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Diaquabis(4,4'-bipyridine-*N*)bis(dihydrogenphosphato-*O*)copper(II): blocking of extended metal–ligand coordination by hydrogen bonding

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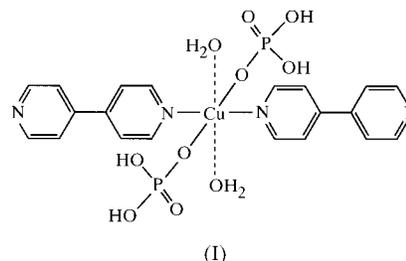
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The title compound, $[\text{Cu}(\text{H}_2\text{PO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]$, is a mononuclear complex in which the Cu atom is square-planar coordinated by two dihydrogenphosphate anions and two monodentate 4,4'-bipyridine (4,4'-bipy) groups, and by two more distant aqua ligands to complete a distorted octahedral coordination. Metal–metal bridging by 4,4'-bipy is blocked by intermolecular hydrogen bonding from the dihydrogenphosphate to the second N atom of 4,4'-bipy. The crystal packing is controlled both by additional hydrogen bonding between the aqua and phosphate ligands and by π -stacking. These hydrogen-bonding interactions create two-dimensional networks which are connected by the bipyridine ligands.

Comment

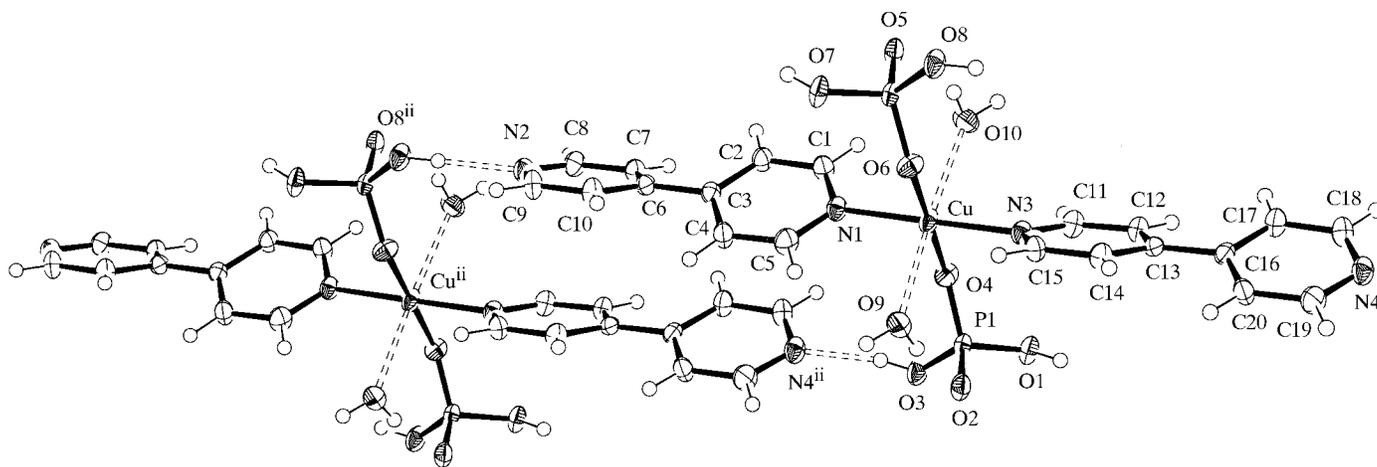
There is widespread interest in achieving control of the aggregation of organic ligands and metal ions into oligo- or polynuclear coordination structures *via* covalent metal–ligand bonds and non-covalent interactions (Wu *et al.*, 1999; Janiak *et al.*, 1999). Recent years have seen an appreciable number of studies on the coordination of phosphate ions to transition metals (Choudhuy *et al.*, 2000; Finn & Zubieta, 2000; Neeraj *et al.*, 2000; Shi *et al.*, 2000; Yan *et al.*, 2000). Amine phosphates, for example, react with metal ions under hydrothermal conditions to give open-framework metal phosphates (Neeraj *et al.*, 1999; Cheetham *et al.*, 1999; Oliver *et al.*, 1998). Mono- and dihydrogenphosphate ligands are good candidates for participation in structure-directing hydrogen-bonding interactions (Subramanian & Zaworotko, 1994). Moreover, 4,4'-bipyridine (4,4'-bipy) is an often used building block and an excellent bridging ligand for the construction of polymeric coordination frameworks (Hagman *et al.*, 1999; Li *et al.*, 2000; Janiak *et al.*, 1999; Wu *et al.*, 1999, and references therein). Little work has been carried out on the simultaneous coor-

dination of 4,4'-bipy and phosphate with metals (Hagman *et al.*, 1999). Hydrothermal reaction of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, H_3PO_4 and 4,4'-bipy in *n*-butanol produced $[\text{In}_4(4,4'\text{-bipy})_3(\text{H}_2\text{PO}_4)_4(\text{HPO}_4)_4] \cdot 4\text{H}_2\text{O}$ (Lii & Huang, 1999). The extended inorganic–organic hybrid material $[\text{M}(4,4'\text{-bipy})_2(\text{VO}_2)_2(\text{HPO}_4)_4]$ ($\text{M} = \text{Co}, \text{Ni}$) was also obtained by a hydrothermal reaction (Shi *et al.*, 2000).



