

# Poly[[diaquacobalt(II)]- $\mu$ -4,4'-bipyridine- $\kappa^2$ N:N'- $\mu$ -*p*-phenylenebis(oxyacetato)- $\kappa^2$ O:O']

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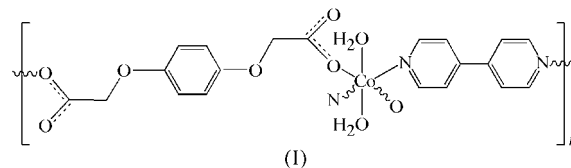
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The title compound,  $[\text{Co}^{\text{II}}(\text{C}_{10}\text{H}_8\text{O}_6)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]_n$ , was obtained by the hydrothermal reaction of  $\text{CoSO}_4$  with benzene-1,4-dioxydiacetate [systematic name: *p*-phenylenebis(oxyacetate)] and 4,4'-bipyridine (4,4'-bpy). The Co atom lies at an inversion center and the benzene-1,4-dioxydiacetate and 4,4'-bipyridine moieties lie about other inversion centers. The benzene-1,4-dioxydiacetate ligands bridge the octahedral  $\text{Co}^{\text{II}}$  coordination centers, forming a one-dimensional zigzag chain. The chains are further bridged by 4,4'-bpy ligands, forming a novel two-dimensional supramolecular architecture. Hydrogen-bonding interactions between the coordinated water molecules and the carboxylate O atoms lead to the formation of a three-dimensional network structure.

## Comment

In recent years, the crystal engineering and construction of metal-organic coordination polymers with fascinating structural topologies have attracted much attention owing to the potential functions of these compounds as microporous solids for molecular adsorption, ion exchange and heterogeneous catalysis (Matsumoto *et al.*, 1999; Chui *et al.*, 1999). The majority of reported work is based on the use of multidentate ligands to bind to the *d*-block transition metal ions through self-assembly processes. It has also been proved that careful selection of appropriate ligands is crucial to the construction of specific supramolecular architectures. This concept is demonstrated by the great variety of structural topologies of discrete supramolecular complexes or infinite supramolecular arrays, such as molecular grids, racks, bricks, rings, boxes, honeycombs and helicates (Fei *et al.*, 2000; Caradoc-Davies *et al.*, 2000). In general, (i) the multiple coordination sites of the ligand incline towards forming higher dimensions and (ii) the

long chain of the ligand may generate a larger cavity or channel in the assembly reaction with metal ions. On the basis of the above considerations, we chose benzene-1,4-dioxydiacetic acid and 4,4'-bipyridine (4,4'-bpy) as bridging ligands in this work. We report here the novel two-dimensional framework structure of the title compound, (I), which is built up by connecting the crystallographically unique  $\text{Co}^{\text{II}}$  atom with its neighbors *via* bridging 4,4'-bpy ligands and benzene-1,4-dioxydiacetate. To the best of our knowledge, although benzene-1,4-dioxydiacetic acid is a multidentate ligand in that it has the potential to coordinate to metals in a number of different ways, few compounds of benzene-1,4-dioxydiacetic acid have been reported.



Polymer (I), which crystallizes in the space group  $P\bar{1}$ , contains infinite grid-like layers. The molecular structure, with

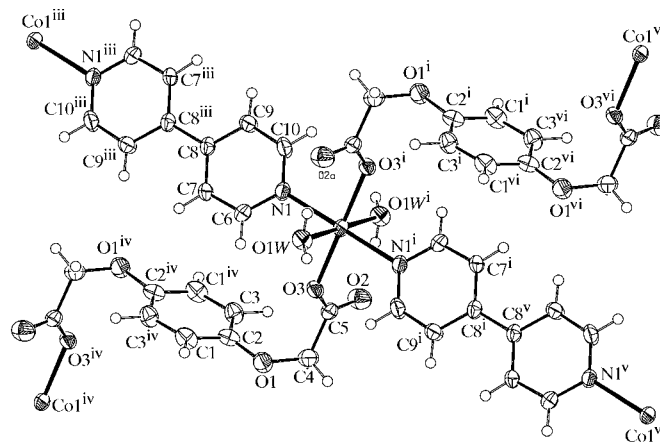


Figure 1

A view of the title compound, showing the atomic labeling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (i)  $-x, -y, -z$ ; (iii)  $-x, 1-y, 1-z$ ; (iv)  $1-x, -y, 1-z$ ; (v)  $x, y-1, z-1$ ; (vi)  $x-1, y, z-1$ .]

