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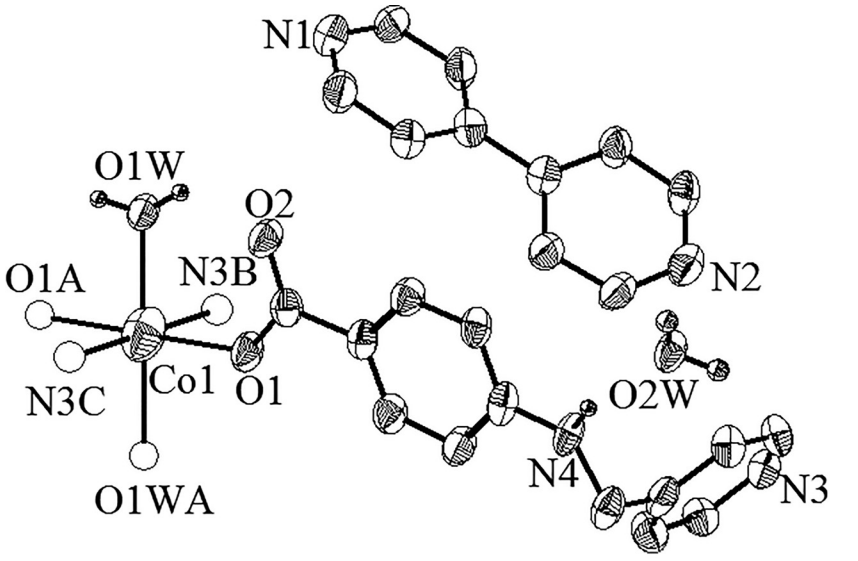
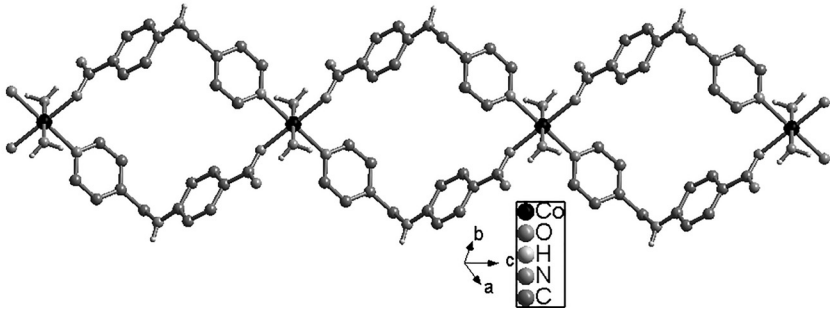
Hydrothermal synthesis and crystal structure of *catena*-poly[diaqua-bis(μ_2-4-((pyridin-4-ylmethyl)amino)benzoato-κ^2*N:O*)cobalt(II)] – 4,4′-bipyridine – water (1/2/2)





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Abstract

$C_{23}H_{23}Co_{0.5}N_4O_4$, triclinic, $P\bar{1}$ (no. 2), a = 9.6428(5) Å, b = 10.3191(5) Å, c = 11.8710(6) Å, α = 86.664 (4)°, β = 69.399 (5)°, γ = 79.429 (4)°, V = 1086.90(10) Å^3, Z = 2, $R_{gt}(F)$ = 0.0432, $wR_{ref}(F^2)$ = 0.1454, T = 293(2) K.

CCDC no.: 2290490

Table 1: Data collection and handling.