We describe here the structure of the monomeric complex $[\text{Cu}(4,4'\text{-bipy})_2(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})_2]$, (I) (Fig. 1). The molecular symmetry is D_{2h} when H_2PO_4 is treated as a point ligand and C_{2h} when the latter is taken into account as a full group. The coordination geometry around the Cu^{II} atom is a Jahn–Teller-distorted elongated octahedron. The two bipy N atoms and the two phosphate O atoms form the equatorial plane around copper. The two aqua ligands comprise the elongated axial coordination. There are intramolecular hydrogen bonds between the aqua and phosphate ligands (Fig. 2). The in-plane distances for $\text{Cu}-\text{N}1$ [2.024 (3) Å], $\text{Cu}-\text{N}3$ [2.007 (3) Å], $\text{Cu}-\text{O}4$ [1.945 (2) Å] and $\text{Cu}-\text{O}6$ [1.944 (2) Å] are normal. For $\text{Cu}-\text{N}_{\text{py}}$, the expected range is 2.046 ± 0.032 Å (Orpen *et al.*, 1989). There are few examples of copper–phosphate bonds. Nevertheless, the copper–phosphate (phos) distances are comparable to those in $[\{\text{Cu}(2,2'\text{-bipy})\}_2(\text{VO})_3(\text{PO}_4)_2(\text{HPO}_4)_2] \cdot 2\text{H}_2\text{O}$ [average $\text{Cu}-\text{O}_{\text{phos}} = 1.975$ (4) Å], in $[\{\text{Cu}(\text{terpy})\}_2(\text{VO}_2)_3(\text{PO}_4)(\text{HPO}_4)_2]$ [$\text{Cu}-\text{O}_{\text{phos}} = 1.921$ (4) Å; Finn & Zubieta, 2000], and in $[\{\text{Cu}_2(\text{HL})(\text{H}_2\text{PO}_4)_2\}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [$\text{H}_2\text{L} = \text{bis}(\text{pyridine-2-aldehyde}) \text{thiocarbohydrazone}$; $\text{Cu}-\text{O}_{\text{phos}} = 1.890$ (3) and 1.933 (3) Å; Moubaraki *et al.*, 1998]. The axial distances from Cu to the aqua ligands with O9 [2.690 (3) Å] and O10 [2.605 (2) Å] lie at the top end of the expected range. For the terminal $\text{Cu}-\text{OH}_2$ bonds, the range is 2.399 ± 0.154 Å (Orpen *et al.*, 1989).

The 4,4'-bipy group functions as a monodentate ligand towards a metal atom in (I). This appears to be a rare phenomenon. Two known examples of monodentate 4,4'-bipy binding involve coordination to manganese (Attia & Pierpont, 1995; Tong *et al.*, 1999). Much more common for 4,4'-bipy is a bidentate bridging coordination between metal atoms, which usually gives rise to extended metal–ligand structures, such as chains or grids. This is also normally observed in copper compounds with 4,4'-bipy (Blake *et al.*, 1999; Hagman *et al.*, 1998; You *et al.*, 2000; Tong *et al.*, 1998; Zhang *et al.*, 1999). In (I), one of the *N*-donor atoms of 4,4'-bipy is, however, engaged in intermolecular hydrogen bonding to a dihydrogenphosphate ligand of an adjacent complex (*cf.* Fig. 1). Without the protonated phosphate group, an extended copper–4,4'-bipy chain could have been envisioned, as found in $[\text{Cu}(4,4'$ -

