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catena-poly[[[tetraaquacobalt(II)]-μ-4,4′-bipyridine-κ^2N:N'] phthalate dihydrate]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.084
Data-to-parameter ratio = 13.1

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

A polymeric cobalt complex, $\{[Co(C_{10}H_8N_2)(H_2O)_4]-(C_8H_4O_4)\cdot 2H_2O\}_n$, was synthesized and its crystal structure has been determined by X-ray diffraction. The complex exhibits a polymeric structure consisting of six-coordinated Co^{II} units linked *via* 4,4′-bipyridine (4,4′-bpy) to form a linear chain. The asymmetric unit contains only one half-molecule of the bridging ligand and two coordinated water molecules, the Co^{II} ion and the bridging ligand lying on a twofold rotation axis. Each cobalt(II) ion is in a distorted octahedral environment with a CoN_2O_4 core; 4,4′-bpy acts as a bridging ligand and four O atoms from coordinated water molecules act as terminal ligands. The chains are linked to (which also lie on twofold axes) uncoordinated phthalate anions and water molecules by extensive hydrogen bonds to form a three-dimensional supramolecular structure.

Comment

In recent years, metal-organic coordination polymers with one-, two- or three-dimensional structures have attracted much attention for their potential applications as photoelectric functional materials, catalysis carriers, sensors *etc.* (Fyfe & Stoddart, 1997; Swieqers & Malefetse, 2000; Cheetham *et al.*, 1999; Kiang *et al.*, 2000; Guilera & Steed, 1999; Prior & Rosseinsky, 2001). In the design and synthesis of polymeric complexes, various bridging and chelating ligands have been used extensively. Coordination and hydrogen bonds are the major linkages in these assembly systems.

Carboxylates (Yaghi *et al.*, 1996; Eddaoudi *et al.*, 2001) and pyridyls (Noro *et al.*, 2002) frequently provide rigid frameworks, although the carboxylates tend to form relatively more rigid frameworks as a result of the potential bidentate coordination of their carboxylate groups. Recently, the mixed-linker systems of both carboxylates and pyridyls have proved effective for the preparation of novel coordination polymers

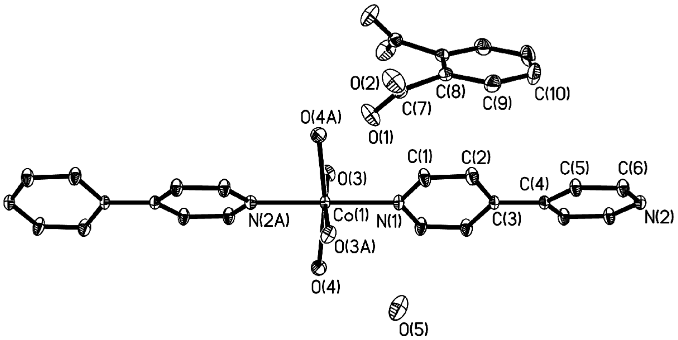


Figure 1
View of $[Co(4,4'\text{-bpy})(H_2O)_4]_n\cdot n(\text{phth})\cdot 2nH_2O$, with the unique atom-labelling scheme (phth is phthalate). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted

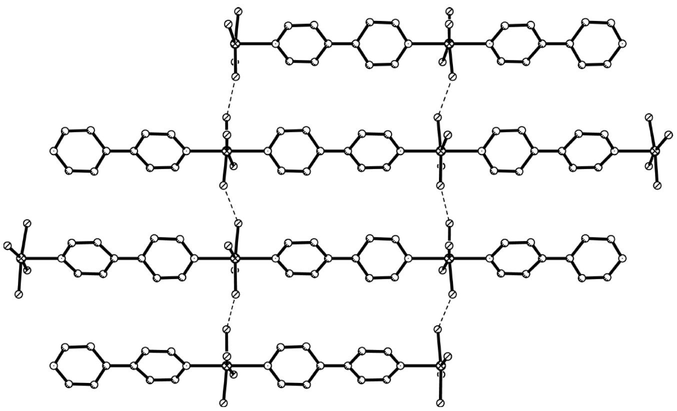
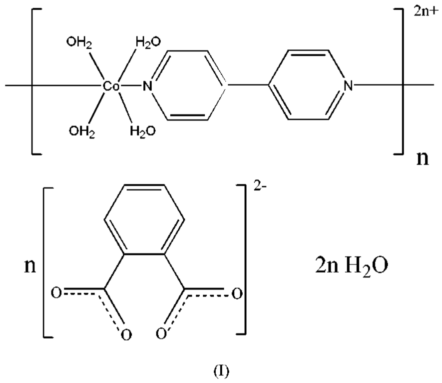


Figure 2
Packing diagram showing the two-dimensional structure; for clarity, uncoordinated phth anions and water molecules have been omitted. Dashed lines indicate hydrogen bonds.

