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## Key indicators

Single-crystal X-ray study  
 $T = 180$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.046  
 $wR$  factor = 0.121  
Data-to-parameter ratio = 11.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis(4,4'-bipyridine)tetraaquacobalt(II)  
2,6-naphthalenedicarboxylate dihydrate

The title compound,  $[\text{Co}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_4](\text{C}_{12}\text{H}_6\text{O}_4) \cdot 2\text{H}_2\text{O}$  (where  $\text{C}_{10}\text{H}_8\text{N}_2$  is 4,4'-bipyridine, BPY, and  $\text{C}_{12}\text{H}_6\text{O}_4$  is 2,6-naphthalenedicarboxylate,  $\text{NDC}^{2-}$ ), (CUMof-6), was synthesized under mild hydrothermal conditions. The structure contains  $[\text{Co}(\text{BPY})_2(\text{H}_2\text{O})_4]^{2+}$  complex cations, which stack along the  $a$  axis through close face-to-face contacts. Uncoordinated  $\text{NDC}^{2-}$  anions are strongly hydrogen bonded to the complex cations. The  $\text{Co}^{2+}$  cation and the centre of gravity of  $\text{NDC}^{2-}$  are located on crystallographic centres of symmetry.

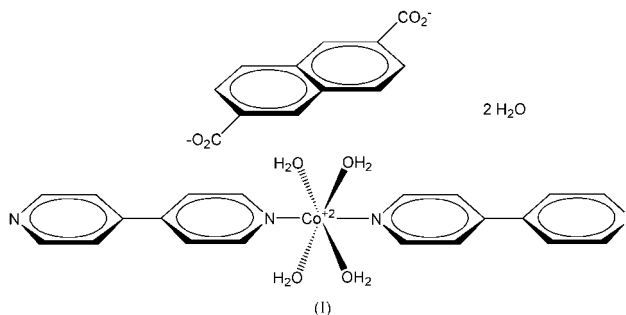
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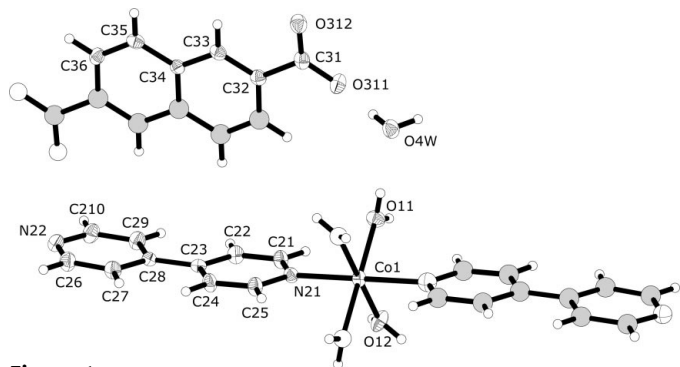
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## Comment

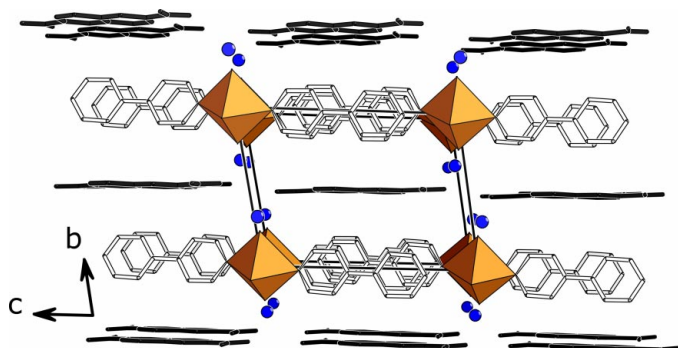
The construction of inorganic–organic hybrid frameworks containing  $d$ -block transition metal ions and ligands with 4-pyridyl donor groups has developed significantly in recent years (see, for example, Batten & Robson, 1998; Moulton & Zaworotko, 2001). We are interested in the synthesis of novel hybrid compounds which contain not only 4-pyridyl but also carboxylate groups in the crystal structure (Almeida Paz, Khimyak *et al.*, 2002). Recently, we also reported a novel one-dimensional  $\text{Co}^{2+}$  coordination polymer containing 1,2-bis(4-pyridyl)ethane (BPE), CUMof-4 (Almeida Paz, Bond *et al.*, 2002).



Just as for CUMof-4, the title compound,  $[\text{Co}(\text{BPY})_2(\text{H}_2\text{O})_4](\text{NDC}) \cdot 2\text{H}_2\text{O}$ , CUMof-6, (I), was synthesized under mild hydrothermal conditions and contains only one crystallographically unique  $\text{Co}^{2+}$  centre, occupying a centre of symmetry in  $P\bar{1}$ . The metal ion shows an almost regular octahedral chemical environment, composed of four water molecules (forming the equatorial plane) and two *trans*-coordinated 4-pyridyl N atoms (from BPY) at the apical positions (Table 1 and Fig. 1). Individual  $[\text{Co}(\text{BPY})_2(\text{H}_2\text{O})_4]^{2+}$  complex cations stack in an offset manner along the  $a$  direction through close BPY contacts. The average distance between adjacent aromatic rings is *ca* 3.5 Å (Fig. 2). Interestingly, and unlike the situation in CUMof-4, the  $\text{NDC}^{2-}$  ions do not participate in these interactions. This is explained by the fact that the metal-to-metal distance imposed by a BPY spacer is not sufficient to accommodate the  $\text{NDC}^{2-}$  anions.

