Poly[4,4'-(propane-1,3-diyl)dipyridinium bis{tetraaquabis(μ2-5-carboxybenzene-1,2,4-tricarboxylato)bis[μ2-1,3-bis(4-pyridyl)propane]dicobalt(II)} pentahydrate]

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The title polymeric compound, $\{(C_{13}H_{16}N_2)[Co(C_{10}H_3O_8)(C_{13}H_{14}N_2)(H_2O)_2]_2 \cdot 5H_2O\}_n$, is an ionic structure comprising an anionic two-dimensional mesh characterized by a $\{[Co(Hbtc)(bpp)(H_2O)_2]^-\}_2$ motif [Hbtc is 5-carboxybenzene-1,2,4-tricarboxylate and bpp is 1,3-bis(4-pyridyl)propane], with interspersed 4,4'-(propane-1,3-diyl)dipyridinium cations, denoted $(H_2bpp)^{2+}$, and water molecules providing the charge balance and structure stabilization. The reticular mesh consists of two independent types of $[Co(H_2O)_2]^{2+}$ cationic nodes (lying on inversion centres), interconnected in the $[\bar{1}01]$ direction by two independent sets of neutral bridging bpp ligands, both types of ligands being split by non-equivalent twofold axes. One set is formed by genuinely symmetric moieties, while those in the second set are only symmetric by disorder in the central propane bridge. These chains contain only one type of Co^{II} centre and one type of bpp ligand; the metal cations therein are laterally bridged by Hbtc anions, thus forming transverse chains of alternating types of Co^{II} cations. The elemental motif of the resulting grid is a highly distorted parallelogram, with metal–metal distances of 13.5242 (14) Å in the bpp direction and 9.105 (2) Å in the Hbtc direction, and a large internal angle of 138.42 (18)°. These two-dimensional structures have a profusion of hydrogen-bonding interactions with each other, either directly (with the aqua molecules as donors and the Hbtc anions as acceptors) or mediated by the unbound $(H_2bpp)^{2+}$ cations and water molecules of hydration. These interactions generate a very complex hydrogen-bonding scheme involving all of the available N—H and O—H groups and which links these two-dimensional grids into a three-dimensional network.

Comment

Multidentate ligands are fundamental in the design of metal–organic coordination polymers, not only because they can produce unexpected structural motifs (Archer, 2001), but also because the resulting compounds may contain some interesting properties with potential applications as functional materials (Kitagawa *et al.*, 2004; Kondo *et al.*, 1997; Fujita *et al.*, 1994; Moulton & Zaworotko, 2001). Some of the properties analysed in these ligands are flexibility and multidenticity, which when adequately combined in the same compound often lead to intriguing structural topologies. 1,3-Bis(4-pyridyl)propane (bpp) is an excellent example of a flexible ligand. An analogue of 4,4'-bipyridine, it possesses variable flexibility and functionality owing to the introduction of three methylene groups between the two pyridine (py) rings (Zhang *et al.*, 2010; Carlucci *et al.*, 1997; Plater *et al.*, 2000). Its binding diversity is limited, since it can present only two possible coordination modes, *viz.* either through its two pyridine N atoms [by far the most frequent mode, accounting for an overwhelming 95% of the reported cases in the Cambridge Structural Database (CSD; Version 5.3; Allen, 2002)] or through just one of them. However, even within this almost unique μ_2-mode, the flexibility allowed by the central (saturated) bridge allows for at least two different conformations, very clearly differentiated by their internal N···N distance: (i) bridging, covering more than 90% of the entries in the CSD, with the ligand displaying a fully stretched geometry, reflected in an N···N range of 7.5–10.5 Å and (ii) chelating, with the ligand heavily bent onto itself. Even if this second group is in the minority, there is a clear bimodal distribution of N···N distances within the group: a subgroup falling into an N···N distance range of 5.5–6.5 Å, displaying a rather 'twisted' chelating geometry with no direct interaction between offset pyridine groups, and the conformation with an N···N distance range of 3.8–4.2 Å, which could be termed face-to-face chelating with a clear π–π interaction between stacking pyridine groups.