Crystal:	Pink block
Size:	0.33 × 0.22 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.46 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.5°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11,718, 3987, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3510
$N(param)_{refined}$:	289
Programs:	Olex2 [1], SHELX [2, 3]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.5000	0.02797 (18)
O1	0.36593 (18)	0.56658 (17)	0.67157 (14)	0.0374 (4)
O1W	0.54267 (17)	0.69171 (16)	0.44558 (14)	0.0365 (4)
H1WA	0.5218	0.7129	0.3824	0.055*
H1WB	0.5050	0.7556	0.4953	0.055*
O2	0.33858 (19)	0.78536 (17)	0.65731 (15)	0.0423 (4)
N3	0.3076 (2)	0.5370 (2)	1.43896 (17)	0.0341 (5)
N4	−0.0366 (2)	0.7196 (2)	1.21399 (17)	0.0409 (5)
H4	−0.0866	0.7966	1.2391	0.049*
C1	0.3162 (2)	0.6810 (2)	0.7168 (2)	0.0297 (5)
C2	0.2281 (2)	0.6902 (2)	0.84817 (19)	0.0299 (5)
C3	0.2095 (3)	0.5786 (2)	0.9179 (2)	0.0375 (6)
H3	0.2542	0.4965	0.8818	0.045*
C4	0.1265 (3)	0.5848 (3)	1.0397 (2)	0.0394 (6)
H4A	0.1174	0.5076	1.0842	0.047*
C5	0.0564 (2)	0.7066 (2)	1.0960 (2)	0.0319 (5)
C6	0.0790 (3)	0.8202 (3)	1.0266 (2)	0.0371 (6)
H6	0.0371	0.9025	1.0629	0.044*
C7	0.1625 (2)	0.8125 (2)	0.9048 (2)	0.0333 (5)
H7	0.1750	0.8894	0.8602	0.040*
C8	−0.0563 (3)	0.6125 (3)	1.2990 (2)	0.0413 (6)
H8A	−0.0604	0.5343	1.2595	0.050*
H8B	−0.1513	0.6355	1.3646	0.050*
C9	0.0699 (2)	0.5822 (3)	1.3493 (2)	0.0332 (5)
C10	0.1700 (3)	0.4660 (3)	1.3284 (2)	0.0417 (6)
H10	0.1597	0.3995	1.2838	0.050*
C11	0.2865 (3)	0.4471 (3)	1.3735 (2)	0.0428 (6)
H11	0.3535	0.3675	1.3572	0.051*
C12	0.2088 (3)	0.6496 (3)	1.4606 (2)	0.0422 (6)
H12	0.2193	0.7134	1.5078	0.051*
C13	0.0927 (3)	0.6763 (3)	1.4170 (2)	0.0428 (6)
H13	0.0289	0.7576	1.4327	0.051*
N1	0.7693 (3)	0.9349 (3)	0.5992 (2)	0.0593 (7)
N2	0.5241 (3)	0.7615 (3)	1.2177 (2)	0.0528 (6)
C14	0.4614 (4)	0.7275 (4)	1.1437 (3)	0.0705 (10)
H14	0.3825	0.6808	1.1756	0.085*
C15	0.5044 (4)	0.7561 (4)	1.0233 (3)	0.0628 (9)
H15	0.4562	0.7280	0.9761	0.075*
C16	0.6206 (3)	0.8275 (3)	0.9722 (2)	0.0391 (6)
C17	0.6863 (3)	0.8631 (3)	1.0487 (2)	0.0544 (8)
H17	0.7648	0.9106	1.0199	0.065*
C18	0.6352 (3)	0.8281 (3)	1.1692 (3)	0.0542 (8)
H18	0.6822	0.8530	1.2187	0.065*
C19	0.6722 (3)	0.8638 (3)	0.8434 (2)	0.0377 (6)
C20	0.8158 (3)	0.8900 (3)	0.7836 (3)	0.0579 (8)
H20	0.8835	0.8836	0.8242	0.069*
C21	0.8588 (4)	0.9256 (4)	0.6640 (3)	0.0671 (9)
H21	0.9554	0.9441	0.6267	0.081*
C22	0.6332 (3)	0.9090 (3)	0.6555 (3)	0.0535 (7)
H22	0.5687	0.9148	0.6120	0.064*
C23	0.5798 (3)	0.8736 (3)	0.7758 (2)	0.0451 (7)
H23	0.4823	0.8566	0.8108	0.054*
O2W	−0.1821 (3)	0.9664 (2)	1.34689 (17)	0.0612 (6)
H2WA	−0.2295	1.0421	1.3381	0.092*
H2WB	−0.1949	0.9537	1.4210	0.092*

