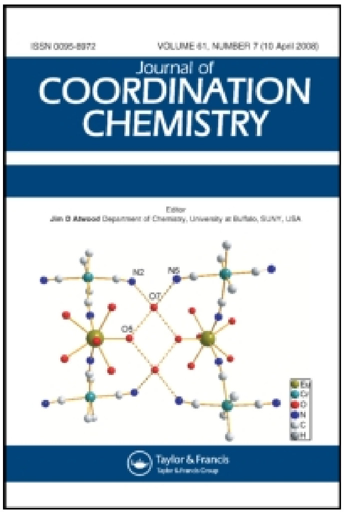

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Hydrogen bonding in triamine copper(II) P,P′-Diphenylmethylenediphosphinate (pcp^{2-}) hybrids. Syntheses and crystal structures of [Cu(pcp)(2,2′-dipyridylamine)(H_2O)]·2H_2O and [Cu(pcp)(2,2′:6′,2″terpyridine)]·4H_2O

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Two hybrid materials [Cu(pcp)(dipyam)(H_2O)]·2H_2O (**1**) and [Cu(pcp)(terpy)]·4H_2O (**2**), have been prepared by reaction of copper(II) acetate monohydrate with P,P′ diphenylmethylenephosphinic acid (H_2pcp) and 2,2′ dipyridylamine (dipyam) or 2,2′:6′,2″ terpyridine (terpy), and have been structurally characterized by X-ray analyses. Both structures have a three-dimensional architecture, created by a close network of hydrogen bonding interactions. The copper centers present approximate square-pyramidal coordination, surrounded by pcp, dipyam and one water molecule in **1**, and by pcp and terpyridine in **2**. In both complexes the pcp ligand chelates only one metal, so that the free phenylphosphinate oxygens remain available for hydrogen-bonding interactions with water molecules, present in coordinated and solvated forms in **1** and solely as the solvated form in **2**.

Keywords: Copper(II); Diphosphinate; Hydrogen bond; Hybrid materials; X-ray structure

1. Introduction

Organic phosphorus acids play a fundamental role in crystal engineering and the architecture of supramolecular arrays. Metal phosphonates (or phosphinates), with the ability to bridge metal ions, constitute a rich class of inorganic–organic hybrid materials that are capable of adopting a wide variety of structural motifs, with a wide range of applications [1–7]. In addition, phosphonic (or phosphinic) acids associate through strong hydrogen bonds between the P–O and P–O–H groups [8, 9]. Nitrogen containing aromatic ligands also are prominent building blocks in the design of supramolecular networks, through important non-covalent forces such as π–π stacking interactions [10–12]. Thus the combination of phosphonate (or phosphinate) metal ions, coordinated and uncoordinated molecules suitable for hydrogen bonding such as water,

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amines etc., and possible π–π interactions from aromatic ring electrons seems to be a good basis to form extended architectures.

Here we present the syntheses and the X-ray structures of two new copper(II) inorganic–organic hybrids [Cu(pcp)(dipyam)(H_2O)] · $2H_2O$ **1** and [Cu(pcp)(terpy)] · $4H_2O$ **2**, where pcp^{2-} is the bifunctional P,P′-diphenylmethylenediphosphinate ligand, dipyam is 2,2′dipyridylamine and terpy is 2,2′ : 6′,2″terpyridine. In both cases extended 3D networks are achieved through strong hydrogen bonds between the P–O moieties of pcp^{2-}, the coordinated and uncoordinated water molecules, and the N–H group of dipyam.

A series of hybrids with pcp^{2-} have been reported, with metal ions such as Be(II) [13], Mn(II), Co(II), Ni(II) [14], Cu(II) [15–16], Zn(II) [17], Pb(II) [18] and Sn(II) [16]. Such complexes show a variety of extended structural arrays, with different dimensionality. For copper(II), variously hydrated forms, where the structure is arranged in the form of 2D hydrogen bonded layers [15], and an anhydrous species featuring a monodimensional array [16], have been obtained.

2. Experimental

2.1. *General procedures*

H_2pcp was prepared as previously described [19] and then purified by recrystallization from ethanol. All other reagents were purchased commercially and used without further purification. IR spectra were recorded, as Nujol mulls, on a Perkin-Elmer BX FT-IR spectrometer, in the 4000–400 cm^{-1} region.