On the other hand, benzene-1,2,4,5-tetracarboxylic acid (H_4btc) is an outstanding representative of multidentate ligands with eight possible active sites available for coordination and/or hydrogen bonding (Chu *et al.*, 2001; Rochon Fernande & Massarweh, 2000; Bok *et al.*, 2005). In addition, the rotational degree of freedom of its four carboxylate groups gives the ligand an astonishing variety of binding modes, in a surprising mixture of bridging and chelation. It was clear then that the simultaneous presence of these two ingredients in a single complex should in principle give rise to interesting (and at the same time unpredictable) crystal structures, and therefore we decided to investigate the system. We report herein our first successful result, the title Co^{II} polymeric complex formulated as $\{(H_2bpp)[Co(Hbtc)(bpp)(H_2O)_2]_2 \cdot 5H_2O\}_n$, (I).

Fig. 1 shows the asymmetric unit of (I), which consists of two independent metal ions residing on two different centres of symmetry, two halves of coordinated bpp ligands, two coordinated water molecules and one singly protonated Hbtc. The halving of both coordinated bpp ligands takes place by

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way of two different twofold rotation axes: in unit 2 (as defined by its final digit in Fig. 1), the axis bisects the central propyl C atom, and thus defines a true symmetry for the ligand, while in unit 3 (after its final digit in Fig. 1), this is an 'averaged symmetry' built up around a disordered central propane group (shown with dashed lines in Fig. 1) (see *Refinement* for details). The independent set is completed by half of a doubly protonated H_2bpp^{2+} cation (hereafter unit 4), also split through the central propyl C atoms by the same

(I)
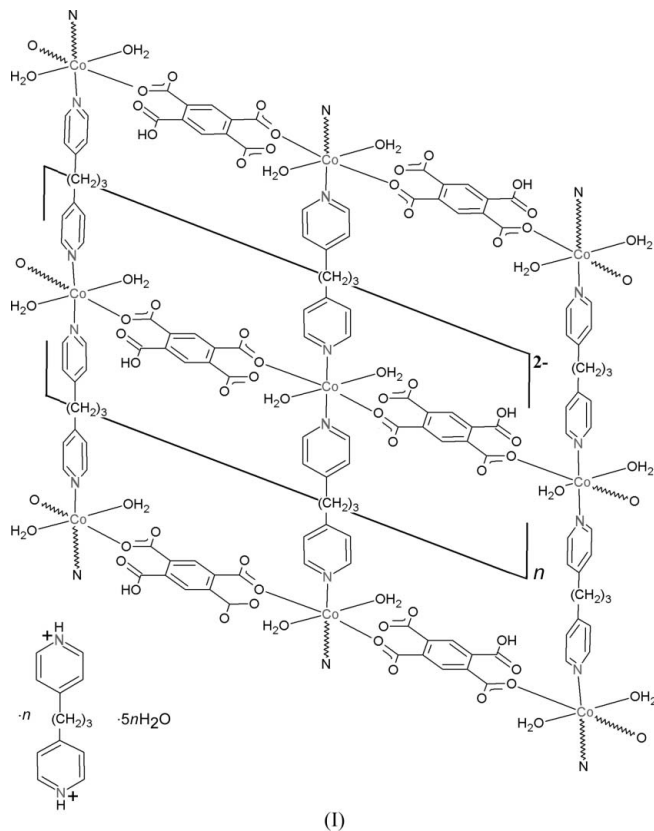
twofold axis halving unit 2, and two and a half water solvent molecules. Fig. 1 presents the minimum formula unit having chemical sense, formulated as $(H_2bpp)[Co(Hbtc)(bpp)(H_2O)_2]_2 \cdot 5H_2O$; in this figure, the effect of the symmetry operations involved ($\bar{1}$ on Co1 and Co2, and a twofold rotation through C72, C74 and O5W on one side and C73″ on the other) is apparent. Both Co^{II} cations present similar CoN_2O_4 octahedral environments, with the same ligands: one N atom from bpp, one O atom from Hbtc and one aqua molecule, plus their symmetry-related counterparts. The octahedra are quite regular and display similar mean Co—O/N distances [with ranges from 2.1215 (14) to 2.1463 (19) Å], apart from Co2—O81 of 2.0755 (14) Å. The maximum angular deviations from 90° for *cis* coordination angles are also larger for Co2 [4.18 (7)° *versus* 3.06 (6)° for Co1]. All three ligands (one Hbtc and two bpp) act in a similar μ_2-bridging mode: the two bpp ligands in the usual role as a spacer, through the two outermost N atoms; the Hbtc anion binding laterally through two noncontiguous carboxylates and offering the opposite side for hydrogen bonding. This $\mu_2,\kappa O,O'$ mode in H_nbtc ($n = 0$–4) is found rather infrequently in the literature; a search of the

CSD (Allen, 2002) showed 309 complexes having the group as a ligand, with only four of them presenting this binding mode. On the other hand, the $\mu_2,\kappa N,N'$ mode in bpp is by far the most common; 379 cases out of 403 complexes in the CSD exhibit this mode. The averaging effect of resonance in the C—O distances in the nonprotonated carboxylates is uneven, though clear, with percentage C—O bond differences of 0.4, 2.6 and 2.8%, as compared with 8.0% for the protonated carboxylate group.

