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Polymeric diaqua(μ_2-2,2′-bipyrimidinyl-$\kappa^4N^1,N^{1'}:N^3,N^{3'}$)-di-$\mu_3$-hydroxybis($\mu_5$-benzene-1,3,5-tricarboxylato-$\kappa^5O^1:O^2:O^3:O^3:O^5$)tetracobalt(II) dihydrate

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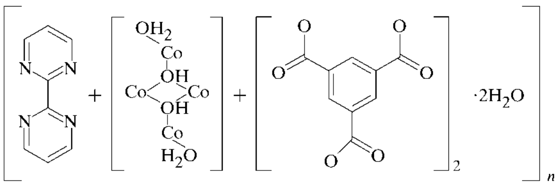
The structure of the title compound, $[Co_4(C_9H_3O_6)_2(OH)_2(C_8H_6N_4)(H_2O)_2]\cdot 2H_2O$, contains three separate species, namely the μ_5-bridging $C_9H_3O_6{}^{3-}$ anion, the doubly chelating and therefore μ_2-bridging $C_8H_6N_4$ ligand (bipyrimidine, BPM), and the dihydrated diaquadihydroxy tetranuclear cationic cluster, $[Co_4(OH^-)_2(H_2O)_2]^{6+}\cdot 2H_2O$, which lies on a crystallographic centre of symmetry, as does the BPM ligand with, in this case, the centre of symmetry coincident with the midpoint of the C—C bond joining the six-membered rings. Within the cation cluster, the Co atoms of one pair are five-coordinate and those of the other six-coordinate.

Comment

The plethora of relevant entries in the Cambridge Structural Database (CSD, Release 23; Allen & Kennard, 1993) is a clear indication of the popularity of benzene-1,3,5-tricarboxylic acid, H_3BTC, for the preparation of materials by self-assembly, also referred to, perhaps optimistically, as crystal engineering. In many cases, as shown for example by Plater *et al.* (2001, and references therein), transition metal elements and additional ligand species are also involved. Some structures of this type have provoked the use of nomenclature which is positively lyrical, as in the 'molecular floral lace conformer' of tris[diaqua(cyclam)nickel(II)] bis(1,3,5-benzenetricarboxylate) hydrate clathrate (CSD refcode GOQTIP; Choi *et al.*, 1999) or the 'molecular honeycomb conformer' of *catena*-{bis(μ_3-1,3,5-benzenetricarboxylato-*O*,*O*′,*O*″)tris[1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]-nickel(II) pyridine solvate tetradecahydrate} (JEDQOY; Choi & Suh, 1998).

While the title compound, (I), is clearly generally similar in type to the examples cited above, its structure possesses some special features. The first and perhaps most obvious of these is the centrosymmetric site symmetry of both the cationic cluster and the 2,2′-bipyrimidine (BPM) ligand. The choice of atom-labelling scheme to accommodate this is shown in Fig. 1, and selected bond lengths and angles are given in Table 1.



(1)

The dihydrated diaquadihydroxytetracobalt cation, $[Co_4(OH^-)_2(H_2O)_2]^{6+}\cdot 2H_2O$ (Fig. 2 and Table 1), displays its own special features. Among these, other than merely the presence of four Co atoms, are (i) the μ_3-hydroxyl atom O7, (ii) the trigonal–bipyramidal coordination of atom Co1 with axial atoms O1 and O3 from two different BTC^{3-} anions [Co1—O1 = 2.3031 (9) Å, notably the longest of any Co—O/N bond in this structure] and equatorial atom O5 from a third anion, along with hydroxyl atom O7 and water molecule O8, and (iii) the octahedral Co2 atom with the chelated BPM ligand, with both N atoms *trans* to hydroxyl atom O7, and carboxylate atoms O1 and O6, again from two different anions, completing its coordination.

The centrosymmetric site symmetry of the BPM ligand demands that it chelates not one but two Co2 atoms. Thus, BPM has a μ_2-bridging function in addition to its chelate action. The shortest Co···Co distances within the cluster [Co2···Co2^{iv} = 3.0392 (3) and Co1···Co2 = 3.2196 (2) Å; symmetry code: (iv) $1 - x, -y, -z$] lie across the shared edges of the coordination polyhedra. The hydrate water molecule, O9, is not shown in Fig. 2, but is associated with the cluster by virtue of its participation as acceptor in the O8—H···O9 hydrogen bond (Table 2).

