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A dinuclear Co^{II} complex: bis(μ-dihydrogen phosphato-κ^2O:O')-bis[(bipyridine-κ^2N,N')(dihydrogen phosphato-κO)cobalt(II)]

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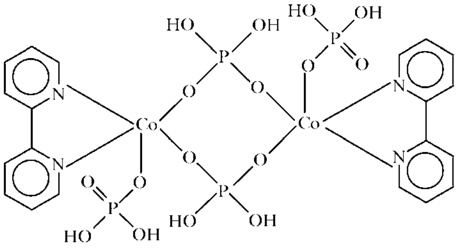
The title compound, $[Co_2(H_2PO_4)_4(C_{10}H_8N_2)_2]$, is dinuclear, centred on a symmetry centre of the $P\overline{1}$ space group. Each Co atom has a distorted square-pyramidal coordination involving two N atoms from a bipyridine molecule and three O atoms from two bridging and one terminal dihydrogen orthophosphate anion. The molecular structure and packing are stabilized by intermolecular hydrogen-bond interactions.

Comment

Metal phosphonate or orthophosphate materials are of increasing interest due to their potential applications in ion exchange, catalysis and sensing (Liang *et al.*, 2003; Wang *et al.*, 2002). An extraordinarily large number of orthophosphates have been characterized in the past two decades (Wilson *et al.*, 1982; Gier & Stucky, 1991). We report here the crystal structure of the title compound, (I).



(I)

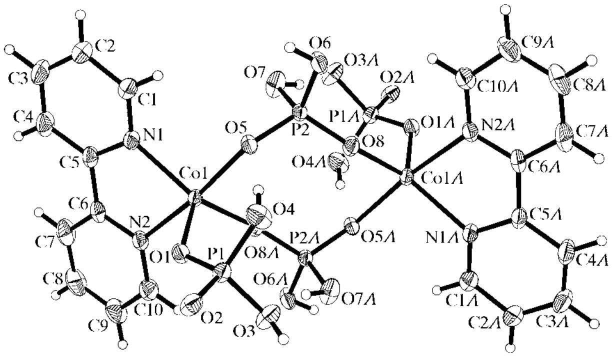


Figure 1
The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (*A*) $-x$, $-y$, $-z$.]

The structure of (I) contains two Co^{II} ions, two 2,2′-bipyridine ligands and four dihydrogen orthophosphate anions, and is built up of centrosymmetric dinuclear entities. The coordination sphere of the Co^{II} ions is best described as a distorted square pyramid. The basal coordination positions are occupied by two N atoms and two O atoms belonging to two bridging dihydrogen orthophosphate anions. The axial position is occupied by an O atom from the terminal dihydrogen orthophosphate anions.

The 2,2′-bipyridine ligands chelate the Co atom and form a five-membered CoN_2C_2 ring. The Co—N bond lengths of 2.067 (3) and 2.117 (3) Å are in good agreement with the corresponding five-coordination Co—N distances reported previously (Du *et al.*, 2001). The N1—Co1—N2 bite angle is 77.15 (10)°, which is narrower than that in $[Co(phen)_2(H_2O)_2](NO_3)_3\cdot 2H_2O$ [84.5 (1)°; Ye *et al.*, 1994].

The two Co atoms are bridged by two orthophosphate anions. The O atoms are bound asymmetrically to cobalt, with distances of 1.968 (2) and 2.064 (2) Å, and axial Co—O bond