(Geraghty *et al.*, 1999; Kitagawa *et al.*, 1995; Liu *et al.*, 2002; Lu *et al.*, 1999; Shi *et al.*, 2000; Tao *et al.*, 2002). In this research, we planned to synthesize a multidimensional complex structure constructed from a bidentate 4,4′-bipyridine ligand (4,4′-bpy) and multidentate phthalate ligand (phth). However, contrary to our expectation, the phth ligand did not participate in the coordination. Thus we obtained a new one-dimensional polymeric complex $[Co(4,4'\text{-bpy})(H_2O)_4]_n\cdot n(\text{phth})\cdot 2nH_2O$, (I). Its structure consists of a linear chain, which is linked to uncoordinated phth anions and water molecules by extensive hydrogen bonds to form a three-dimensional supramolecular structure.



(I)

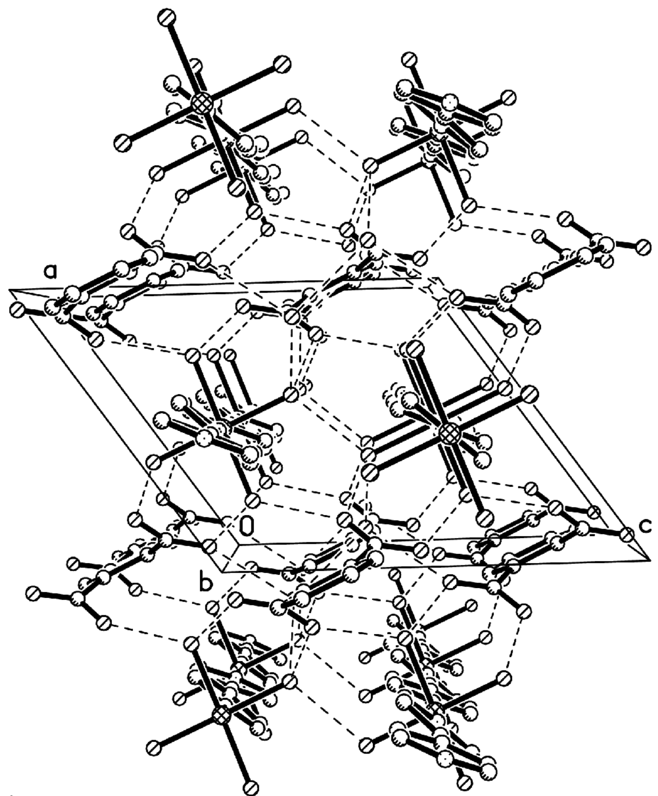


Figure 3
Packing diagram showing the three-dimensional structure, with inter-chain hydrogen bonds (dashed lines); for clarity, H atoms have been omitted.

The structure of the title complex is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The asymmetric unit contains only one half of the chemical formula unit, which consists of half a phthalate anion, half a 4,4′-bpy molecule, two coordinated water molecules and one uncoordinated water molecule in addition to half a cobalt(II) ion. The cobalt(II) ion lies on a rotation axis, which also runs along the axis of the bridging ligand. The coordination geometry around the cobalt ion is a distorted octahedral. Four O atoms from coordinated water molecules, which act as the terminal ligands, lie in the equatorial plane [Co(1)—O(3) = 2.0529 (17) Å and Co(1)—O(4) = 2.1158 (17) Å], while two independent pyridine N-atom donors are in the axial sites [Co(1)—N(1) = 2.172 (3) Å and Co(1)—N(2)^{ii} = 2.197 (3) Å; symmetry code: (ii) $x, y-1, z$]. The bridge *trans* angle N(1)—Co(1)—N(2)^{ii} is constrained to 180° by symmetry; the other *trans* O—Co—O angles and all of the *cis* N—Co—O angles are nearly 180 and 90° (Table 1), respectively. In the phthalate anion, which also lies on a twofold rotation axis, the two independent C—O bonds are approximately equivalent, the double bond being delocalized over both C—O bonds [C(7)—O(1) = 1.250 (3) Å and C(7)—O(2) = 1.242 (3) Å].