All three carboxylate groups of the BTC^{3-} anion contribute, in different ways, to the coordination of the Co atoms (Fig. 3). Atom O1 of the C11/O1/O2 carboxylate group bonds

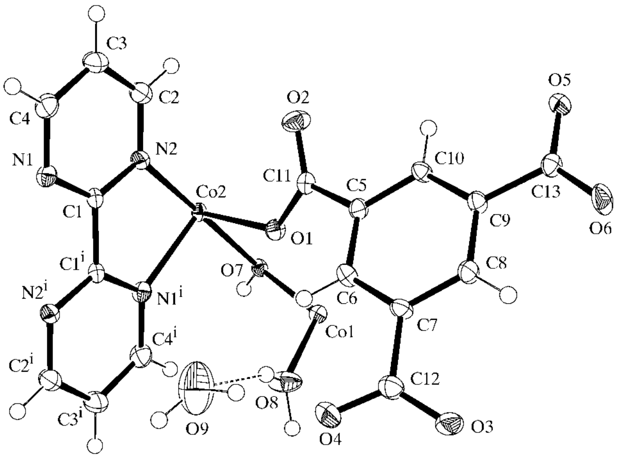


Figure 1
The asymmetric unit of (I), extended in order to complete the BPM molecule by symmetry [symmetry code: (i) $2 - x, -y, -z$], showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line represents the O8—H8*B*···O9 hydrogen bond.

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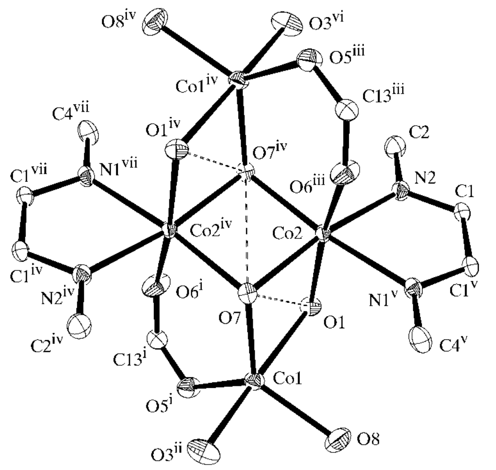

Figure 2
The centrosymmetric tetranuclear cation cluster of (I), showing the coordination of the Co atoms. Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms have been omitted and only fragments of the BPM ligand and the BTC^{3-} anion are shown. Dashed lines indicate the shared edges of the coordination polyhedra [symmetry codes: (i)–(v) as in Table 1; (vi) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $x - 1, y, z$].

to two Co atoms in a monodentate but bridging manner, while atom O2 acts purely as a hydrogen-bond acceptor. In the C12/O3/O4 group, which is also monodentate, atom O3 bonds to a single Co atom, while atom O4 participates in hydrogen-bond formation. The C13/O5/O6 group, on the other hand, has a bidentate but bridging function. Thus, overall, the BTC^{3-} anion, in terms of the Co—O bonds it forms, is a μ_5 species, but is μ_3 in terms of the tetracobalt clusters.

The three carboxylate groups differ also in the angles between the planes defined by their constituent atoms and that of the benzene-ring nucleus of the anion, with values, based on unit-weight least-squares plane calculations, of 33.09 (8), 15.8 (2) and 2.84 (19)°, respectively, for carboxylate groups C11/O1/O2, C12/O3/O4 and C13/O5/O6. The disparity between these values and the relevant torsion angles in Table 1 is indicative of a displacement of the atoms from the plane of the benzene ring, in addition to any rotation of the carboxylate groups relative to the benzene ring about the C—C bond joining them. The effect of this displacement is particularly marked for the C11/O1/O2 group.

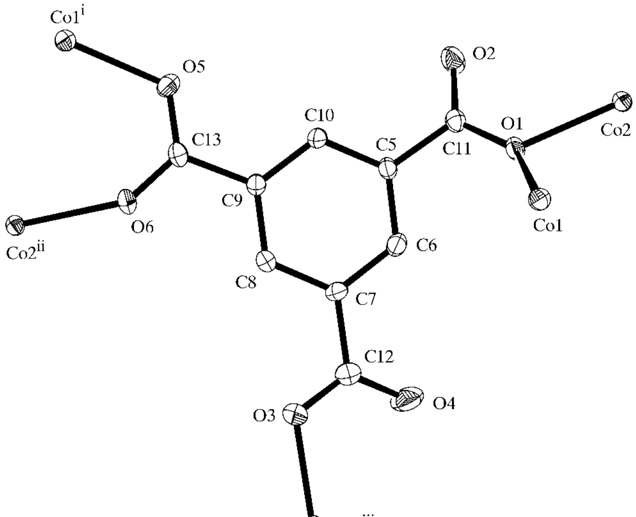

Figure 3
View of the BTC^{3-} anion of (I) and the Co—O bonds it forms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity [symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, y, z + 1$; (iii) $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$].

