

**A new trinuclear cobalt(II) complex:  
 decaqua- $1\kappa^3O,2\kappa^4O,3\kappa^3O$ -  
 bis(benzene-1,3,5-tricarboxylato)-  
 $1\kappa O,3\kappa O$ -di- $\mu$ -4,4'-bipyridine-  
 $1:2\kappa^2N:N'$ ;  $2:3\kappa^2N:N'$ -di-4,4'-  
 bipyridine- $1\kappa N,3\kappa N$ -tricobalt(II)  
 4,4'-bipyridine solvate octahydrate**

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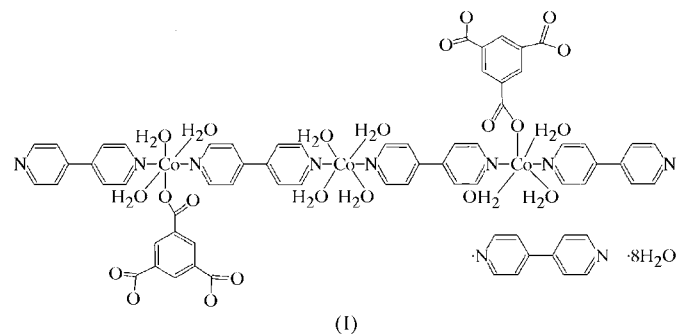
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The principal building units in the title compound,  $[\text{Co}_3(\text{C}_9\text{H}_3\text{O}_6)_2(\text{C}_{10}\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})_{10}] \cdot \text{C}_{10}\text{H}_8\text{N}_2 \cdot 8\text{H}_2\text{O}$ , are the linear centrosymmetric tricobalt(II) complex molecules resulting from two square-pyramidal  $[\text{Co}(\text{btc})(\text{bpy})(\text{H}_2\text{O})_3]^-$  entities (bpy is 4,4'-bipyridine and btc is the benzene-1,3,5-tricarboxylate trianion) bridged by one *trans*- $[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4]^{2+}$  unit. The trinuclear complex molecules are assembled into infinite chains through intermolecular O—

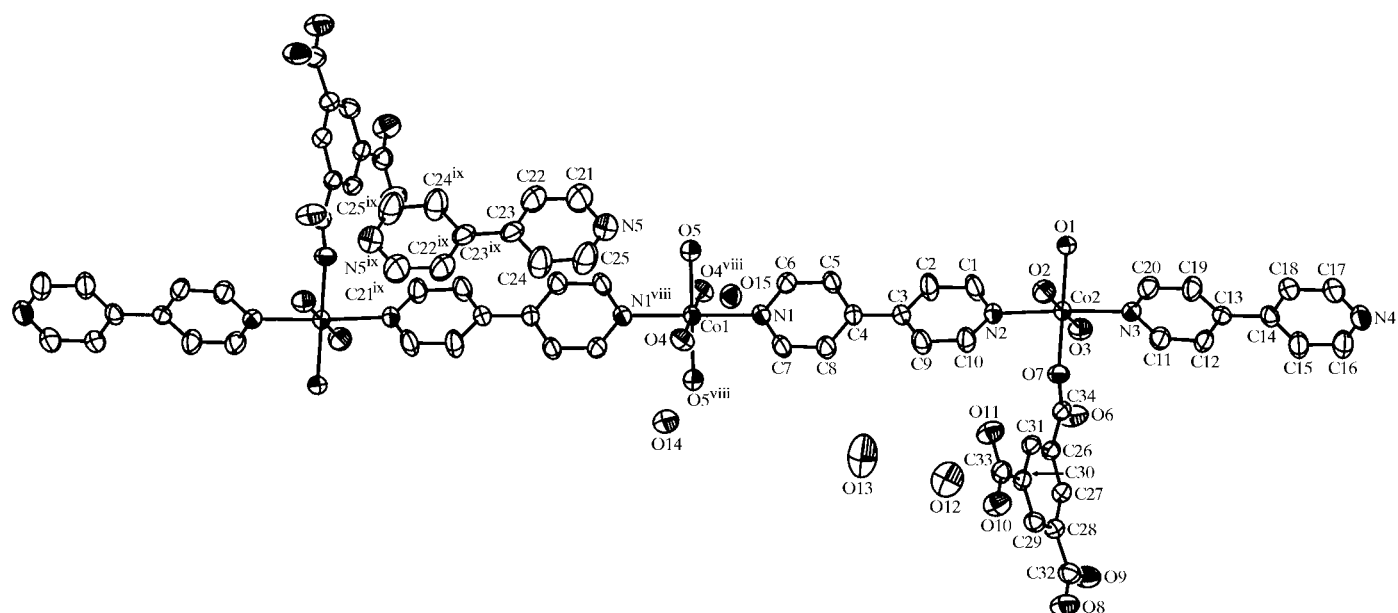
H...N hydrogen bonds and  $\pi$ – $\pi$  stacking interactions between adjacent monodentate bpy ligands. The chains and uncoordinated bpy molecules are further assembled into two-dimensional open layers, which are stacked in a staggered manner to give a three-dimensional supramolecular architecture with the solvent water molecules in the cavities.

