catena-Poly[bis[tetraaquacobalt(II)-μ-4,4′-bipyridine-κ²N:N′] benzene-1,2,4,5-tetracarboxylate(4−) dihydrate]

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The title compound, $[Co(C_{10}H_8N_2)(H_2O)_4]_2(C_{10}H_2O_8)\cdot2H_2O$, consists of two crystallographically independent Co^{II} atoms linked by 4,4′-bipyridine ligands into one-dimensional chains, which are further connected into a three-dimensional framework linked by $[C_6H_2(COO)_4]^{4-}$ anions and water molecules, achieved through complex hydrogen bonding.

Comment

Polymetallic materials, which are normally constructed by linking transition metal atoms through multidentate bridging ligands, have attracted much attention because of their intriguing topological structures and their potential for interesting applications (Yaghi *et al.*, 1998; Hagrman *et al.*, 1999; Philp & Stoddart, 1996). Complexes with the bridging ligand 4,4′-bipyridine (4,4′-bpy) are particularly interesting because of their interesting topological structures, as well as their potential application in areas such as ion exchange, catalysis, separation and magnetism (Kondo *et al.*, 1997; Yaghi & Li, 1995; Fujita *et al.*, 1994; Julve *et al.*, 1987). Various preparative methods have been employed to obtain such materials. As part of our investigations into the hydrothermal synthesis of new polymeric complexes containing 4,4′-bpy and benzene-1,2,4,5-tetracarboxylic acid (H_4btc), red single crystals of the title compound, (I), were obtained.

(I)
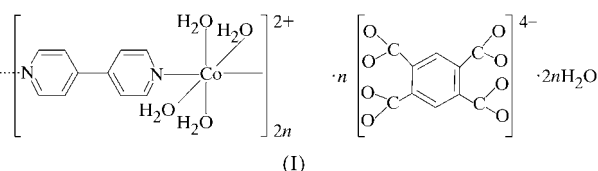
As shown in Fig. 1, the crystal structure of (I) comprises two 4,4′-bpy-bridged crystallographically symmetry-independent Co^{II} centres, water molecules and btc(4−) anions. Bond distances and angles are in good agreement with the values reported for related one-dimensional Co^{II}–4,4′-bpy complexes (Tong *et al.*, 1998; Lu *et al.*, 1998; Dong *et al.*, 2000).

One Co^{II} atom is located at an inversion centre and the other is on a crystallographic twofold axis. Each crystallographically independent Co^{II} centre displays six-coordinate octahedral geometry, coordinated by two N atoms from 4,4′-bpy at the axial positions [Co—N 2.136 (4)–2.207 (3) Å] and four water molecules at the equatorial positions [Co—O 2.043 (3)–2.145 (3) Å], with bond angles involving neighbouring atoms ranging from 87.2 (1) to 92.8 (1)°. These slightly distorted octahedral Co^{II} centres are connected into one-dimensional chains through intervening 4,4′-bpy ligands and are separated by about 11.44 Å.

It is interesting to note that these two one-dimensional polymeric cation arrays, which have a fold of about 60°, are packed into a beautiful three-dimensional architecture
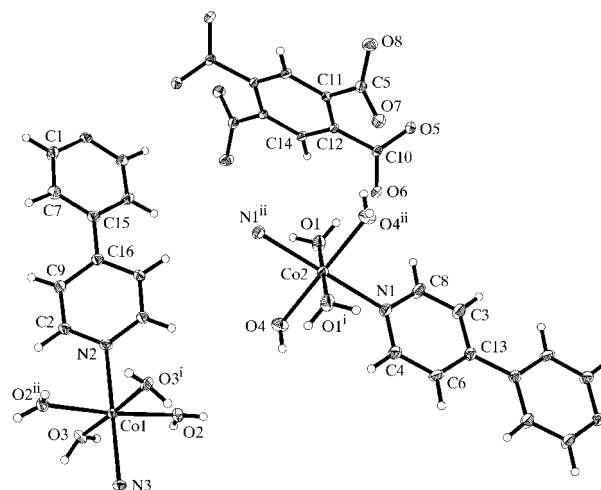

Figure 1
A perspective view of the locally expanded unit for (I). Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii. Solvent water molecules have been omitted for clarity [symmetry code: (i) $1 - x$, y, $\frac{1}{2} - z$; (ii) $\frac{1}{2} - x$, $-\frac{1}{2} - y$, $1 - z$].
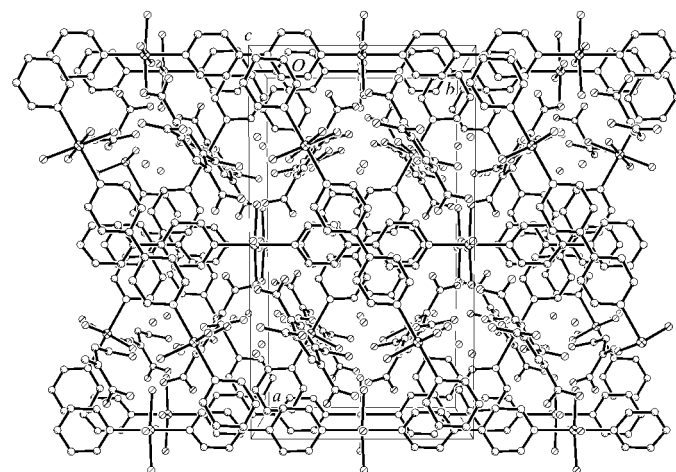
Figure 2
A packing diagram for (I) viewed down the *c* axis. For clarity, H atoms and hydrogen bonds have been omitted. Co atoms are indicated by cross-hatched circles, O atoms by hatched circles, N atoms by open circles and C atoms by shaded circles.