2.2. *Syntheses*

2.2.1. [Cu(pcp)(dipyam)(H_2O)] · $2H_2O$ (1). H_2pcp (0.1 g, 0.34 mmol) was dissolved in 70 mL of boiling water and then a solution of copper(II) acetate monohydrate (0.068 g, 0.34 mmol) in 10 mL of water was added. Solid 2,2′dipyridylamine (0.058 g, 0.34 mmol) was added, and green needles of the complex rapidly started to separate. Standing the solution at 80°C, without stirring, the precipitation was complete (ca. 2 h). The complex was filtered off, washed with water and dried in air at room temperature (88% yield). Anal. Calcd for $C_{23}H_{27}CuO_7N_3P_2$(%): C, 47.39; H, 4.67; N, 7.21. Found: C, 47.45; H, 4.75; N, 7.15.

2.2.2. [Cu(pcp)(terpy)] · $4H_2O$ (2). H_2pcp (0.1 g, 0.34 mmol) was dissolved in 70 mL of boiling water and then a solution of copper(II) acetate monohydrate (0.068 g, 0.34 mmol) in 10 mL of water was added. After addition of solid 2,2′ : 6′,2″ terpyridine (0.079 g. 0.34 mmol) the resulting solution was concentrated by evaporation to a volume of ca. 20 mL. Further slow evaporation of the water, at room temperature, allowed the precipitation of well-shaped turquoise crystals. These were filtered, washed with cold water and dried in air at room temperature (74% yield). Anal. Calcd for $C_{28}H_{31}CuO_8N_3P_2$(%): C, 50.73; H, 47.12; N, 6.34. Found: C, 50.65; H, 47.25; N, 6.28.

2.3. *Crystal structure determinations*

Diffraction data for **1** and **2** were collected at room temperature on a Philips PW1100 and on an Enraf Nonius CAD4 automatic diffractometer respectively. Unit cell parameters for both compounds were determined by least-squares refinement of the setting angles of 25 carefully centered reflections. Crystal data and data collection details of **1** and **2** are given in table 1. The intensities I were assigned standard deviations $\sigma(I)$ calculated by using a value of 0.03 for the instability factor k [20]. They were corrected for Lorentz-polarization effects and for absorption [21]. Atomic scattering factors for neutral atoms were taken from ref. [22]. Both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [23]. The structures were solved by direct methods and refined by full-matrix F^2 refinement, with anisotropic thermal parameters assigned to all non-carbon and non-hydrogen atoms for a good *ratio* of data/variables. In both structures the hydrogen atoms were introduced in their calculated positions riding on their carbon atoms, with thermal parameters 20% larger. The function minimized during the refinement was $\Sigma \mathrm{w}(F_o^2 - F_c^2)^2$, with $w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 13.07P]$ and $w = 1/[\sigma^2(F_o^2) + (0.0003P)^2]$ $(P = (\max(F_o^2,\ 0) + 2F_c^2)/3)$ for **1** and **2**, respectively. The absolute configuration of **1** was determined on the basis of the Flack parameter [24]. All calculations were performed using the package WINGX [25] (SIR97 [26], SHELX97 [27] and ORTEP-III [28]). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 274839 and 274840. Copies of the data can be obtained free of charge on

Table 1. Crystal data and structure refinement.

	1	**2**
Empirical formula	$C_{23}H_{27}CuN_3O_7P_2$	$C_{56}H_{62}Cu_2N_6O_{16}P_4$
Formula weight	582.96	1326.08
Temperature (K)	293(2)	293(2)
Wavelength (λ, Å)	1.54180	0.71073
Crystal system, space group	orthorhombic, $P2_12_12_1$	monoclinic, $C2/c$
Unit cell dimensions (Å, °)	$a = 20.266(6)$	45.569(9)
	$b = 18.076(8)$	10.604(5)
	$c = 7.063(2)$	34.056(9)
	$\alpha = 90$	$\alpha = 90$
	$\beta = 90$	$\beta = 133.64(2)$
	$\gamma = 90$	$\gamma = 90$
Volume (Å^3)	2587.4(16)	11909(7)
Z, Calculated density (Mg m^{-3})	4, 1.497	8, 1.479
Absorption coefficient (mm^{-1})	2.777	0.895
$F(000)$	1204	5488
Crystal size (mm^3)	0.40 × 0.05 × 0.05	0.20 × 0.10 × 0.10
ν range for data collection (°)	3.28 to 49.97	2.01 to 20.00
Limiting indices	$0 < h < 20$, $0 < k < 17$, $0 < l < 7$	$-43 < h < 31$, $0 < k < 10$, $0 < l < 32$
Reflections collected/unique	1555/1555	5542/5542
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1555/0/187	5542/0/474
Goodness-of-fit on F^2	1.069	0.805
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0574$	$R_1 = 0.0479$
	$wR_2 = 0.1118$	$wR_2 = 0.0606$
R indices (all data)	$R_1 = 0.0832$	$R_1 = 0.1353$
	$wR_2 = 0.1244$	$wR_2 = 0.0718$
Largest diff. peak and hole (e Å^{-3})	0.375 and −0.323	0.308 and −0.316

