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Poly[diaquabis(μ_2-4,4′-bipyridine)bis(μ_3-5,5′-dicarboxybiphenyl-2,2′-dicarboxylato)-dicobalt(II) tetrahydrate]

Ji-Yang Xu,[a] Damacio S. Contreras,[b] Frank R. Fronczek[c] and Banglin Chen[b]*

[a]Department of Biochemistry, China Pharmaceutical University, Nanjing 210009, People's Republic of China, [b]Department of Chemistry, The University of Texas-Pan American, Edinburg, TX 78541-2999, USA, and [c]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

Correspondence e-mail: banglin@utpa.edu

Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 87%
R factor = 0.065
wR factor = 0.140
Data-to-parameter ratio = 15.4

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

In the title compound, $\{[Co_2(C_{16}H_8O_8)_2(C_{10}H_8N_2)_2(H_2O)_2]\cdot 4H_2O\}_n$, two types of Co atoms are bridged by 5,5′-dicarboxybiphenyl-2,2′-dicarboxylate and 4,4′-bipyridine ligands to form a rectangular two-dimensional (4,4) grid. Packing of these grids mediated by hydrogen bonding leads to a three-dimensional porous metal–organic framework with water molecules inside the cavities. Both of the independent Co atoms lie on a twofold axes, upon which the long axes of both bipyridine ligands also lie, forming chains in the [010] direction. Both Co atoms have a *trans*-O_4N_2 coordination, but one has four carboxylate O atoms in the equatorial plane, while the other has two carboxylates and two water molecules in this plane.

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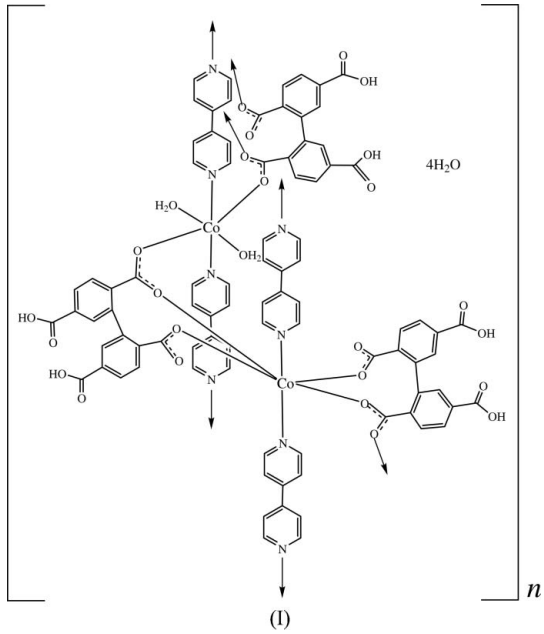
Comment

There has been extensive research interest in porous metal–organic frameworks (MOFs) for their potential applications in gas storage, separation, molecular recognition, magnetism and catalysis (Eddaoudi *et al.*, 2001; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003; Janiak, 2003). These kinds of porous MOFs can not only be constructed from single organic linkers (Chen *et al.*, 2005), but can also be self-assembled from mixed organic linkers (Rather & Zaworotko, 2003; Chun *et al.*, 2005; Ma *et al.*, 2005; Chen *et al.*, 2006). The title compound, (I), is one of the MOFs constructed from cobalt(II) nitrate and the organic linkers biphenyl-2,2′,5,5′-tetracarboxylic acid (H_4BPTC) and 4,4′-bipyridine, and its structure is reported here.



(I)