**Comment**

Recently, the design and synthesis of metal–organic frameworks (MOFs) has been a field of increasing interest due to their potential applications as functional materials (Tu *et al.*,



2003; Mandal *et al.*, 2000; Reynolds & Coucouvanis, 1998). In general, the strategy to design MOFs relies on the utilization of multidentate O- and/or N-donor bridging ligands. For this, benzenecarboxylic acids, such as terephthalic acid, benzene-1,3,5-tricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid and mellitic acid, in combination with some linear N-donor ligands, such as 4,4'-bipyridine, 1,2-di-4-pyridylethane, are extensively employed to construct one-, two- and three-dimensional coordination polymers (Groeneman *et al.*, 1999; Shattock *et al.*, 2005; Wu *et al.*, 2002; Cui, 2005; Chui *et al.*, 1999). However, few reports of polynuclear complex mol-



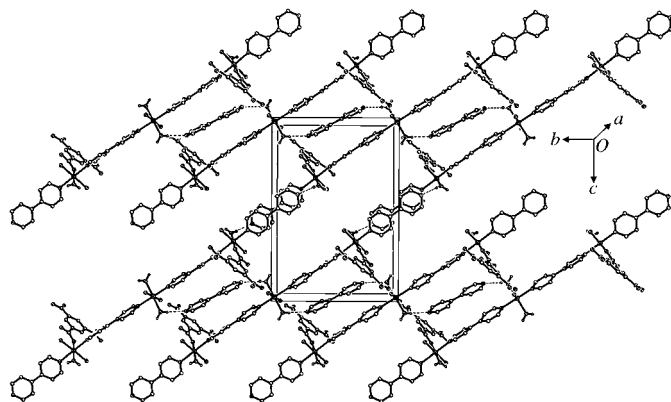
**Figure 1**  
 A view of the complex molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 45% probability level and H atoms have been omitted for clarity. [Symmetry codes: (x)  $-x + 2, -y + 1, -z + 1$ ; (xi)  $-x, -y, -z + 1$ .]

ecules from the self-assembly of transition metal cations with benzene-1,3,5-tricarboxylic acid ( $H_3btc$ ) and 4,4'-bipyridine (bpy) have been published to date. We present here the title novel trinuclear cobalt complex,  $[Co_3(C_9H_3O_6)_2(C_{10}H_8N_2)_4(H_2O)_{10}] \cdot C_{10}H_8N_2 \cdot 8H_2O$ , (I), which was obtained from the hydrothermal reaction of bpy,  $H_3btc$  and  $CoCl_2 \cdot 6H_2O$  at 443 K.

As shown in Fig. 1, compound (I) consists of solvent water molecules, bpy molecules and linear centrosymmetric trinuclear  $[Co_3(btc)(bpy)(H_2O)_{10}]$  complex molecules, where the middle Co1 atom at an inversion centre is bridged to two distal Co2 atoms by two bidentate bpy ligands. Both crystallographically independent Co atoms are in nearly identical *trans*- $CoN_2O_4$  environments with normal Co–N and Co–O bond lengths (Lightfoot & Snedden, 1999). The octahedral  $N_2O_4$  donor set around the Co1 atoms arises from two N atoms of different bridging bpy ligands and four aqua O atoms, while the coordination geometry of the Co2 atoms is defined by three aqua O atoms, one O atom of the monodentate btc trianion, and two N atoms of a bridging bidentate bpy and a monodentate bpy ligand, respectively. The monodentate btc anions are nearly perpendicular to the principal axis through the Co atoms of the trinuclear molecule. To the best of our knowledge, complex (I) represents a rare example of a compound with the btc anion acting as a monodentate ligand (Guillou *et al.*, 2000).

The carboxylate groups are found to be twisted from the plane defined by the C atoms to different extents. The largest dihedral angle of  $13.3(3)^\circ$  is found for the coordinated group, due to the formation of an intramolecular hydrogen bond between uncoordinated atom O6 and an aqua ligand, with  $O3 \cdots O6 = 2.775(4) \text{ \AA}$ ; the dihedral angles for the uncoordinated groups are  $4.7(8)$  and  $5.0(7)^\circ$ , respectively. The uncoordinated carboxylate O atoms are each involved in double hydrogen bonds to both aqua ligands and uncoordinated water molecules.