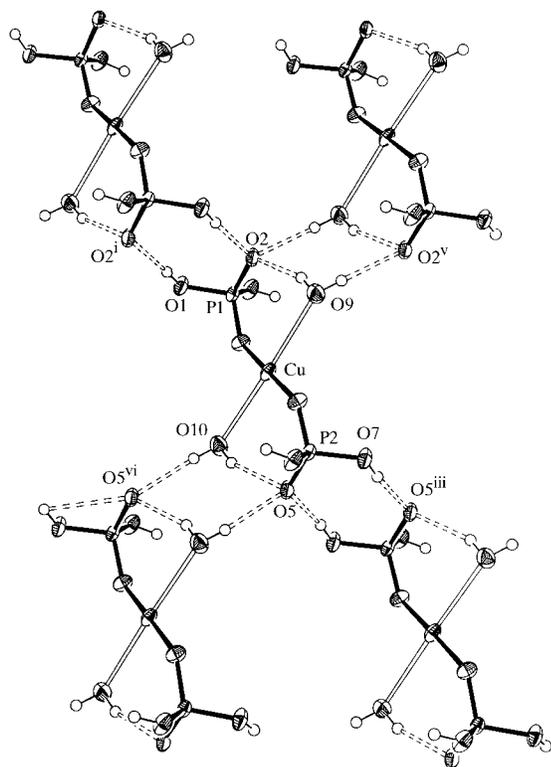

Figure 1

An ORTEP-3 (Farrugia, 1997) view of the title compound illustrating some of the intermolecular hydrogen bonding and π -interactions. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (ii) $1 + x, y - 1, z$.]

bipy)(SO₄)(H₂O)₃·2H₂O and compounds with related bipyridine ligands (Hagman *et al.*, 1998). Hydrogen bonding from metal-aqua ligands to both N atoms of uncoordinated 4,4'-bipy molecules has been observed in [Co(4,4'-bipy)(H₂O)₄](PF₆)₂·3(4,4'-bipy) (Dong *et al.*, 2000), in [Mn(4,4'-bipy)₂(H₂O)₄](ClO₄)₂·4(4,4'-bipy) (Tong *et al.*, 1999),

and in a series of [M(4,4'-bipy)(H₂O)_m]*X*₂·*n*(4,4'-bipy) compounds (*M* = Fe, Zn; *m* = 3, 4; *X* = ClO₄, NO₃, O₃SCF₃; *n* = 1, 1.5, 2; Carlucci *et al.*, 1997). An example with metal coordination to one end of 4,4'-bipy and hydrogen bonding from an aqua ligand to the other end is [Cd₂(4,4'-bipy)₅(H₂O)₄(NO₃)₂(PF₆)₂] (Dong *et al.*, 2000). The pyridyl rings of the 4,4'-bipy molecules in (I) are non-coplanar and are twisted by interplanar angles of 30.6 (1)° (rings with N1 and N2) and 22.6 (1)° (rings with N3 and N4).

The crystal packing is further controlled by hydrogen bonding among the phosphate ligands and between the aqua and phosphate ligands, as shown in Fig. 2. Hydrogen bonding between the phosphate ligands gives rise to a ring with inversion symmetry. The sole hydrogen-bond acceptor is the formally P=O double-bonded O atom. It accepts three hydrogen bonds, *i.e.* one intra- and two intermolecular. These hydrogen-bonding interactions create two-dimensional networks parallel to the *xz* plane, which are then connected by the 4,4'-bipy ligands. The crystal packing also seems to be influenced by π -stacking between the 4,4'-bipy ligands. They feature offset or slipped π - π interactions, with an interplanar separation of about 3.64 Å (Janiak, 2000). These latter packing interactions can be seen in Fig. 1.


Figure 2

The hydrogen-bonding network between the aqua and phosphate ligands in (I). The 4,4'-bipy ligands have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The symmetry codes are as given in Table 2.

Experimental

Copper nitrate trihydrate (0.241 g, 1.00 mmol) and 4,4'-bipy (0.156 g, 1.00 mmol) were mixed in distilled water (25 ml). To this slurry was carefully added a 1 mol l⁻¹ solution of H₃PO₄ with constant stirring until the 4,4'-bipy had completely dissolved. The pH was adjusted to 4.3 using tetra-*n*-butylammonium hydroxide. The mixture was then stirred for 6 h. The solution was left to stand for three days at room temperature and some of the solvent evaporated. After this time, blue crystals of the title compound were collected by filtration (yield 280 mg, 46%). IR (KBr): 3444 (*br*, OH), 1607 (C=C), 1416 (P=O), 963 (P-O); calculated for C₂₀H₂₄CuN₄O₁₀P₂: C 39.66, H 3.96, N 9.25%; found C 39.21, H 2.95, N 8.90%.