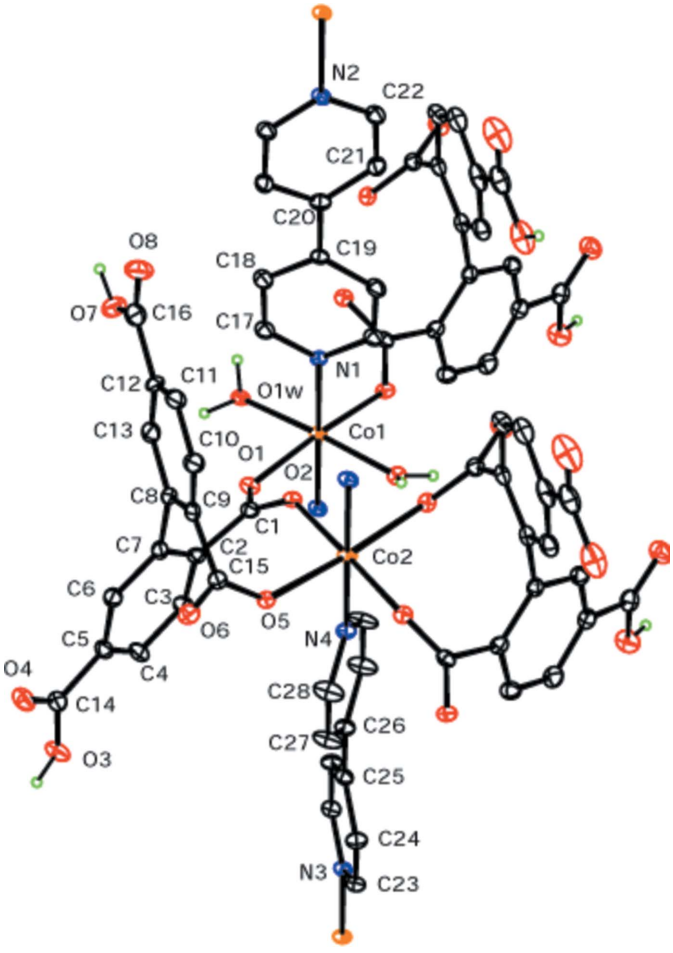


Figure 1
A portion of the structure of (I), with the asymmetric unit labelled, apart from the uncoordinated water molecules, and with displacement ellipsoids drawn at the 40% probability level. C-bound H atoms have been omitted for clarity. The twofold axis through Co1 relates atoms by the symmetry operator $(\frac{1}{2}-x, y, \frac{3}{2}-z)$, while the twofold axis through Co2 relates atoms by the symmetry operator $(\frac{3}{2}-x, y, \frac{3}{2}-z)$. Bipyridine molecules in each coordination environment are related by translation in the *b* direction.

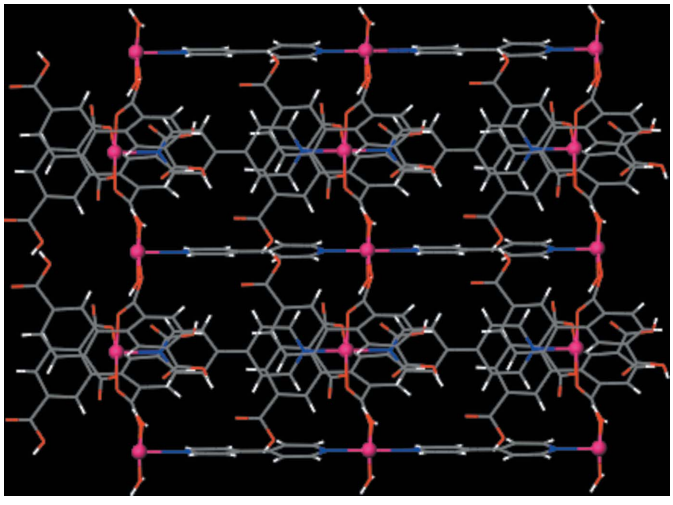


Figure 2
The distorted rectangular two-dimensional (4,4) grid sheet of (I). Co atoms are pink, C atoms grey, N atoms blue and O atoms red.

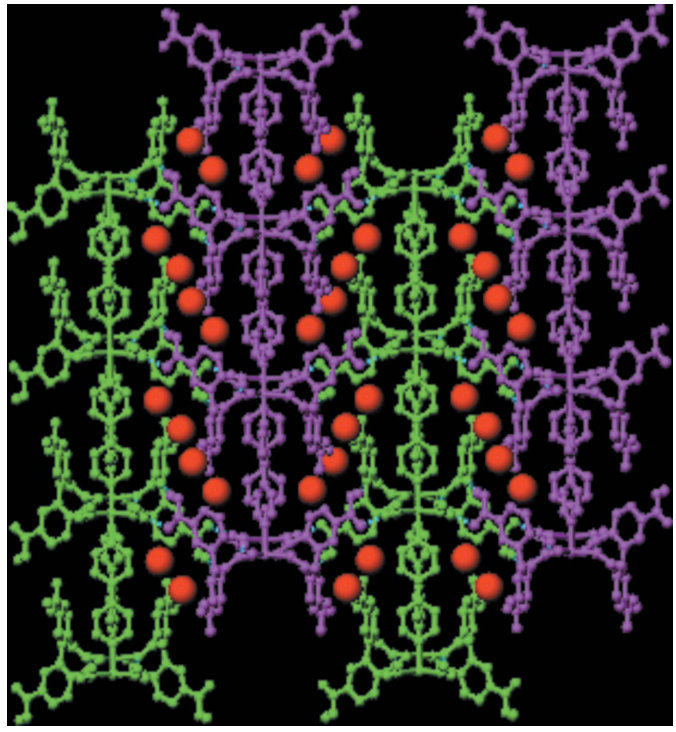


Figure 3
The crystal packing in (I), indicating the *ABAB* arrangement to form a three-dimensional porous MOF, with water molecules residing in the cavities.

A portion of the structure of (I) is shown in Fig. 1. There are two types of Co atoms, both of which lie on a twofold axis, both having an O_4N_2 coordination, with the N atoms *trans*. Atom Co1 has two water molecules and two carboxylate O atoms in the equatorial plane, while atom Co2 has four carboxylate O atoms in this plane. Also along these twofold axes lie two independent 4,4′-bipyridine bridging ligands, forming parallel ···bipy–Co–bipy–Co··· chains in the [010] direction. One BPTC ligand has two of its COOH groups deprotonated (at C1 and C15), while the other two (at C14 and C16) remain protonated. The C1 COO^- group bridges the Co1 and Co2 chains through two O atoms, while the C15 COO^- group is monodentate to Co2, with atom O6 uncoordinated and accepting two hydrogen bonds, discussed below.

