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Synthesis and Crystal Structure of Diaquabis(4-iodinebenzoato-κO)bis-(nicotinamide-κN)cobalt(II)

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The title compound $[Co(C_7H_4O_2I)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$ is a two-dimensional hydrogen-bonded supramolecular complex. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit-cell parameters a = 7.2964(13), b = 8.6047(17), c = 16.745(3)Å, α = 93.034(15), β = 101.574(15), γ = 111.975(14)° and Z = 1. 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 C–H···O and O–H···O hydrogen bonds produce $R_2^2(16)$, $R_2^2(18)$ and $R_2^2(20)$ rings, which lead to one-dimensional polymeric chains. An extensive two-dimensional network of C–H···O and O–H···O hydrogen bonds, π-π and C–H···π interactions are responsible for crystal stabilization.

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Our recent research has concentrated on the construction of coordination polymers with specific topologies based on co-bridging of rigid 4,4′-bipyridine and α,ω-dicarboxylates.[1] Some interesting coordination polymers assembled with 4,4′-bipyridine (bipy) have been reported, showing various structural motifs, including two-dimensional layers[2] and three-dimensional nets.[3] We report here on the structure of diaquabis(4-iodinebenzoato-κO)bis(nicotinamide-κN)cobalt(II), (I), in which hydrogen bonds, π-π and C–H···π interactions lead to a two-dimensional supramolecular network.

A solution of na (nicotinamide) (2 mmol) in distilled water (30 mL) was added dropwise with stirring to a solution of Co(4-Iba)$_2$(H$_2$O)$_n$ (1 mmol) in hot distilled water (50 mL). The solution was heated to 50°C in a temperature-controlled bath and stirred for 4 h, and then cooled to room temperature and allowed 10 – 12 days for crystallization. The crystals formed were filtered and washed with cold water and acetone and dried *in vacuo*. Mixed-ligand complexes were prepared according to the following equations: Co(4-Iba)$_2$(H$_2$O)$_n$ + 2na → Co(4-Iba)$_2$(na)$_2$(H$_2$O)$_2$

The structure was solved by direct methods with SHELXS-97[4] and refined by full-matrix least-squares procedures on F^2, using the program SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically. The H atoms of the water O atom were located in a Fourier difference map and freely refined. Other hydrogen atom positions were refined using a riding model. The crystal was twinned by a two-fold rotation axis perpendicular to (001). Reflection data were measured for the two twin domains, scaled and combined together, but overlapping reflections could not be satisfactorily measured and were discarded, leading to a data completeness of only slightly over 52%.

The molecular structure (Fig. 1) and atom-numbering scheme are shown in Fig. 2; selected bond lengths are given in Table 3. The Co(II) ion is located on a symmetry center, and is coordinated by two O atoms from two identical carboxylate groups and two O atoms from two water molecules and by two

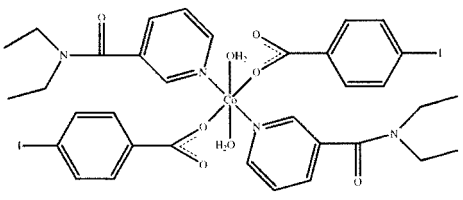

Fig. 1 Schematic diagram of the title compound.

Table 1 Crystal and experimental data

Formula: $C_{34}H_{40}CoI_2N_4O_8$	
Formula weight: 945.43	
Crystal system: triclinic	
Space group: $P\bar{1}$	Z = 1
a = 7.2964(13)Å	α = 93.034(15)°
b = 8.6047(17)Å	β = 101.574(15)°
c = 16.745(3)Å	γ = 111.975(14)°
V = 945.6(3)Å^3	
D_c = 1.660 g cm^{-3}	
No. of reflections used = 2238	
θ_{max} = 27.3° Mo K_α	
R = 0.048	
wR = 0.180	
$(\Delta\rho)$ = 0.46 eÅ^{-3}	
$(\Delta\rho)$ = –0.44 eÅ^{-3}	
Measurement: STOE IPDS II	
Program system: STOE X-RED	
Structure determination: Direct methods	
Refinement: full matrix	
CCDC number: CCDC 658936	

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Table 2 Atomic coordinates and temperature factors

Atom	*x*	*y*	*z*	U_{eq}
C1	0.6053(13)	0.6770(10)	0.1746(5)	0.064(2)
C2	0.5123(13)	0.6991(11)	0.2442(6)	0.063(2)
C3	0.6198(15)	0.7187(13)	0.3264(6)	0.070(3)
C4	0.5342(16)	0.7372(14)	0.3891(6)	0.088(3)
C5	0.3445(16)	0.7451(14)	0.3729(7)	0.075(3)
C6	0.2305(17)	0.7200(15)	0.2919(8)	0.070(3)
C7	0.3203(13)	0.7028(11)	0.2293(6)	0.066(2)
C8	0.1938(13)	0.2873(10)	0.0901(5)	0.0613(19)
C9	0.0815(13)	0.1508(10)	0.1243(5)	0.0574(18)
C10	0.1078(14)	-0.0015(10)	0.1147(6)	0.066(2)
C11	0.2412(15)	-0.0082(13)	0.0688(6)	0.068(2)
C12	0.3471(12)	0.1305(11)	0.0364(5)	0.062(2)
C13	-0.0808(14)	0.1678(12)	0.1636(6)	0.062(2)
C14	0.075(2)	0.1114(19)	0.2963(10)	0.096(4)
C15	0.205(3)	0.255(2)	0.3582(13)	0.153(8)
C16	-0.2548(18)	0.1539(14)	0.2729(8)	0.089(3)
C17	-0.241(2)	0.3318(15)	0.2943(10)	0.108(5)
N1	0.3265(10)	0.2770(8)	0.0470(4)	0.0605(16)
N2	-0.0802(13)	0.1460(11)	0.2419(5)	0.077(2)
O1	0.4943(9)	0.6471(7)	0.1025(4)	0.0624(14)
O2	0.7839(9)	0.6834(9)	0.1914(4)	0.0728(17)
O3	-0.2128(10)	0.2033(8)	0.1197(4)	0.0759(17)
O4	0.7847(10)	0.4977(8)	0.0606(4)	0.0683(15)
Co1	0.5000	0.5000	0.0000	0.0565(4)
I1	0.21430(13)	0.77096(13)	0.47156(5)	0.1174(5)