Through an intermolecular hydrogen bond between the uncoordinated pyridyl N atom and the aqua ligand opposite to the coordinated carboxylate O7 atom [ $O1 \cdots N4^i = 2.828(5) \text{ \AA}$ ; symmetry code: (i)  $-x + 2, -y - 1, -z + 2$ ], the trinuclear



**Figure 2**  
The two-dimensional supramolecular layer in (I), viewed parallel to (100).

complex molecules are assembled into infinite chains extending in the  $[021]$  and  $[02\bar{1}]$  directions. The resulting chains are stabilized by intermolecular  $\pi$ – $\pi$  stacking interactions between adjacent monodentate bpy ligands (mean interplanar distance =  $3.56 \text{ \AA}$ ). The uncoordinated bpy molecules are each sandwiched between two adjacent bridging bpy ligands of different chains, and are engaged in  $\pi$ – $\pi$  stacking interactions and in hydrogen bonds to one aqua ligand bonded to the middle Co1 atom, with  $O5 \cdots N5 = 2.895(5) \text{ \AA}$ , leading to a two-dimensional open supramolecular layer parallel to (100) with the btc ligands pendent on both sides (Fig. 2).

The layers are stacked in a staggered manner, with btc ligands of one layer occupying the apertures of a neighbouring layer, and interlocked by interlayer hydrogen bonds [ $O2 \cdots O9^{iv} = 2.733(4) \text{ \AA}$  and  $O5 \cdots O11^{iv} = 2.858(4) \text{ \AA}$ ; symmetry code: (iv)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ]. The uncoordinated water molecules are located between the layers and participate in extensive hydrogen bonding, which makes a substantial contribution to the stabilization of the crystal structure. The uncoordinated bpy molecule is twisted, with a dihedral angle of  $8.8(2)^\circ$  between the two pyridyl components, while the mono- and bidentate bpy ligands are twisted with dihedral angles between the component rings of  $4.9(1)$  and  $12.8(2)^\circ$ , respectively, indicating significant coordination effects.

## Experimental

A 23 ml Teflon-lined autoclave charged with a mixture of  $CoCl_2 \cdot 6H_2O$  (0.237 g, 1.0 mmol), benzene-1,3,5-tricarboxylic acid (0.105 g, 0.5 mmol), NaOH (0.03 g, 1.5 mmol) and  $H_2O$  (10.0 ml) was heated at 443 K for 120 h, then cooled to 373 K at a rate of  $5 \text{ K h}^{-1}$  and held at this temperature for 10 h, followed by further cooling to room temperature. The mixture was filtered and slow evaporation of the pink filtrate at room temperature yielded rose-coloured crystals of (I) (yield *ca* 5%, based on the initial  $CoCl_2 \cdot 6H_2O$  input).

### Crystal data

$[Co_3(C_9H_3O_6)_2(C_{10}H_8N_2)_4(H_2O)_{10}] \cdot C_{10}H_8N_2 \cdot 8H_2O$   
 $M_r = 1696.23$   
 Monoclinic,  $P2_1/n$   
 $a = 13.193(3) \text{ \AA}$   
 $b = 13.982(3) \text{ \AA}$   
 $c = 20.193(4) \text{ \AA}$   
 $\beta = 91.36(3)^\circ$

$V = 3723.8(13) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.513 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.75 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Block, red  
 $0.31 \times 0.27 \times 0.22 \text{ mm}$

### Data collection

Siemens P4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{min} = 0.527, T_{max} = 0.601$   
 (expected range = 0.743–0.847)  
 10423 measured reflections

8535 independent reflections  
 4457 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.043$   
 $\theta_{max} = 27.5^\circ$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.064$   
 $wR(F^2) = 0.154$   
 $S = 1.00$   
 8535 reflections  
 502 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.3118P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.41 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.41 \text{ e \AA}^{-3}$

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...N4 <sup>i</sup>	0.77	2.10	2.828 (5)	156
O1—H1B...O14 <sup>ii</sup>	0.81	2.09	2.812 (4)	149
O2—H2A...O15 <sup>iii</sup>	0.80	2.15	2.916 (5)	162
O2—H2B...O9 <sup>iv</sup>	0.75	2.00	2.732 (5)	166
O3—H3A...O13 <sup>iii</sup>	0.72	1.98	2.651 (4)	157
O3—H3B...O6	0.83	2.10	2.773 (4)	138
O4—H4A...O15	0.84	1.89	2.709 (4)	167
O4—H4B...O14	0.89	1.89	2.741 (5)	164
O5—H5A...O11 <sup>iv</sup>	0.85	2.03	2.858 (5)	162
O5—H5B...N5	0.72	2.18	2.895 (4)	173
O12—H12A...O10	0.79	2.14	2.862 (4)	153
O12—H12B...O8 <sup>v</sup>	0.83	2.29	2.994 (5)	142
O13—H13A...O10 <sup>v</sup>	0.76	2.07	2.787 (4)	158
O13—H13B...O12	0.78	1.89	2.664 (4)	177
O14—H14A...O9 <sup>vi</sup>	0.81	2.06	2.848 (5)	166
O14—H14B...O8 <sup>vii</sup>	0.78	1.96	2.728 (5)	167
O15—H15A...O11 <sup>iv</sup>	0.82	1.94	2.751 (5)	171
O15—H15B...O6 <sup>vi</sup>	0.78	1.92	2.677 (4)	172

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

H atoms bonded to C atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Water H atoms were found in a difference Fourier synthesis and refined with the O—H distances fixed as initially found and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3039). Services for accessing these data are described at the back of the journal.

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