metal-organic compounds

through hydrogen bonding (Fig. 2). The btc(4−) anions link the chains through hydrogen bonds involving the non-metallate O atoms of the carboxylate groups and the aqua ligands, with O···O distances in the range 2.650 (4)–2.890 (4) Å.

Finally, it should be noted that the average distance between the O atoms of the solvent water molecules and those of the aqua ligands is about 2.745 (5) Å, while the distances between the solvent O atoms and the O atoms of the carboxylate groups of the btc ligands range from 2.797 (5) to 2.893 (5) Å. Obviously, there is a complex hydrogen-bonding scheme in the packing of (I).

Experimental

A mixture of $CoSO_4 \cdot 7H_2O$ (0.10 g, 0.36 mmol), 4,4′-bipyridine·$2H_2O$ (0.05 g, 0.26 mmol) and benzene-1,2,4,5-tetracarboxylic acid anhydride (0.10 g, 0.46 mmol) in H_2O (18 ml) was sealed in a 30 ml Teflon-lined stainless steel vessel and heated at 443 K for 6 d under autogeneous pressure. After the reaction, the vessel was cooled slowly to room temperature and red crystals of (I) were produced.

Crystal data

$[Co(C_{10}H_8N_2)(H_2O)_4]_2$-$(C_{10}H_2O_8) \cdot 2H_2O$	$D_x = 1.610$ Mg m^{-3}
$M_r = 860.50$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3537
$a = 20.0909 (4)$ Å	reflections
$b = 11.3466 (1)$ Å	$\theta = 2.0–25.0°$
$c = 15.6407 (4)$ Å	$\mu = 1.02$ mm^{-1}
$\beta = 95.476 (1)°$	$T = 293 (2)$ K
$V = 3549.2 (1)$ Å^3	Prism, red
$Z = 4$	$0.43 \times 0.28 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	3129 independent reflections
φ and ω scans	2634 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{int} = 0.026$
	$\theta_{max} = 25°$
$T_{min} = 0.640$, $T_{max} = 0.815$	$h = -19 \rightarrow 23$
5567 measured reflections	$k = -11 \rightarrow 13$
	$l = -11 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 19.8931P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
3129 reflections	$\Delta\rho_{max} = 0.86$ e Å^{-3}
258 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
H-atom: see below	Extinction correction: SHELXL97
	Extinction coefficient: 0.000071 (1)

Table 1
Selected geometric parameters (Å, °).

Co1—O3	2.072 (3)	Co2—O1	2.043 (3)
Co1—N2	2.136 (4)	Co2—O4	2.133 (3)
Co1—N3	2.138 (4)	Co2—N1	2.207 (3)
Co1—O2	2.145 (3)		
O3—Co1—O3^i	176.8 (2)	O1—Co2—O4^{ii}	92.6 (1)
O3—Co1—N2	88.4 (1)	O1—Co2—O4	87.4 (1)
O3—Co1—N3	91.6 (1)	O4^{ii}—Co2—O4	180.0
O3—Co1—O2	90.3 (1)	O1—Co2—N1	92.6 (1)
N2—Co1—O2	87.2 (1)	O4—Co2—N1	92.0 (1)
N3—Co1—O2	92.8 (1)	O1—Co2—N1^{ii}	87.4 (1)
O3—Co1—O2^i	89.6 (1)	O4—Co2—N1^{ii}	88.0 (1)
O2—Co1—O2^i	174.3 (1)		

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1A···O6	0.82	1.92	2.650 (4)	148
O1—H1B···O101	0.91	1.84	2.745 (5)	176
O2—H2A···O6^i	0.82	2.10	2.890 (4)	161
O2—H2B···O7^{ii}	0.78	1.96	2.742 (4)	179
O3—H3B···O5^{iii}	0.82	1.86	2.663 (4)	168
O3—H3A···O6^i	0.82	1.91	2.704 (4)	166
O4—H4B···O7^{ii}	0.82	2.15	2.843 (4)	142
O4—H4A···O8^{iv}	0.94	1.87	2.805 (4)	173
O101—H10A···O7^{iv}	1.03	1.78	2.797 (5)	168
O101—H10B···O8^v	0.95	1.95	2.893 (5)	170

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

All H atoms were clearly visible in difference maps. All H atoms except the solvent H atoms were positioned geometrically and included as riding atoms, with O—H = 0.78–1.03 Å and C—H = 0.93 Å. The solvent H atoms were handled in the subsequent refinement with fixed isotropic displacement parameters. The highest residual peak is 1.03 Å from O1 and the deepest hole is 0.48 Å from H1A.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: SMART and SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXL97.

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