

A one-dimensional Co<sup>II</sup> coordination polymer exhibiting an unusual conformation for 1,2-bis(4-pyridyl)ethaneFilipe A. Almeida Paz,  
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## Key indicators

Single-crystal X-ray study

T = 180 K

Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$ 

R factor = 0.042

wR factor = 0.109

Data-to-parameter ratio = 7.9

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound, *catena*-poly[[[tetraaquacobalt(II)]- $\mu$ -1,2-bis(4-pyridyl)ethane- $\kappa^2$ N:N] 2,6-naphthalenedicarboxylate],  $[\{\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})_4\}(\text{C}_{12}\text{H}_6\text{O}_4)]_n$  or  $[\{\text{Co}(\text{BPE})(\text{H}_2\text{O})_4\}(\text{NDC})]_n$  [BPE is 1,2-bis(4-pyridyl)ethane and NDC is 2,6-naphthalenedicarboxylate], denoted CUMof-4, was synthesized under mild hydrothermal conditions. The crystal structure contains one-dimensional  $[\text{Co}(\text{BPE})(\text{H}_2\text{O})_4]_n^{2n+}$  coordination polymers, which stack along the *b* direction, alternating with uncoordinated NDC anions. The Co atom is located on a centre of symmetry. Hydrogen bonds between the cationic polymer and the anions give rise to a three-dimensional network.

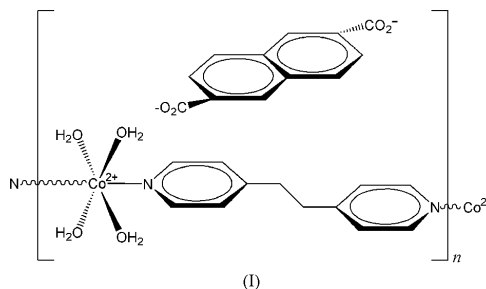
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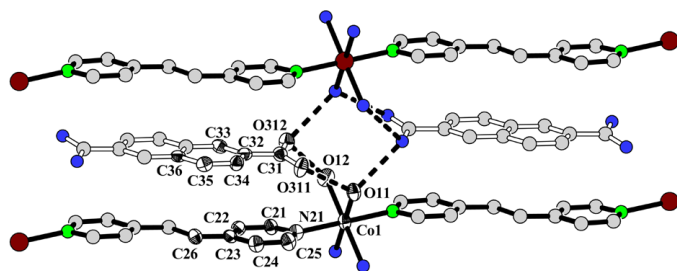
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## Comment

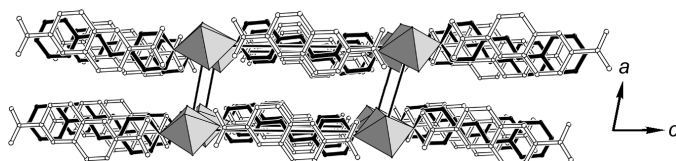
We are interested in the synthesis of novel coordination compounds which contain both carboxylate and 4-pyridyl groups coordinated to metal centres (Almeida Paz *et al.*, 2002). In particular, the use of 1,2-bis(4-pyridyl)ethane (BPE), which has increased flexibility compared to 4,4'-bipyridine (BPY), due to the two methylene ( $-\text{CH}_2-$ ) groups between the 4-pyridyl rings, may lead to supramolecular isomerism (Hennigar *et al.*, 1997).



The title compound, CUMof-4, (I), contains one crystallographically unique cobalt(II) centre, which occupies a centre of symmetry in  $P\bar{1}$  and exhibits an almost ideal octahedral environment, composed of four water molecules in the equatorial plane and two *trans*-coordinated 4-pyridyl N atoms in axial positions (Fig. 1 and Table 1). A one-dimensional cationic  $[\text{Co}(\text{BPE})(\text{H}_2\text{O})_4]_n^{2n+}$  coordination polymer runs along the *c* direction (Fig. 2, top), with BPE ligands establishing bridges between metal centres [ $\text{Co}1 \cdots \text{Co}1^i = 13.529(2) \text{ \AA}$ ; symmetry code: (i)  $x, y, z - 1$ ]. These one-dimensional polymers alternate with NDC ions along the *b* direction (Fig. 1), with the anions being brought into close face-to-face contact with the BPE ligands (the average separation between adjacent aromatic rings is *ca* 3.5 Å) (Fig. 2). These interactions may account for the unusual conformation of the BPE ligand, within which both 4-pyridyl


**Figure 1**

View approximately along the *a* direction, showing alternation along *b* between one-dimensional cationic  $[\text{Co}(\text{BPE})(\text{H}_2\text{O})_4]^{2n+}$  coordination polymers and NDC anions. Hydrogen bonds are drawn as dashed lines. The asymmetric unit of CUMof-4 is represented with ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Colour scheme: C grey, N blue, O blue, Co brown.


**Figure 2**

Perspective view of CUMof-4 along the *b* direction.  $\text{Co}^{\text{II}}$  centres are represented as octahedra, BPE ligands with filled bonds, and NDC ions with hollow bonds.

groups lie in the same plane.  $\text{O}-\text{H}\cdots\text{O}^-$  hydrogen bonds connect the NDC anions to the coordinated water molecules, giving rise to a three-dimensional network (Fig. 3 and Table 2).