The crystal structure can be described as an anionic two-dimensional mesh characterized by a $\{[Co(Hbtc)(bpp)(H_2O)_2]^-\}_2$ motif, with interspersed $(H_2bpp)^{2+}$ cations and water molecules providing for charge balance and structure stabilization. The grid consists of $[Co(H_2O)_2]^{2+}$ nodes (lying on inversion centres), interconnected along the [$\bar{1}$01] direction by two independent sets of bridging bpp ligands. One set is formed by the genuinely symmetric moieties, while those in the second set are formed by the disordered moieties. These chains do not mix cobalt centres or bpp ligands and thus contain exclusively either Co1/bpp2 or Co2/bpp3 units, respectively; metal cations in contiguous chains are laterally bridged by Hbtc anions to form new transverse chains of alternating Co1/Co2 cations (Fig. 2; A···A). The elemental motif of the resulting grid is a highly distorted parallelogram (Fig. 2), with metal–metal distances of 13.5242 (18) Å along [$\bar{1}$01] (the bpp direction) and 9.105 (2) Å along [100] (the Hbtc direction); distortion is best assessed by the parallelogram's internal angle of 138.42 (16)°.
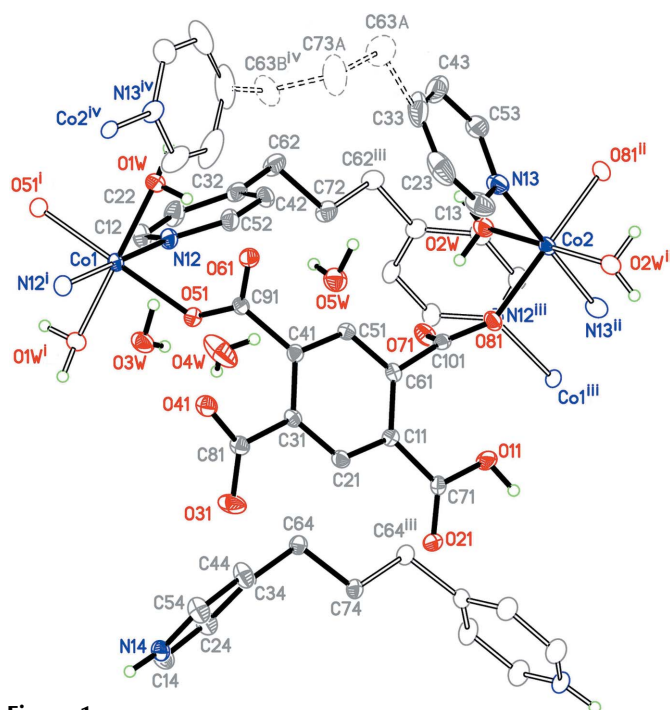

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 40% probability level, with independent (symmetry-related) atoms shown by heavy (hollow) bonds and filled (empty) ellipsoids. The disordered propane group in one of the bpp ligands is drawn with dashed lines. [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x + 1$, $-y + 1$, $-z + 2$; (iii) $-x + \frac{1}{2}$, y, $-z + \frac{3}{2}$; (iv) $-x + \frac{3}{2}$, y, $-z + \frac{3}{2}$.]
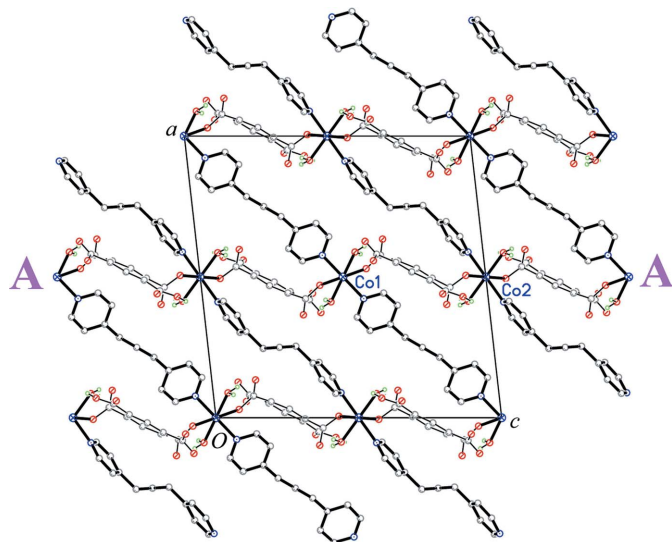
Figure 2
A packing view of (I) along the [010] direction, showing the two-dimensional mesh. In bold are the Co–bpp chains running along [$\bar{1}$01], linked by (slanted) Hbtc anions drawn with thin lines, which define transverse chains (shown as flanking '**A**' labels) along [001].