**Figure 1**

The asymmetric unit of (I), CUmof-6, represented with displacement ellipsoids at the 50% probability level and showing the labelling scheme for non-H atoms. Unlabelled ball-and-stick atoms were generated by symmetry [Symmetry codes: (for BPY)  $-x, -y, -z$  and (for  $\text{NDC}^{2-}$ )  $-x, 1 - y, 1 - z$ ].

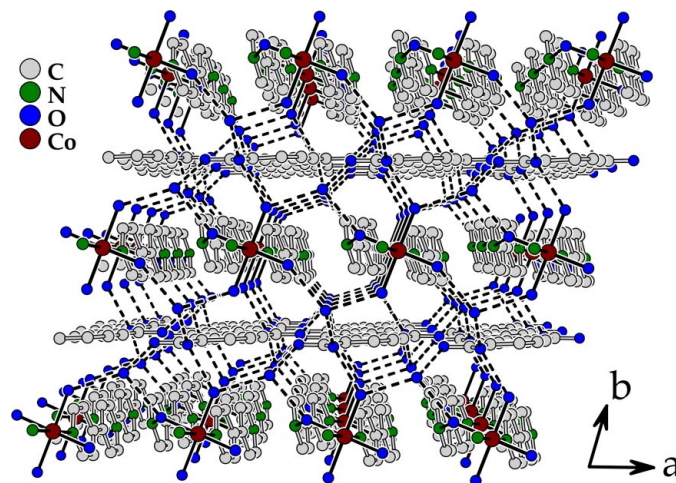
**Figure 2**

Perspective view of CUmof-6 along the  $a$  direction.  $\text{Co}^{2+}$  centres are represented as octahedra, BPY ligands with hollow bonds,  $\text{NDC}^{2-}$  with filled bonds, and water of crystallization in blue.

This may also account for the presence of extra water of crystallization. Compound (I) can be further described by the alternation along the  $b$  direction of layers of the complex cations with layers of  $\text{NDC}^{2-}$  (Fig. 2).  $\text{O}-\text{H}\cdots\text{O}^-$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds between the  $\text{NDC}^{2-}$  ions and the uncoordinated 4-pyridyl group with the water molecules give rise to a three-dimensional network (Table 2 and Fig. 3).

## Experimental

All chemicals were obtained from commercial sources and were used as received. To a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.243 g, Aldrich) in distilled water (6.41 g), 4,4'-bipyridyl (BPY, 0.164 g, Aldrich), 2,6-naphthalenedicarboxylic acid ( $\text{H}_2\text{NDC}$ , 0.218 g, Aldrich) and triethylamine (TEA, 0.208 g, Avocado) were added and the mixture was stirred thoroughly for 1 h at ambient temperature. The suspension, with a  $\text{H}_2\text{NDC}:\text{Co}^{2+}:\text{BPY}:\text{TEA}:\text{H}_2\text{O}$  composition ratio of 1.00:1.01:1.04:2.04:353, was placed inside a Parr stainless steel Teflon-lined reaction vessel (8 ml, 70% 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 (I) were manually separated and preserved in a portion of the reaction vessel solution.

**Figure 3**

Perspective view of CUmof-6 along the  $c$  direction, showing the hydrogen-bonding network (dashed lines). H atoms have been omitted for clarity.

### Crystal data

$\text{C}_{20}\text{H}_{24}\text{CoN}_4\text{O}_4 \cdot \text{C}_{12}\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$   
 $M_r = 693.56$   
 Triclinic,  $P\bar{1}$   
 $a = 6.9856$  (5) Å  
 $b = 9.2926$  (11) Å  
 $c = 12.3538$  (14) Å  
 $\alpha = 78.585$  (5)°  
 $\beta = 84.015$  (7)°  
 $\gamma = 73.740$  (7)°  
 $V = 753.62$  (13) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.528 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 5738 reflections  
 $\theta = 1.0\text{--}25.0^\circ$   
 $\mu = 0.64 \text{ mm}^{-1}$   
 $T = 180$  (2) K  
 Needle, colourless  
 $0.10 \times 0.05 \times 0.05 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 Thin-slice  $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.839$ ,  $T_{\max} = 0.955$   
 5657 measured reflections  
 2574 independent reflections

2083 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.059$   
 $\theta_{\max} = 24.9^\circ$   
 $h = -7 \rightarrow 8$   
 $k = -10 \rightarrow 10$   
 $l = -13 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.121$   
 $S = 1.10$   
 2574 reflections  
 234 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.2073P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.009$   
 $\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.64 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Co1—O12	2.070 (2)	Co1—N21	2.153 (3)
Co1—O11	2.124 (2)		
O12—Co1—O11	91.04 (9)	O12 <sup>i</sup> —Co1—N21	90.66 (9)
O12 <sup>i</sup> —Co1—O11	88.96 (9)	O11—Co1—N21	87.41 (9)
O12—Co1—N21	89.34 (9)	O11 <sup>i</sup> —Co1—N21	92.59 (9)

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

**Table 2**  
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O11—H11A $\cdots$ O4W	0.837 (17)	1.958 (19)	2.785 (3)	169 (3)
O11—H11B $\cdots$ O311 <sup>ii</sup>	0.835 (17)	1.920 (18)	2.754 (3)	175 (4)
O12—H12A $\cdots$ O4W <sup>iii</sup>	0.832 (17)	2.00 (2)	2.798 (3)	162 (3)
O12—H12B $\cdots$ N22 <sup>iv</sup>	0.829 (18)	1.951 (19)	2.772 (4)	170 (4)
O4W—H4A $\cdots$ O312 <sup>v</sup>	0.833 (18)	1.946 (19)	2.767 (3)	169 (4)
O4W—H4B $\cdots$ O311	0.828 (18)	1.932 (19)	2.750 (3)	170 (4)

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

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

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: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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