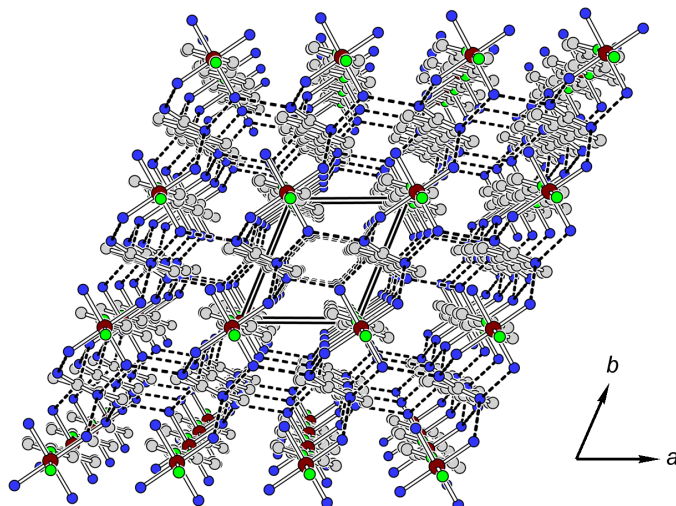
## Experimental

All chemicals were obtained from commercial sources and were used without further purification. To a solution of  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.476 g, Aldrich) in distilled water (12.4 g), 1,2-bis(4-pyridyl)ethane (BPE, 0.378 g, Aldrich), 2,6-naphthalenedicarboxylic acid ( $\text{H}_2\text{NDC}$ , 0.437 g, Aldrich) and triethylamine (TEA, 0.388 g, Avocado) were added, and the mixture was stirred thoroughly for 1 h at ambient temperature. The suspension, with an  $\text{H}_2\text{NDC}:\text{Co}^{2+}:\text{BPE}:\text{TEA}:\text{H}_2\text{O}$  ratio of 1.01:1.00:1.02:1.91:343, was placed in a Parr stainless steel teflon-lined vessel (21 ml, 50% full). The reaction was performed under autogeneous pressure and static conditions in a pre-heated oven at 418 K for 3 h. The vessel was then cooled slowly inside the oven to 298 K at a rate of  $5\text{ K h}^{-1}$  before opening. The crystalline product was collected by vacuum filtration and crystals of the title compound were manually separated and preserved in a portion of the autoclave solution.

### Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_{12}\text{H}_6\text{O}_4)$   
 $M_r = 529.40$   
 Triclinic,  $P\bar{1}$   
 $a = 6.3586$  (12) Å  
 $b = 7.0047$  (10) Å  
 $c = 13.529$  (2) Å  
 $\alpha = 88.463$  (11)°  
 $\beta = 77.165$  (8)°  
 $\gamma = 68.056$  (9)°  
 $V = 543.91$  (15) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.616\text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 6957 reflections  
 $\theta = 1.0\text{--}22.5^\circ$   
 $\mu = 0.85\text{ mm}^{-1}$   
 $T = 180$  (2) K  
 Plate, colourless  
 $0.18 \times 0.12 \times 0.01\text{ mm}$


**Figure 3**

Perspective view of CUMof-4 along the *c* direction, showing the  $\text{O}-\text{H}\cdots\text{O}^-$  hydrogen-bonding network (dashed lines). H atoms have been omitted for clarity.

### Data collection

Nonius KappaCCD diffractometer  
 Thin-slice  $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995)  
 $T_{\text{min}} = 0.943$ ,  $T_{\text{max}} = 0.992$   
 3625 measured reflections  
 1374 independent reflections

1189 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.063$   
 $\theta_{\text{max}} = 22.3^\circ$   
 $h = -6 \rightarrow 6$   
 $k = -7 \rightarrow 7$   
 $l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.109$   
 $S = 1.20$   
 1374 reflections  
 173 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.0618P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.007$   
 $\Delta\rho_{\text{max}} = 0.37\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.42\text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Co1—O11	2.103 (3)	O311—C31	1.264 (5)
Co1—N21	2.111 (3)	O312—C31	1.265 (5)
Co1—O12	2.141 (3)		
O11—Co1—N21	92.29 (11)	O11 <sup>i</sup> —Co1—O12	85.32 (11)
O11 <sup>i</sup> —Co1—N21	87.71 (11)	N21—Co1—O12	91.82 (11)
O11—Co1—O12	94.68 (10)	N21 <sup>i</sup> —Co1—O12	88.18 (11)

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O11—H11A $\cdots$ O312 <sup>ii</sup>	0.82 (2)	2.03 (3)	2.846 (4)	170 (4)
O11—H11B $\cdots$ O311	0.82 (2)	1.83 (3)	2.654 (4)	174 (5)
O12—H12A $\cdots$ O312 <sup>i</sup>	0.83 (2)	2.05 (3)	2.867 (4)	170 (4)
O12—H12B $\cdots$ O311 <sup>iii</sup>	0.83 (2)	1.96 (3)	2.777 (4)	170 (4)

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

H atoms bound to carbon were placed in calculated positions and allowed to ride during subsequent refinement, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Aqua H atoms were located in difference Fourier maps and refined with a single isotropic displacement parameter common to all H atoms, and O–H and H···H distances restrained to ensure a reasonable geometry for the water molecules.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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