Figure 3
A packing view of (I) along [100], orthogonal to the view in Fig. 2. The two-dimensional mesh structures are now seen in projection, as undulating chains (in bold) running horizontally (shown as flanking '**A**' labels). Regarding interplanar hydrogen bonds, only those not involving unbound anions or water solvent molecules are shown, linking planes along [010]. For clarity, coordinated bpp groups evolving upwards/downwards, unbound H_2bpp cations, water solvent molecules and nonrelevant H atoms have been omitted. [Symmetry code: (i) $x, y - 1, z$.]

These two-dimensional structures have a profuse hydrogen-bonding interaction with each other. Fig. 3 presents a simplified packing view where intra/inter-grid hydrogen bonds (not mediated by unbound anions or water solvent molecules) are shown. In particular, there are two interactions internal to the coordination polyhedra (entries 1–2 in Table 1) defining two $R(6)$ rings labelled as '**1**' and '**2**' in Fig. 3. Adjacent two-dimensional structures, in turn, interact directly along the [100] direction through hydrogen bonds involving the remaining H atoms of the two aqua ligands (Table 1), forming three different connecting loops ['**3**' = $R_4^4(20)$, and '**4**' and '**5**' = $R_2^2(18)$]. In addition to these interactions, there are a large number of strong O—H$\cdots$O and N—H$\cdots$O hydrogen bonds, mediated by the 4,4'-(propane-1,3-diyl)dipyridinium cation and the water solvent molecules (Table 1), and some weaker nonclassical C—H$\cdots$O and C—H$\cdots Cg$ hydrogen bonds which give a strong three-dimensional coherence to the structure of (I).

In order to compare the structure of (I) with some related analogues, we searched the CSD (Allen, 2002) and found another compound constructed from the same constituent components as (I), *viz. catena*-[(OH$_2$)(btc)$_2$(bpp)Co$_5$], (II) (Jia *et al.*, 2007). As analysed for (I), a general scheme of cobalt nodes interlinked by btc and bpp ligands is described for (II), but which, irrespective of the basic similarities in components and general architecture, displays an absolutely different structure: while the crystal structure of (I) is the result of the hydrogen-bonding interaction of parallel two-dimensional structures, (II) is definitely three-dimensional through covalent bonding and coordination. In the structure of (II), btc acts in an extremely complex μ_8-mode with all its available O atoms engaged in coordination, and defining on its own the three-dimensional structural cage. The bpp ligands, in turn, even if bound to the metal centres, play only a secondary role,
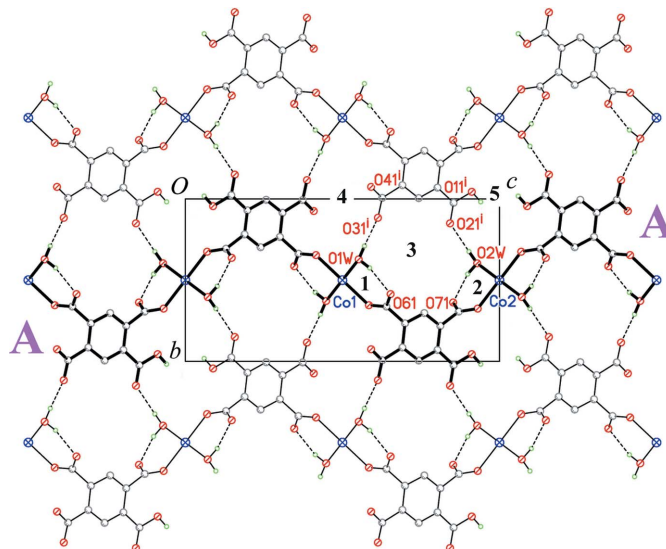
folded into a nearly circular shape [N$\cdots$N = 5.628 (2) Å] and filling the voids within the 'elementary cells' defined by the btc groups which build up the grid.