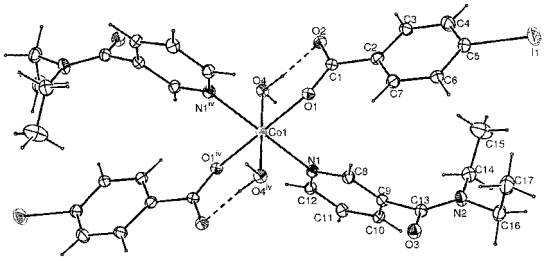

Fig. 2 Molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability. Symmetry transformation used to generate equivalent atoms (iv) 1–*x*, 1–*y*, –*z*.

Table 3 Selected geometric parameters (Å, °)

Bond lengths (Å)			
Co1–N1	2.156 (6)	Co1–O4	2.129 (6)
Co1–O1	2.094 (6)	C1–O2	1.257 (10)
C1–O1	1.265 (11)		
Bond angles (°)			
O1–Co1–N1	88.6 (2)	O1–Co1–O4	91.6 (3)
O4–Co1–N1	93.5 (2)	O4^{iv}–Co1–N1	86.5 (2)

Symmetry code: (iv) 1–*x*, 1–*y*, –*z*.

N atoms from two 4,4′-bpy ligands. The geometry around the Co(II) ion (Table 3) is that of a slightly distorted octahedron, of which the equatorial plane (O1/O4/O1^{iv}/O4^{iv}) is formed by two O atoms of two carboxylate groups (O1 and O1^{iv}) and two O atoms of two water molecules (O4 and O4^{iv}) [symmetry code: (iv) 1–*x*, 1–*y*, –*z*]. The axial positions in the octahedron are occupied by two N atoms of 4,4′-bpy ligands (N1 and N1^{iv}). Significant differences exist between the Co–L bond distances [Co-O1/O1^{iv} = 2.094(6)Å and Co-O4/O4^{iv} = 2.129(6)Å] in the equatorial plane and the Co–L bond distances [Co-N1/N1^{iv} = 2.156(6)Å] in the axial positions.

The intramolecular hydrogen-bond produces S(6) motif.[5] Molecules are linked into sheets by the combination of one of the O–H···O hydrogen bonds and two of the C–H···O hydrogen bonds (Table 4). Each hydrogen bond acting in isolation generates a simple chain motif, and the combination of the three independent chains generates a sheet. Ring atom C10 in the reference molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H10, to atom O2^{iii}, thus forming a C(9)[R_2^2(18)] chain of rings running parallel to the [110] direction and centrosymmetric R_2^2(18) rings centred at (*n*, *n*, 0) (*n* = zero or integer). Similarly, atom C6 in the reference molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H6, to atom O2^{ii}, thus forming a C(6)[R_2^2(20)] chain of rings running parallel to the [100] direction and centrosymmetric R_2^2(20) rings centred at (*n*, 1/2, 0) (*n* = zero or integer) (Fig. 3).

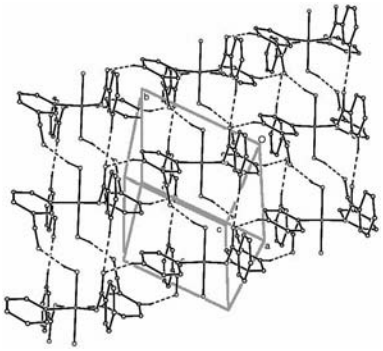

Fig. 3 Stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet built from R_2^2(16), R_2^2(18) and R_2^2(20) rings.

Table 4 Hydrogen-bond and C–H···π interaction geometry (Å)

D-H···A	D-H	H···A	D···A	D-H···A
O4-H4A…O2	0.83(13)	1.82(13)	2.644(9)	170(12)
O4-H4B…O3^{i}	0.83(11)	1.95(11)	2.773(9)	168(12)
C6-H6…O2^{ii}	0.93	2.38	3.244(13)	153
C10-H10…O2^{iii}	0.93	2.46	3.373(10)	166
C15-H15C…Cg2	0.96	3.03	3.921(17)	153
Cg2=C2-C7				

(i = *x*+1, *y*, *z*), (ii = *x*–1, *y*, *z*), (iii = *x*–1, *y*–1, *z*)

Water atom O4 in the reference molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* H4B, to atom O3^{i}, thus forming a C(8)[R_2^2(16)] chain of rings running parallel to the [100] direction and centrosymmetric R_2^2(16) rings centred at (*n*+1, 1/2, 0) (*n* = zero or integer) (Fig. 3). The combination of the C(6) and C(8) chains along [100] generates a chain of edge-fused R^2_2(18) rings.

In the extended structure of (I), there are also weak π-π and π-ring interactions. An intermolecular π-π contact occurs between the two symmetry-related pyridine rings of neighboring molecules. Ring Cg1 is oriented in such a way that the perpendicular distance from Cg1 to Cg1^{v} is 3.407 Å [symmetry code: (v) –*x*, –*y*, –*z*]. The distance between the ring centroids is 3.630(5)Å. The details of the intramolecular C–H···π interaction are given in Table 4. The π-π interaction produces a chain running parallel to the [110] direction.

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