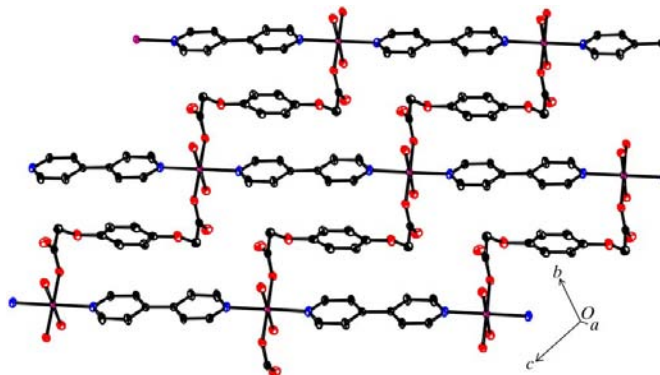
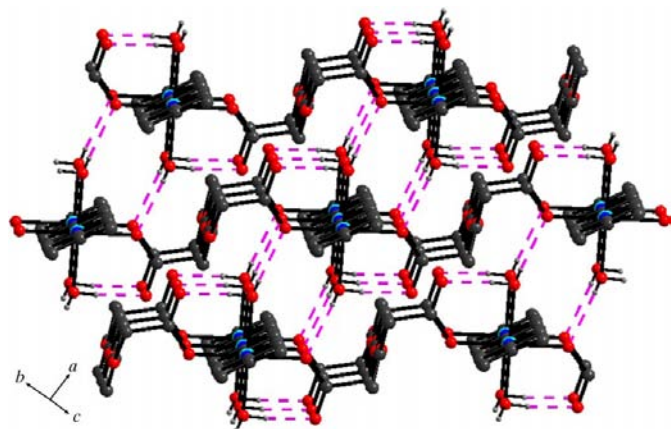


Figure 2

The two-dimensional network in (I) along the *bc* plane. H atoms have been omitted for clarity.



**Figure 3**  
The packing of the title compound. Hydrogen bonds are indicated by dashed lines.

the atomic labeling scheme, is presented in Fig. 1. The Co<sup>II</sup> ion lies at the cell origin and is octahedrally coordinated by two N atoms from two 4,4'-bpy ligands, two identical monodentate carboxylate groups and two water molecules, which are all in *trans* arrangements. It can be seen that the Co<sup>II</sup> ion is coplanar with the plane defined by atoms O3, O3<sup>i</sup>, OW1 and OW1<sup>i</sup> [symmetry code: (i)  $-x, -y, -z$ ]. The Co–O and Co–N distances (Table 1) are similar to those in related cobalt complexes (Wu *et al.*, 2002; Zhu *et al.*, 2003). Each benzene-1,4-dioxydiacetate ligand links two metal centers in a  $\mu_2$ -bridging mode, and each metal center connects two benzene-1,4-dioxydiacetate ligands to form a zigzag chain structure. Each 4,4'-bpy ligand bridges two Co<sup>II</sup> ions from two neighboring zigzag chains, resulting in a two-dimensional lamellar structure.

The structure of (I) contains 44-membered macro-metallo-cyclic rings, comprising four Co<sup>II</sup> ions at the corners, and two 4,4'-bpy ligands and two benzene-1,4-dioxydiacetate ligands as the edges (see Fig. 2).