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

All chemicals for synthesis were of reagent grade and used as received without further purification. The mixtures of 4-[(4-pyridinylmethyl)amino] benzoic acid (0.05 mmol, 12.0 mg), 4,4′-bipyridine (0.1 mmol, 16.2 mg), $Co(Ac)_2$–$4H_2O$ (0.1 mmol, 25.1 mg), NaOH (0.1 mmol, 4.0 mg) and H_2O (6 mL) was placed in a 23 mL Teflon-lined autoclave at 393 K for 4 days, and then slowly cooled down to room temperature for crystallization. Pink block crystals of the title compound were obtained. The yield was 62 % (based on Co). For $C_{23}H_{23}Co_{0.5}N_4O_4$ anal. calcd., % C, 61.54 H, 5.16 N, 12.48 found, % C, 61.45 H, 5.38 N, 12.38.

2 Experimental details

Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program and refined with the ShelXL [3] refinement package. All hydrogen atoms were added to their calculated positions and refined using a riding model. The U_{iso} of the H-atoms were constrained to 1.2 times U_{eq} of their bonding carbon atoms and 1.5 times U_{eq} of their bonding oxygen atoms for the hydrogen atoms in water molecules.

3 Comment

Coordination polymers (CPs) represent a high-speed growing area in coordination and supramolecular chemistry [4–6], and especially for Co(II) compounds [7, 8]. The design and synthesis of coordination polymers via self-assembly of metal ions and organic ligands depend on the selection of metal centers and the organic ligands with controlled chemical and physical properties by the Schiff-base ligands [9, 10], because this class of ligand with O,N-bifunctional group has multiple coordination points and various coordination modes. The HL {HL = 4-[(4-pyridinylmethyl)amino]benzoic acid} starting material has one carboxylic group and one nitrogen atom at the terminal positions and one secondary amine group between the phenyl groups, which can supply more varied coordinating patterns (monodentate, bridging, chelating) to construct coordination frameworks. However, HL

carboxylic acid ligands have not been extensively exploited, except for some limited cases [11–13].

The crystal structure of the compound shows a one-dimensional chain structure. The asymmetric unit contains one half crystallographically Co(II) cation, one completely deprotonated L^- anion and one Bpy molecule and one coordinating water molecule and one crystallization water molecule as shown in the upper part of the figure (A: $1 - x$, $1 - y$, $1 - z$; B: $1 - x$, $1 - y$, $2 - z$; C: x, y, $-1 + z$). In this complex, each Co(II) cation is six-coordinated with a distorted octahedral geometry, [CoN_2O_4] by two N atoms from two symmetry-related Bpy ligand, two oxygen atoms from two symmetry-related L^- anions, two oxygen atoms from two coordination water molecules. The Co–O bond lengths are 2.068(16), and 2.113(18) Å for Co1–O1, Co1–O1W, and one Co–N bond is 2.183(18) Å for Co1–N3, respectively. Two adjacent cobalt(II) are connected together by two L^- anions adopting monodentate coordination mode to form an infinite one-dimensional chain along the *c* axis with the Co⋯Co distance of 11.8710(6) Å (lower part of the structure). There are massive H-bonding interactions in the compound via the participation of coordination waters and carboxylate O atoms (O(1W)–H(1WB)⋯O(2): 2.689(2) Å), between crystallization waters and carboxylate O atoms (O(2W)–H(2WA)⋯O(2): 2.732(3) Å), between coordination waters and N atoms of Bpy molecules (O(1W)–H(1WA)⋯N(2): 2.817(3) Å), between crystallization waters and N atoms of Bpy molecules (O(2W)–H(2WB)⋯N(1): 2.873(3) Å), between crystallization waters and amino N atoms of L^- (N(4)–H(4)⋯O(2W): 2.923(3) Å). The free Bpy molecules as parallel pendent arms are hung on one side of the infinite chain through the hydrogen bonds. At last a three-dimensional supramolecular structure was gained through the H-bonding interactions.

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