Crystal data

[Cu(H ₂ PO ₄) ₂ (C ₁₀ H ₈ N ₂) ₂ (H ₂ O) ₂]	Z = 2
M _r = 605.91	D _x = 1.750 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
a = 7.948 (2) Å	Cell parameters from 3065 reflections
b = 10.208 (2) Å	θ = 1.4–27.5°
c = 14.362 (3) Å	μ = 1.16 mm ⁻¹
α = 85.693 (5)°	T = 210 (2) K
β = 82.008 (5)°	Block, blue
γ = 89.172 (5)°	0.15 × 0.14 × 0.05 mm
V = 1150.6 (4) Å ³	

Data collection

Bruker AXS CCD diffractometer	R _{int} = 0.040
ω scans	θ _{max} = 27.5°
10 246 measured reflections	h = -10 → 10
5200 independent reflections	k = -13 → 13
3065 reflections with I > 2σ(I)	l = -18 → 18

Refinement

Refinement on F ²	H atoms treated by a mixture of independent and constrained refinement
R(F) = 0.036	w = 1/[σ ² (F _o ²) + (0.0348P) ²]
wR(F ²) = 0.096	where P = (F _o ² + 2F _c ²)/3
S = 1.01	(Δ/σ) _{max} < 0.001
5200 reflections	Δρ _{max} = 0.39 e Å ⁻³
358 parameters	Δρ _{min} = -0.62 e Å ⁻³

Table 1 Selected geometric parameters (Å, °).

Cu—O6	1.9435 (19)	Cu—N1	2.024 (3)
Cu—O4	1.9452 (19)	Cu—O10	2.605 (2)
Cu—N3	2.007 (3)	Cu—O9	2.690 (3)
O6—Cu—O4	179.42 (10)	N3—Cu—O10	89.89 (9)
O6—Cu—N3	88.77 (9)	N1—Cu—O10	90.05 (10)
O4—Cu—N3	91.15 (9)	O6—Cu—O9	85.15 (8)
O6—Cu—N1	90.65 (9)	O4—Cu—O9	94.28 (8)
O4—Cu—N1	89.43 (9)	N3—Cu—O9	85.10 (9)
N3—Cu—N1	179.41 (10)	N1—Cu—O9	94.93 (9)
O6—Cu—O10	91.53 (8)	O10—Cu—O9	174.04 (8)
O4—Cu—O10	89.04 (8)		

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

D—H...A	D—H	H...A	D...A	D—H...A
O1—H01...O2 ⁱ	0.82 (2)	1.76 (2)	2.570 (3)	170 (4)
O3—H03...N4 ⁱⁱ	0.83 (2)	1.81 (2)	2.627 (3)	170 (4)
O7—H07...O5 ⁱⁱⁱ	0.83 (2)	1.74 (2)	2.570 (3)	175 (4)
O8—H08...N2 ^{iv}	0.81 (2)	1.84 (2)	2.646 (3)	170 (4)
O9—H9A...O2	0.82 (2)	1.97 (2)	2.780 (3)	168 (4)
O9—H9B...O2 ^v	0.81 (2)	2.13 (2)	2.918 (3)	163 (3)
O10—H10A...O5 ^{vi}	0.82 (2)	2.11 (2)	2.909 (3)	166 (3)
O10—H10B...O5	0.84 (2)	2.02 (2)	2.800 (3)	156 (3)

Symmetry codes: (i) -x, -y, -1 - z; (ii) 1 + x, y - 1, z; (iii) 1 - x, -y, -z; (iv) x - 1, 1 + y, z; (v) 1 - x, -y, -1 - z; (vi) -x, -y, -z.

The H atoms on O atoms were found and refined. The O—H bond distances were restrained to a target value of 0.83±0.02 Å with *DFIX*. Isotropic displacement parameters of U_{iso}(H) = 1.5U_{eq}(O) were used. The H atoms on C atoms could also be found and refined but it was preferred to place them at calculated positions and refine them using appropriate riding models (*HFIX* 43; C—H = 0.94 Å) and isotropic

displacement parameters of U_{iso}(H) = 1.2U_{eq}(C). The structure could also be solved in a smaller triclinic unit cell, with a = 7.707 (1), b = 7.945 (1), c = 10.207 (2) Å, α = 90.839 (3), β = 93.589 (3) and γ = 112.72 (1)°. Solution and refinement in the smaller triclinic cell was successful to R1 = 0.0405 and wR = 0.1122 for 2306 reflections with I > 2σ(I), and R1 = 0.0474 and wR = 0.1179 for all data. The superstructure reflections which give rise to the larger unit cell are clearly visible, however. Furthermore, the pyridyl-ring C atoms have high displacement parameters perpendicular to the ring plane. This corresponds to an averaged structure of the two 4,4'-bipy ligands where the pyridyl groups are tilted differently. Another example of a 4,4'-bipy complex with pseudosymmetry has been reported recently with the polymeric structure [MnCl₂(4,4'-bipy)]_n (Chippindale *et al.*, 2000).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) and *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *SHELXTL-Plus*; 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: JZ1468). Services for accessing these data are described at the back of the journal.

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