

Bis(μ -diphenylphosphinato- $\kappa^2O:O'$)-bis[aqua(diphenylphosphinato- κO)-bis(pyridine- κN)cobalt(II)]

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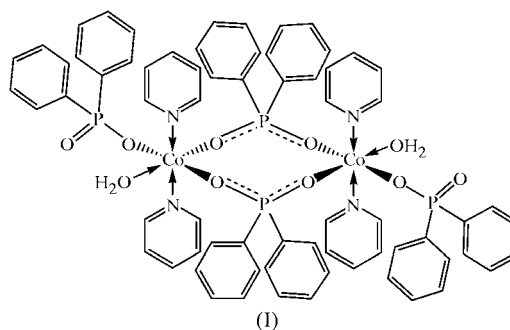
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In the centrosymmetric title compound, $[\text{Co}_2(\text{C}_{12}\text{H}_{10}\text{O}_2\text{P})_4(\text{C}_5\text{H}_5\text{N})_4(\text{H}_2\text{O})_2]$, each approximately octahedral Co atom features two *trans*-coordinated pyridine molecules, one water molecule, a terminally coordinated monodentate diphenylphosphinate ligand, and two bidentate diphenylphosphinate ligands that bridge the two Co atoms across a centre of inversion to form a dimeric binuclear complex. The discrete molecules are linked by double hydrogen bonds between the terminally coordinated diphenylphosphinate ligand and the

water molecule to form a continuous chain along the crystallographic *b* axis.

Comment

Phosphinate ligands have a rich coordination chemistry, often forming polymeric species (Vioux *et al.*, 2004). Coordinating solvents can be used to dissolve these phosphinate-bridged coordination polymers, in a process that breaks the coordination chains, to form oligomeric or monomeric solvent adducts in solution (Siqueira *et al.*, 2006). We have investigated the possibility of forming the pyridine adduct of the diphenylphosphinate-bridged coordination polymer of Co^{II} . However, due to the presence of opportunist water, the title compound, (I), a molecular species incorporating both pyridine and water, was formed, and we present its crystal structure here.



One half-molecule of (I) is found in the asymmetric unit; the entire molecule is generated by the crystallographic centre of inversion, which lies at the mid-point between the two Co