This contrasts with (I), where the 'first rank' structural building blocks can be shown to be the parallel [$\bar{1}$01] chains defined by the bpp ligands [fully stretched, N$\cdots$N = 9.346 (2) Å], and where the Hbtc units appear to act as 'second rank' interchain μ_2-connectors, to form the (010) two-dimensional structures (Fig. 2) and, *via* hydrogen bonding, promote the interactions between planes (Fig. 3).

There are many possible reasons for the varying behaviour of the btc and bpp, such as synthesis conditions and ligand ratio, but their analysis exceeds the scope of this report; the examples given, however, clearly show the versatility with which both ligands can adapt in different circumstances.

Experimental

An aqueous solution (50 ml) of cobalt(II) acetate (0.164 g, 6.6 mmol) was added to a solution of benzene-1,2,4,5-tetracarboxylic acid (0.168 g, 6.6 mmol) and 1,3-bis(4-pyridyl)propane (0.130 g, 6.6 mmol) in an ethanol–water mixture (250 ml), which had previously been stirred under reflux for 30 min. The reaction mixture was heated under reflux for 2 h. Single crystals adequate for X-ray diffraction studies were obtained by slow evaporation at room temperature. All reagents and solvents were commercially available and were used without additional purification. Elemental analysis was performed with a Carlo–Erba 1108 analyser. Analysis required: C 51.39, H 4.97, N 6.09, O 29.00, Co 8.55%; found: C 51.8, H 4.9, N 6.0, O 28.8, Co 8.6%.

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Crystal data

$(C_{13}H_{16}N_2)[Co(C_{10}H_3O_8)$-
$(C_{13}H_{14}N_2)(H_2O)_2]_2 \cdot 5H_2O$
$M_r = 1379.05$
Monoclinic, $P2/n$
$a = 18.068 (4)$ Å
$b = 9.346 (2)$ Å
$c = 18.209 (4)$ Å

$\beta = 96.421 (6)°$
$V = 3055.5 (12)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.63$ mm^{-1}
$T = 150$ K
$0.36 \times 0.35 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector
    diffractometer
Absorption correction: multi-scan
    (*SADABS* in *SAINT-NT*;
    Bruker, 2002)
    $T_{min} = 0.79$, $T_{max} = 0.89$

24669 measured reflections
6749 independent reflections
5280 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.115$
$S = 1.03$
6749 reflections
477 parameters

H atoms treated by a mixture of
    independent and constrained
    refinement
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H11O$\cdots$O3W^i	0.87 (4)	1.79 (4)	2.625 (2)	161 (3)
N14—H14N$\cdots$O41^{ii}	0.96 (3)	1.66 (3)	2.621 (2)	178 (3)
O1W—H1WA$\cdots$O31^{iii}	0.86 (3)	1.87 (3)	2.723 (2)	175 (3)
O1W—H1WB$\cdots$O61	0.82 (3)	1.99 (3)	2.786 (2)	162 (3)
O2W—H2WA$\cdots$O71	0.85 (4)	1.84 (4)	2.646 (2)	158 (3)
O2W—H2WB$\cdots$O21^{iii}	0.78 (3)	2.07 (4)	2.855 (2)	178 (3)
O3W—H3WA$\cdots$O81^{iv}	0.87 (3)	1.91 (3)	2.786 (2)	178 (3)
O3W—H3WB$\cdots$O4W	0.79 (3)	2.02 (3)	2.805 (3)	178 (3)
O4W—H4WA$\cdots$O5W	0.79 (4)	2.14 (4)	2.882 (2)	157 (4)
O4W—H4WB$\cdots$O41	0.87 (3)	1.96 (3)	2.824 (3)	172 (3)
O5W—H5W$\cdots$O61^{iv}	0.81 (3)	2.05 (3)	2.8535 (19)	169 (3)

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

All H atoms were clearly visible in difference Fourier maps. They were, however, treated differently. C—H hydrogens were repositioned at their expected locations, and allowed to ride with respect to both coordinates [C—H = 0.95 (aromatic) and 0.99 Å (methylene)] and isotropic displacement parameters [$U_{iso}(H) = 1.2U_{eq}(host)$]. Those attached to O and N atoms were refined freely. As already stated, the three bpp groups revolve around different twofold axes: in units 2 and 4, the symmetry element passes through the central C atom, and thus the molecules have genuine $C2$ symmetry, while unit 3 has only average symmetry, disordered around the symmetry element. This disorder takes place in such a way as to have the two lateral pyridine groups reasonably well defined, while linked by a disordered propane group split into two separate components of equal occupancy.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2002); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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