The H_2BPTC ligand deviates significantly from planarity, with a torsion angle about its central C7–C8 bond of −114.1 (5)°, while the bipyridyl ligands are slightly nonplanar, with twists about their central C—C bonds of about 20 and 30°, respectively (Table 1).

Topologically, the structure can be viewed as a rectangular two-dimensional (4,4) grid, with Co nodes bridged by H_2BPTC and 4,4′-bipy to form a layer (Fig. 2). These two-dimensional layers are further packed in an ···*ABAB*··· fashion by hydrogen bonding (Table 2) to form a three-dimensional porous structure, in the cavities of which a small number of water molecules reside (Fig. 3). Both COOH groups are donors in the hydrogen-bonding scheme, as are both H atoms of the coordinated water molecule. Hydrogen

bonding by the cavity water molecules is less clear, as only one H atom could be located.

Experimental

The title compound was synthesized by the hydrothermal reaction of $Co(NO_3)_2{\cdot}6H_2O$, biphenyl-2,2′,5,5′-tetracarboxylic acid and 4,4′-bipyridine (1:1:1 mole ratio) in dimethylformamide–ethanol–water (3:3:2 *v*/*v*) at 353 K. Very small pink crystals of the title compound were formed and these were collected in 36% yield.

Crystal data

$[Co_2(C_{16}H_8O_8)_2(C_{10}H_8N_2)_2(H_2O)_2]{\cdot}4H_2O$	V = 2445.0 (17) Å^3
M_r = 1194.78	Z = 2
Monoclinic, $P2/n$	D_x = 1.623 Mg m^{-3}
a = 9.877 (4) Å	Mo $K\alpha$ radiation
b = 11.393 (4) Å	μ = 0.77 mm^{-1}
c = 21.763 (10) Å	T = 105 K
β = 93.25 (2)°	Prism, pink
	0.10 × 0.07 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer (with an Oxford Cryosystems Cryostream cooler)	Minor, 1997)
	T_{min} = 0.932, T_{max} = 0.962
	18159 measured reflections
ω scans with κ offsets	5795 independent reflections
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski &	3130 reflections with $I > 2\sigma(I)$
	R_{int} = 0.085
	θ_{max} = 27.9°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 1.6222P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.065	
$wR(F^2)$ = 0.140	
S = 1.02	$(\Delta/\sigma)_{max} < 0.001$
5795 reflections	$\Delta\rho_{max}$ = 0.95 e Å^{-3}
377 parameters	$\Delta\rho_{min}$ = −0.77 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Co1—O1*W*	2.057 (3)	Co2—O2	2.056 (3)
Co1—O1	2.087 (3)	Co2—N3^{ii}	2.111 (5)
Co1—N1	2.137 (4)	Co2—N4	2.160 (5)
Co1—N2^{i}	2.165 (4)	Co2—O5	2.214 (3)
O1*W*^{iii}—Co1—O1*W*	175.56 (16)	O2—Co2—N3^{ii}	91.12 (7)
O1*W*^{iii}—Co1—O1	97.06 (12)	O2—Co2—N4	88.88 (7)
O1*W*—Co1—O1	82.68 (11)	O2—Co2—O5^{iv}	81.89 (11)
O1—Co1—O1^{iii}	173.34 (15)	N4—Co2—O5^{iv}	93.24 (7)
O1*W*—Co1—N1	92.22 (8)	O2—Co2—O5	98.23 (11)
O1—Co1—N1	93.33 (7)	O2^{iv}—Co2—O5	81.89 (11)
O1—Co1—N2^{i}	86.67 (7)	N4—Co2—O5	93.24 (7)
O2—Co2—O2^{iv}	177.77 (15)	O5^{iv}—Co2—O5	173.52 (14)
C2—C7—C8—C9	−114.1 (5)	C24—C25—C26—C27	−31.0 (3)
C18—C19—C20—C21	−159.9 (3)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O6^{v}	0.84	1.91	2.724 (4)	162
O7—H7*O*···O2*W*^{vi}	0.84	1.83	2.651 (5)	166
O1*W*—H11*W*···O4^{vii}	0.84	1.94	2.775 (4)	172
O1*W*—H12*W*···O5^{viii}	0.84	1.81	2.636 (4)	168
O2*W*—H21*W*···O6^{v}	0.84	1.93	2.768 (5)	171

Symmetry codes: (v) $-x+2, -y+1, -z+1$; (vi) $x-1, y-1, z$; (vii) $-x+1, -y+1, -z+1$; (viii) $x-1, y, z$.

C-bound H atoms were included in the riding-model approximation, with C—H = 0.95–0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C). O-bound H atoms were placed with O—H = 0.84 Å, guided by difference maps, and with U_{iso}(H) = 1.5U_{eq}(O). One of the H atoms on water molecule O2*W* and both of those on water molecule O3*W* could not be located with certainty and were not included in the model.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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