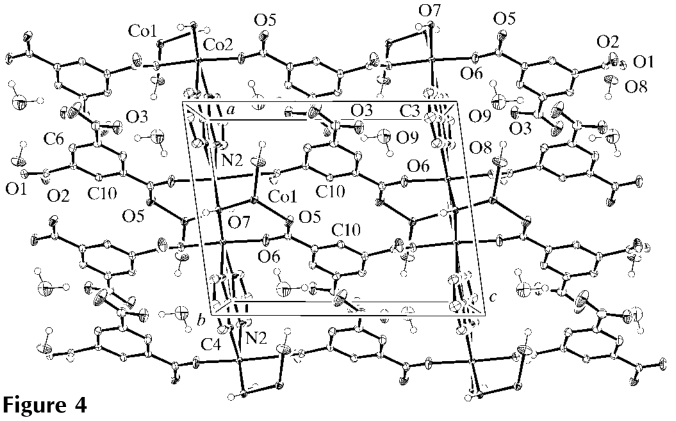

Figure 4
A layer of the polymeric structure of (I) viewed down *b* (out of the page), *b*/2 in thickness and centred on $y = 0$. Displacement ellipsoids are drawn at the 50% probability level and the H atoms of the water and hydroxyl groups are shown as small spheres of arbitrary radii. The directions of the cell edges are indicated.

The overall connectivity of the structure can be thought of in terms of layers parallel to (010) (Fig. 4), in which the hexavalent diaquadihydroxytetracobalt cations are interconnected to form two sets of mutually orthogonal chains. The sets of chains differ in the way in which the cations are connected. In one case, the cation clusters are linked by centrosymmetric doubly bidentate μ_2-bridging BPM ligands. In the other, bridging connectivity is achieved by means of one edge of each of two centrosymmetrically related BTC^{3-} triangles, where the triangle concept is a gross simplification of the overall μ_3 connectivity of the BTC^{3-} anions noted above. The layers are then stacked in the *b* direction in such a way that the remaining vertices of the anion triangles bond to cation clusters in *n*-glide-related (or equivalent twofold screw-axis-related) neighbouring layers. In this way, the anion triangles of one layer are oriented antiparallel to those in neighbouring layers and the cation clusters are distributed in a body-centred manner. Further, with this arrangement, the cation clusters and BTC^{3-} anions by themselves suffice to provide a completely connected three-dimensional structure, with cavities which accommodate the BPM ligands and allow them to complete the coordination of the Co2 atoms.

Experimental

A mixture of benzene-1,3,5-tricarboxylic acid (102 mg, 0.485 mmol), cobalt(II) acetate tetrahydrate (122 mg, 0.489 mmol), 2,2′-bipyrimidine (37 mg, 0.234 mmol) and water (10 ml) was sealed in a 23 ml PTFE-lined metal Parr acid digestion bomb. The bomb was then heated at a rate of 100 K h^{-1} to 453 K and maintained at this temperature for 2 h. Thereafter, the bomb was cooled at a rate of 3 K h^{-1} to 293 K. After opening, the solid products were collected by filtration, washed with copious amounts of water and air dried. A few dark-red crystals of (I), suitable for analysis, were separated mechanically from the largely non- or microcrystalline product.

Table 1
Selected geometric parameters (Å, °).