There are extensive hydrogen-bonding and short-contact interactions (Table 2), namely (i) intramolecular hydrogen-bonding between the coordinated water molecules and the uncoordinated carboxyl O atoms, with an O $\cdots$ O distance of 2.609 (7) Å, (ii) interlayer hydrogen-bonding interactions between the coordinated water molecules and the coordinated carboxyl O atoms, with an O $\cdots$ O distance of 2.958 (6) Å, and (iii) weak short-contact interactions between the coordinated water molecules and carboxyl O atoms, with O $\cdots$ O distances ranging from 3.045 (6) to 3.078 (6) Å. As stated above, the structure contains a two-dimensional coordination polymer. However, the hydrogen bonding in the structure allows the formation of an extended three-dimensional supramolecular framework (see Fig. 3).

## Experimental

The pH of a mixture of CoSO<sub>4</sub>·7H<sub>2</sub>O (0.50 mmol, 0.14 g), 4,4'-bpy (0.5 mmol, 0.078 g), benzene-1,4-dioxydiacetic acid (0.5 mmol, 0.113 g) and H<sub>2</sub>O (15 ml) was adjusted to 6–7 with 10% NaOH under vigorous stirring. The mixture was sealed in a Teflon-lined stainless steel vessel and heated at 393 K for 96 h, and then cooled slowly to

303 K at a rate of 1.39 K h<sup>-1</sup>. Deep-red crystals were obtained (yield 48%, based on Co).

## Crystal data

[Co(C<sub>10</sub>H<sub>8</sub>O<sub>6</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]  
*M<sub>r</sub>* = 475.31  
 Triclinic, *P* $\bar{1}$   
*a* = 5.760 (1) Å  
*b* = 8.177 (1) Å  
*c* = 10.639 (2) Å  
 $\alpha$  = 106.10 (1)°  
 $\beta$  = 96.91 (1)°  
 $\gamma$  = 97.40 (1)°  
*V* = 470.98 (14) Å<sup>3</sup>

*Z* = 1  
*D<sub>x</sub>* = 1.676 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1535 reflections  
 $\theta$  = 2.0–25.1°  
 $\mu$  = 0.97 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, red  
 0.60 × 0.38 × 0.30 mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.650, *T<sub>max</sub>* = 0.748  
 2498 measured reflections

1663 independent reflections  
 1409 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.040  
 $\theta_{max}$  = 25.1°  
*h* = –6 → 6  
*k* = –9 → 6  
*l* = –11 → 12

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.072  
*wR* (*F*<sup>2</sup>) = 0.183  
*S* = 1.11  
 1664 reflections  
 156 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 3.5833P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.61 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -0.83 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Co1–O3 <sup>i</sup>	2.086 (4)	Co1–N1 <sup>i</sup>	2.174 (5)
Co1–O1W	2.138 (5)		
O3 <sup>i</sup> –Co1–O1W	92.23 (17)	O1W–Co1–N1 <sup>i</sup>	91.88 (18)
O3 <sup>i</sup> –Co1–N1 <sup>i</sup>	90.18 (17)		

Symmetry code: (i)  $-x, -y, -z$ .

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H $\cdots$ <i>A</i>	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
O1W–H1WB $\cdots$ O2 <sup>i</sup>	0.83 (6)	1.79 (7)	2.609 (7)	174 (8)
O1W–H1WB $\cdots$ O3 <sup>i</sup>	0.83 (6)	2.59 (7)	3.045 (6)	116 (7)
O1W–H1WA $\cdots$ O3 <sup>ii</sup>	0.82 (7)	2.22 (4)	2.958 (6)	149 (7)
O1W–H1WA $\cdots$ O1 <sup>ii</sup>	0.82 (7)	2.58 (7)	3.078 (6)	120 (7)

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $1 - x, -y, -z$ .

The C-bound H atoms, except those on atoms C1 and C3, were positioned geometrically and refined using a riding model [*C*–H = 0.93 and 0.97 Å, and *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(C)]. The aqua H atoms and the H atoms bonded to C1 and C3 were located from difference maps and refined with an O–H distance restraint of 0.82 (2) Å [*U<sub>iso</sub>*(H) = 1.5*U<sub>eq</sub>*(O)] and a C–H distance restraint of 0.97 (7) Å [*U<sub>iso</sub>*(H) = 1.5*U<sub>eq</sub>*(C)].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SAINT*, and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: AV1215). Services for accessing these data are described at the back of the journal.

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