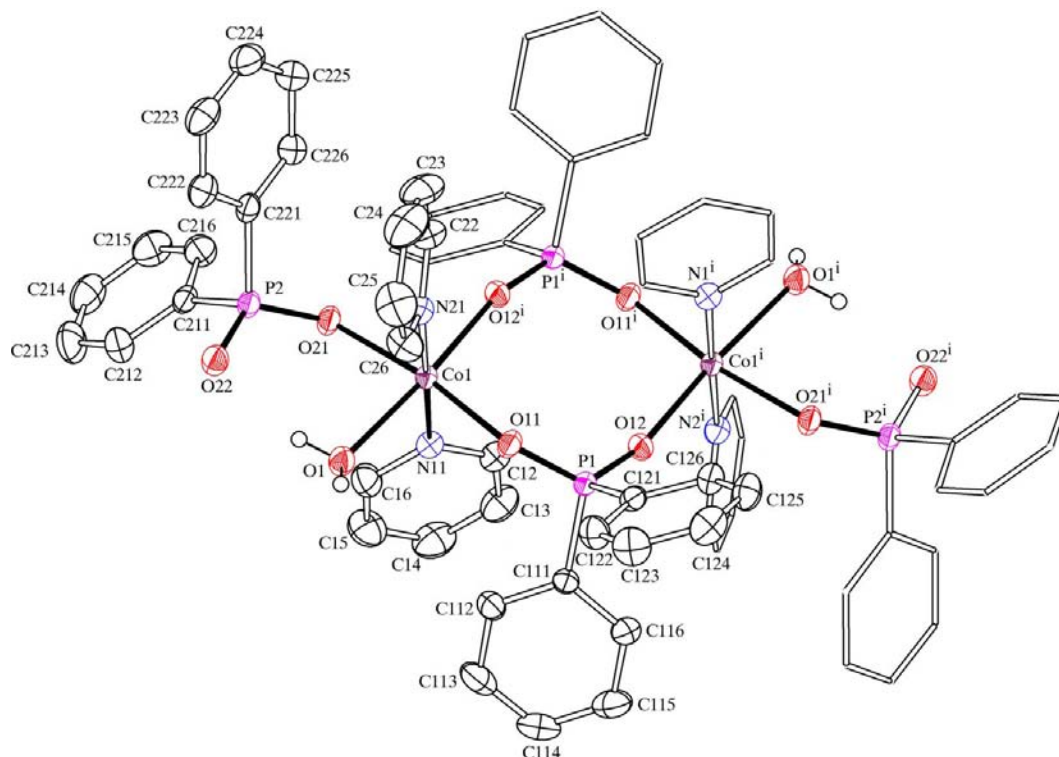


Figure 1

The structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. Symmetry-equivalent phenyl groups are shown as sticks. [Symmetry code: (i) $-x, 2 - y, 1 - z$.]

atoms (Fig. 1). Two diphenylphosphinate ligands bridge the two Co atoms to form an eight-membered ring. The octahedral coordination sphere is completed by two *trans* pyridine ligands, a water molecule, and a terminally coordinated monodentate diphenylphosphinate ligand.

The very long Co...Co distance in (I) (Table 1) precludes metallic bonding. This distance is slightly longer than that in the parent coordination polymer [4.704 (5) Å; Liu *et al.*, 1992]. The very slightly different Co—O distances involved in the bridging diphenylphosphinate ligand in (I) are considerably longer than those for the parent polymer [1.905 (16)–1.927 (16) Å], which is likely to be due to the change from tetrahedral to octahedral geometry of the Co centre. The P...O distances are almost equal, showing a delocalization of the negative charge. The monodentate diphenylphosphinate ligand has a slightly longer P—O bond for the O atom coordinated to the Co centre than for the non-coordinated O atom, consistent with a partial localization of the negative charge on the O atom that forms the formally covalent bond. These values correspond well to the few examples found in the Cambridge Structural Database (Version 5.26, update of August 2005; Allen, 2002), where the average terminal P...O distance is 1.500 (13) Å and the coordinated P...O distance is 1.514 (15) Å for 14 observations.

The pyridine molecules are coordinated to the Co centre, with Co—N distances identical to within experimental error and N—Co—N angle close to the ideal value of 180°. The rings are rotated by 66.96 (7)° with respect to one another but are almost perpendicular to the CoO₄ plane, with angles of 86.71 (5)° for the N11-containing pyridine ring and 89.51 (5)° for the N21-containing ring.

A water molecule, presumably present in the methanol preparation solvent, completes the coordination sphere of the Co centre, preventing the formation of a polymeric chain as found for similar solvent adducts of coordinating polymers (Siqueira *et al.*, 2006). Double hydrogen bonds between the terminal diphenylphosphinate ligand and the water molecule across a centre of inversion (Table 2) link discrete molecules to form a continuous chain along the crystallographic *b* axis (Fig. 2). The water molecule also participates in an intramolecular hydrogen bond to the terminal O atom of a neighbouring diphenylphosphinate ligand, presumably stabilizing the monodentate coordination mode.

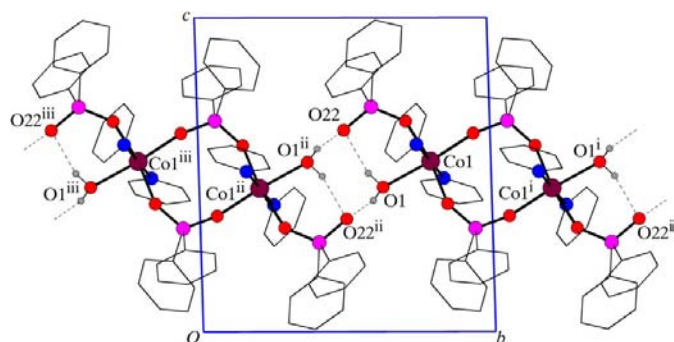


Figure 2
A view of the hydrogen bonding in (I) (dashed lines). [Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $x, y - 1, z$.]