The most striking feature of the title compound, as depicted in Fig. 2, is that it consists of a linear chain. Extensive hydrogen bonds are formed between the O atoms of the coordinated water atoms [O(3)] of cobalt ions in adjacent chains, forming two-dimensional layers. Through extensive hydrogen bonds between the cobalt(II) chains, uncoordinated phth anions and uncoordinated water molecules, a three-dimensional supramolecular network is formed (Fig. 3).

Experimental

A mixture of $CoCl_2\cdot 6H_2O$ (0.4 mmol, 95.2 mg), phthalate acid (0.4 mmol, 66.4 mg), 4,4′bpy (0.4 mmol, 76.9 mg) imidazole (0.4 mmol, 27.2 mg) and H_2O (18.0 ml) in a 1:1:1:2500 molar ratio was sealed in a 25 ml stainless steel reactor with a Teflon liner; the mixture was heated to 443 K, kept at 443 K for 72 h, and then cooled slowly to 303 K at a rate of 3 K h^{-1}. Red block-shaped crystals of the title complex were collected by filtration and washed with ethanol (2 × 5 ml).

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Crystal data

$[Co(C_{10}H_8N_2)(H_2O)_4]$-$(C_8H_4O_4)·2H_2O$
M_r = 487.32
Monoclinic, $P2/c$
a = 9.511 (3) Å
b = 11.496 (3) Å
c = 11.528 (4) Å
β = 125.287 (5)°
V = 1028.9 (5) Å^3
Z = 2

D_x = 1.573 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 925 reflections
θ = 2.8–26.1°
μ = 0.89 mm^{-1}
T = 293 (2) K
Block, red
0.18 × 0.16 × 0.12 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.794, T_{max} = 0.898
5821 measured reflections

2111 independent reflections
1665 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 26.4°
$h = -7 \rightarrow 11$
$k = -13 \rightarrow 14$
$l = -14 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 1.04
2111 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.3271P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Co1—O3	2.0529 (17)	Co1—N2^{ii}	2.197 (3)
Co1—O4	2.1158 (17)	O1—C7	1.250 (3)
Co1—N1	2.173 (3)	O2—C7	1.242 (3)
O3^{i}—Co1—O3	175.18 (10)	O4—Co1—N1	95.09 (5)
O3^{i}—Co1—O4	86.62 (7)	O3—Co1—N2^{ii}	92.41 (5)
O3—Co1—O4	93.81 (7)	O4—Co1—N2^{ii}	84.91 (5)
O4—Co1—O4^{i}	169.82 (9)	N1—Co1—N2^{ii}	180.0
O3—Co1—N1	87.59 (5)		

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $x, y - 1, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5C···O3	0.8501 (11)	2.019 (9)	2.856 (3)	168 (4)
O5—H5B···O5^{iii}	0.8501 (11)	2.007 (10)	2.843 (5)	167 (4)
O5—H5A···O2^{iv}	0.8501 (11)	1.98 (2)	2.780 (3)	156 (4)
O4—H4B···O2^{v}	0.85	1.92	2.771 (3)	174
O3—H3C···O1^{vi}	0.8502 (11)	1.663 (6)	2.507 (2)	172 (3)
O3—H3B···O5	0.8499 (11)	2.081 (15)	2.856 (3)	151 (3)
O3—H3A···O3^{vi}	0.8499 (11)	1.904 (12)	2.716 (3)	159 (3)

Symmetry codes: (iii) $2 - x, y, \frac{3}{2} - z$; (iv) $1 + x, y, z$; (v) $x, -y, z - \frac{1}{2}$; (vi) $1 - x, -y, 1 - z$.

The coordinates of the H atoms of the water molecules were determined from difference Fourier maps and refined subject to restrained O—H distances of 0.85 Å. H atoms bound to C atoms could also be located in difference maps and were placed using the HFIX commands in *SHELXL*97 (Sheldrick, 1997). Other H atoms were positioned geometrically and refined riding (C—H = 0.93 Å, O—H = 0.85 Å). U_{iso}(H) values were fixed at $1.2U_{eq}$(C) and $1.5U_{eq}$(O).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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