (4)	2.810 (4)	145 (5)
O2—H2$A\cdots$O7	0.834 (19)	1.88 (2)	2.677 (5)	158 (5)
O2—H2$B\cdots$O9^{v}	0.82 (4)	2.23 (4)	2.906 (4)	140 (5)
C18—H18$\cdots$O5^{vi}	0.93	2.41	3.311 (6)	165
C3—H3$\cdots Cg1^{vii}$	0.93	2.68	3.520 (4)	151
C9—H9$\cdots Cg2^{iii}$	0.93	2.82	3.614 (4)	144

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

The combination of the chains along [100], [10$\overline{1}$], [010] and [001] suffices to generate a three-dimensional structure of considerable complexity.

Experimental

As a first step, the sodium salt of salicylic acid (SA) was prepared and cobalt salicylate was synthesized from the Na(SA) salt. A solution of Co(SA)$_2\cdot n$H$_2$O in water was left for 15 d at room temperature for crystallization. In a second step, a solution of nicotinamide (2 mmol) in distilled water (30 ml) was added dropwise to a stirred solution of Co(SA)$_2\cdot n$H$_2$O (1 mmol) in hot distilled water (50 ml). The resulting solution was heated to 323 K in a temperature-controlled bath and stirred for 4 h, then cooled to room temperature and left for 15–17 d for crystallization. The brown crystals which formed were filtered off, washed with cold water and acetone and dried *in vacuo* (yield 84%, 0.51 g). Analysis found: C 50.38, H 4.12%; calculated for $C_{26}H_{28}CoN_4O_{10}$: C 50.86, H 4.57%.

Crystal data

$[Co(C_7H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$
$M_r = 613.44$
Monoclinic, $P2_1$
$a = 7.0484$ (4) Å
$b = 19.4249$ (7) Å
$c = 10.3331$ (5) Å
$\beta = 109.774$ (4)°
$V = 1331.33$ (11) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.71$ mm^{-1}
$T = 296$ K
0.48 × 0.39 × 0.36 mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min} = 0.549$, $T_{max} = 0.811$
9880 measured reflections
5360 independent reflections
4725 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.115$
$S = 1.05$
5360 reflections
383 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}
Absolute structure: Flack (1983), with 2533 Friedel pairs
Flack parameter: 0.012 (16)

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, and with U_{iso}(H) = 1.2U_{eq}(C,N). Water H atoms were located in a difference map and refined subject to a DFIX (*SHELXL97*; Sheldrick, 2008) restraint of O—H = 0.83 (2) Å. The H atoms of the hydroxy groups (O6 and O8) were allowed for with a fixed O—H distance of 0.82 Å [U_{iso}(H) = 1.5U_{eq}(O)].

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3085). Services for accessing these data are described at the back of the journal.

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