Experimental

Co(O₂PPh₂)₂ was suspended in methanol and pyridine was added dropwise until the blue solid disappeared and the solution was clear light-pink in colour. Red crystals of (I) formed on slow evaporation of the solution.

Crystal data

[Co ₂ (C ₁₂ H ₁₀ O ₂ P) ₄ (C ₅ H ₅ N) ₄ (H ₂ O) ₂]	Z = 1
<i>M_r</i> = 1338.97	<i>D_x</i> = 1.374 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 10.7871 (4) Å	Cell parameters from 8177 reflections
<i>b</i> = 11.8221 (4) Å	θ = 3.0–25.9°
<i>c</i> = 12.7061 (5) Å	μ = 0.67 mm ⁻¹
α = 91.609 (2)°	<i>T</i> = 294 (2) K
β = 90.390 (2)°	Rectangular plate, red
γ = 92.774 (2)°	0.25 × 0.15 × 0.07 mm
<i>V</i> = 1617.77 (10) Å ³	

Data collection

Bruker X8 Kappa-APEX-II CCD area-detector diffractometer	9046 independent reflections
φ and ω scans	6553 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 2004); values rescaled by 0.95	<i>R</i> _{int} = 0.027
<i>T</i> _{min} = 0.745, <i>T</i> _{max} = 0.950	θ _{max} = 29.6°
30066 measured reflections	<i>h</i> = -15 → 14
	<i>k</i> = -16 → 16
	<i>l</i> = -17 → 15

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.0829P]$
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.034	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>wR</i> (<i>F</i> ²) = 0.091	(Δσ) _{max} = 0.001
<i>S</i> = 1.06	Δρ _{max} = 0.36 e Å ⁻³
9046 reflections	Δρ _{min} = -0.34 e Å ⁻³
405 parameters	
H atoms: see below	

Table 1

Selected geometric parameters (Å, °).

Co1—O1	2.2076 (12)	Co1—Co1 ⁱ	5.0718 (4)
Co1—O11	2.0687 (11)	P1—O11	1.5004 (11)
Co1—O12 ⁱ	2.0615 (10)	P1—O12	1.4944 (11)
Co1—O21	2.0957 (10)	P2—O21	1.5081 (11)
Co1—N11	2.1736 (12)	P2—O22	1.4982 (12)
Co1—N21	2.1740 (12)		
O11—Co1—O12 ⁱ	98.71 (4)	O21—Co1—N21	91.15 (5)
O12 ⁱ —Co1—O21	90.72 (4)	O11—Co1—O1	86.42 (5)
O11—Co1—O21	170.41 (4)	O21—Co1—O1	84.18 (5)
O12 ⁱ —Co1—N11	91.74 (5)	N11—Co1—O1	87.34 (5)
O11—Co1—N11	92.90 (5)	N21—Co1—O1	91.56 (5)
O21—Co1—N11	88.52 (5)	O11—P1—O12	118.11 (6)
O12 ⁱ —Co1—N21	89.33 (5)	O21—P2—O22	117.37 (6)
O11—Co1—N21	87.26 (5)		

Symmetry code: (i) $-x, 2 - y, 1 - z$.

Table 2

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...O22	0.81 (3)	2.02 (3)	2.8072 (18)	163 (3)
O1—H1B...O22 ⁱⁱ	0.93 (2)	1.84 (2)	2.7464 (17)	165 (2)

Symmetry code: (ii) $-x, 1 - y, 1 - z$.

All H atoms on the phenyl and pyridine rings were refined using a riding model, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The H atoms of the water molecule were found in a difference Fourier map and allowed to refine freely.

Data collection: *COSMO* (Bruker, 2004), *APEX2* (Bruker, 2004) and *BIS* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1241). Services for accessing these data are described at the back of the journal.

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