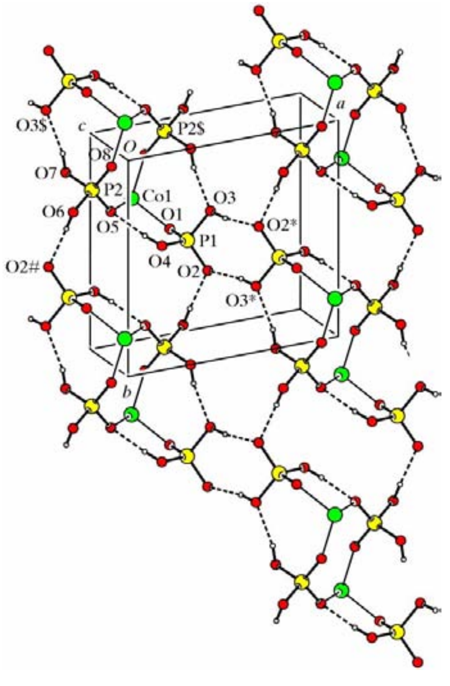


Figure 2
A view of part of the sheet of molecules of (I) linked by O—H···O hydrogen bonds in the *ab* plane. Labels appended with an asterisk (*), a hash (#) or a dollar sign ($) are at the equivalent positions ($1-x$, $1-y$, $1-z$), ($-x$, $1-y$, $-z$) and ($-x$, $-y$, $-z$), respectively. For clarity, atoms of the bipyridine ligands are not shown.

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length is 1.993 (2) Å. The Co—O bond lengths in this structure are slightly longer than found in a similar structure (Murugavel *et al.*, 2001).

The five-membered chelate ring (*P*1) is fairly planar, the displacement of atom Co1 from the weighted least-squares plane through N1/C5/C6/N2 being 0.029 (2) Å. The dihedral angles between *P*1 and the planes N2/C6–C10 (*P*2) and N1/C1–C5 (*P*3) are 5.3 (1) and 4.7 (1)°, respectively; planes *P*2 and *P*3 form a dihedral angle of 8.5 (1)°.

All four hydroxy groups of the asymmetric unit take part in a two-dimensional O—H···O hydrogen-bond network (Table 2) which links the centrosymmetric dimers to form sheets of molecules in the *ab* plane, as shown in Fig. 2.

Experimental

The title compound was prepared by hydrothermal synthesis by the reaction of cobalt dichloride with 2,2′-bipyridine in phosphoric acid solution (1:2 molar ratio) in a stainless-steel reactor with a Teflon liner at 383 K over a period of 24 h.

Crystal data

$[Co_2(H_2PO_4)_4(C_{10}H_8N_2)_2]$
$M_r = 818.17$
Triclinic, $P\overline{1}$
$a = 8.6797$ (17) Å
$b = 8.7749$ (18) Å
$c = 10.057$ (2) Å
$\alpha = 96.09$ (3)°
$\beta = 100.55$ (3)°
$\gamma = 100.89$ (3)°
$V = 731.6$ (3) Å^3

$Z = 1$
$D_x = 1.857$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 2$–11°
$\mu = 1.44$ mm^{-1}
$T = 293$ (2) K
Block, red
0.20 × 0.20 × 0.10 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.758$, $T_{\max} = 0.866$
3435 measured reflections

2902 independent reflections
2415 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 26.2°$
$h = -10 \rightarrow 10$
$k = -8 \rightarrow 11$
$l = -12 \rightarrow 12$

Table 1
Selected geometric parameters (Å, °).

Co1—O8^{i}	1.968 (2)	P1—O3	1.572 (2)
Co1—O1	1.993 (2)	P1—O4	1.554 (2)
Co1—O5	2.064 (2)	P2—O5	1.505 (2)
Co1—N1	2.067 (3)	P2—O6	1.554 (2)
Co1—N2	2.117 (3)	P2—O7	1.553 (2)
P1—O1	1.497 (2)	P2—O8	1.481 (2)
P1—O2	1.497 (2)		
O8^{i}—Co1—O1	108.57 (9)	O5—Co1—N1	96.96 (9)
O8^{i}—Co1—O5	93.73 (9)	O8^{i}—Co1—N2	87.81 (10)
O1—Co1—O5	93.94 (9)	O1—Co1—N2	92.14 (10)
O8^{i}—Co1—N1	134.82 (11)	O5—Co1—N2	172.90 (9)
O1—Co1—N1	114.27 (10)	N1—Co1—N2	77.15 (10)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O2^{i}	0.82	1.71	2.522 (4)	170
O4—H4*A*···O5	0.82	1.79	2.603 (3)	170
O6—H6*A*···O2^{ii}	0.82	1.78	2.589 (3)	169
O7—H7*A*···O3^{iii}	0.82	1.90	2.694 (4)	161

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

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.091$
$S = 1.00$
2902 reflections
208 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances of 0.93 Å and O—H distances of 0.82 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1662). Services for accessing these data are described at the back of the journal.

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