Co1—O7	1.9985 (9)	Co2—N2	2.1230 (11)
Co1—O5^{i}	2.0075 (10)	Co2—N1^{v}	2.1658 (11)
Co1—O8	2.0168 (12)	Co2—Co2^{iv}	3.0392 (3)
Co1—O3^{ii}	2.0326 (10)	O1—C11	1.2902 (15)
Co1—O1	2.3031 (9)	O2—C11	1.2379 (15)
Co1—Co2	3.2196 (2)	O3—C12	1.2667 (17)
Co2—O6^{iii}	2.0609 (10)	O4—C12	1.2391 (18)
Co2—O7^{iv}	2.0702 (9)	O5—C13	1.2640 (15)
Co2—O7	2.0838 (9)	O6—C13	1.2502 (16)
Co2—O1	2.0899 (9)		
O7—Co1—O5^{i}	114.50 (4)	O6^{iii}—Co2—O1	167.60 (4)
O7—Co1—O8	122.34 (5)	O7^{iv}—Co2—O1	98.07 (4)
O5^{i}—Co1—O8	120.43 (5)	O7—Co2—O1	79.98 (4)
O7—Co1—O3^{ii}	102.61 (4)	O6^{iii}—Co2—N2	93.26 (5)
O5^{i}—Co1—O3^{ii}	93.57 (4)	O7^{iv}—Co2—N2	99.68 (4)
O8—Co1—O3^{ii}	90.51 (5)	O7—Co2—N2	170.10 (4)
O7—Co1—O1	76.79 (3)	O1—Co2—N2	91.11 (4)
O5^{i}—Co1—O1	88.19 (4)	O6^{iii}—Co2—N1^{v}	80.63 (4)
O8—Co1—O1	88.43 (4)	O7^{iv}—Co2—N1^{v}	172.58 (4)
O3^{ii}—Co1—O1	178.23 (4)	O7—Co2—N1^{v}	97.61 (4)
O6^{iii}—Co2—O7^{iv}	92.63 (4)	O1—Co2—N1^{v}	88.98 (4)
O6^{iii}—Co2—O7	94.62 (4)	N2—Co2—N1^{v}	77.76 (4)
O7^{iv}—Co2—O7	85.95 (4)		
C6—C5—C11—O2	149.92 (14)	C6—C7—C12—O3	162.88 (14)
C10—C5—C11—O2	−34.06 (19)	C8—C7—C12—O3	−13.2 (2)
C6—C5—C11—O1	−31.16 (17)	C8—C9—C13—O6	−0.03 (18)
C10—C5—C11—O1	144.86 (12)	C10—C9—C13—O6	−177.21 (13)
C6—C7—C12—O4	−15.8 (2)	C8—C9—C13—O5	178.81 (12)
C8—C7—C12—O4	168.16 (16)	C10—C9—C13—O5	1.63 (19)

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

Crystal data

$[Co_4(C_9H_3O_6)_2(OH)_2(C_8H_6N_4)(H_2O)_2]\cdot 2H_2O$
$M_r = 914.20$
Monoclinic, $P2_1/n$
$a = 8.7476$ (4) Å
$b = 15.3691$ (6) Å
$c = 11.0972$ (4) Å
$\beta = 97.759$ (1)°
$V = 1478.28$ (10) Å^3
$Z = 2$
$D_x = 2.054$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5004 reflections
$\theta = 2.7$–32.5°
$\mu = 2.30$ mm^{-1}
$T = 298$ (2) K
Block, dark red
0.50 × 0.40 × 0.22 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.507$, $T_{max} = 0.603$
15 056 measured reflections
5315 independent reflections
4765 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 32.5°$
$h = -13 \rightarrow 11$
$k = -23 \rightarrow 23$
$l = -13 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.067$
$S = 1.04$
5315 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 0.6519P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Aryl H atoms were placed in calculated positions, with C—H = 0.93 Å, and were refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. Hydroxyl (O7) and water (O8 and O9) H atoms were found in difference maps. The H atoms attached to O7 and O8 were refined isotropically in the usual manner, but with O—H and H···H of the latter constrained to, respectively, 1.0 and 1.54 times a free variable whose final refined value was 0.74 (2) Å. The H atoms associated with the hydrate water molecule (O9) were refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(O9)$. The positions of atoms H9*A* and H9*B* coincide with the second and third largest features in the difference map obtained prior to their introduction into the model. While they create a reasonable representation of the water molecule, no suitable acceptor is available to permit atom H9*B* to participate in hydrogen-bond formation. The largest feature at this stage, and still present in the final difference map as a peak of 1.02 e Å^{-3}, 0.76 Å from O4, was considered as one, and indeed the most likely, of several possible alternative sites for H9*B* in a number of unsuccessful attempts to provide a more complete hydrogen-bonding scheme. This particular site, however, is too close to C12 (approximately 1.46 Å) and must therefore be regarded as an artefact.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7···O2^{i}	0.76 (2)	2.50 (2)	3.0980 (14)	136 (2)
O7—H7···O4^{ii}	0.76 (2)	2.52 (2)	2.9718 (17)	120 (2)
O8—H8*A*···O2^{iii}	0.74 (2)	1.95 (2)	2.6749 (15)	164 (3)
O8—H8*B*···O9	0.72 (2)	2.11 (2)	2.815 (2)	164 (3)
O9—H9*A*···O4	0.89	1.84	2.709 (2)	165

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1519). Services for accessing these data are described at the back of the journal.

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