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44) 1223 336-033. E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal structures*

The structure of **1** consists of [Cu(pcp)(dipyam)(H_2O)] molecular units and solvent water molecules, held together by hydrogen bonding interactions in a complicated polymeric array. In figure 1 is shown the asymmetric unit of **1**, whose selected bond distances and angles are reported in table 2. In particular the copper center is surrounded in a distorted square pyramidal geometry with two nitrogen donors from the dipyam ligand, two oxygen atoms from the phosphinate groups of the pcp^{2-} ligand and one water molecule in an apical position. The latter is involved in strong hydrogen bonds with the free oxygens of an adjacent pcp ligand, creating an extension of the structure in the z direction (see figure 2). Additionally two solvent water molecules (O6 and O7), with the important cementing action of hydrogen bonds, link together the chains in a three-dimensional architecture. The protonated nitrogen (N2) of the dipyam ligand also plays a role in the network and interacts with one free oxygen (O2) of the phosphinate (see figure 3, which shows a portion of the packing of **1** with the hydrogen bondings network). The most important hydrogen bonding interactions < 3.0 Å are the followings: $O5 \cdots O2^{I}$ 2.64 Å (I x, y, $-1+z$), $O5 \cdots O4^{I}$ 2.70 Å, $O5 \cdots O7$ 2.99 Å, $O2 \cdots N2^{II}$ 2.91 Å (II 1.5 $-x$, $-y$, $0.5+z$), $O4 \cdots O6$ 2.83 Å, $O6 \cdots O7^{III}$ 2.97 Å (III $1-x$, $0.5+y$, 1.5 $-z$).

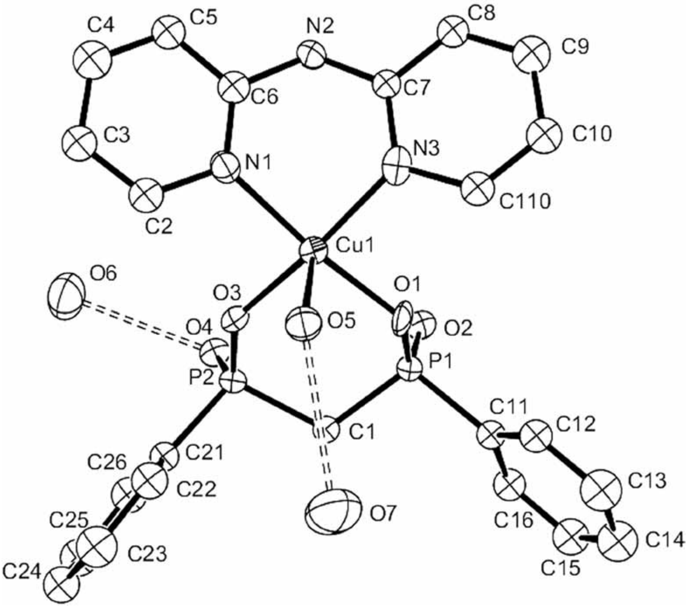

Figure 1. Perspective view of the asymmetric unit of **1**, comprising the solvent water molecules, hydrogen-bond linked. Ortep drawing with 30% probability ellipsoids.

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(dipyam)(pcp)(H_2O)] · $2H_2O$.

Cu(1)–O(3)	1.947(8)	P(1)–C(1)	1.788(10)
Cu(1)–O(1)	1.953(8)	P(1)–C(11)	1.813(6)
Cu(1)–N(3)	1.987(9)	P(2)–O(3)	1.498(8)
Cu(1)–N(1)	2.009(9)	P(2)–O(4)	1.520(9)
Cu(1)–O(5)	2.234(8)	P(2)–C(21)	1.796(6)
P(1)–O(1)	1.504(9)	P(2)–C(1)	1.815(10)
P(1)–O(2)	1.531(10)		
O(3)–Cu(1)–O(1)	92.4(3)	O(1)–P(1)–C(11)	106.4(4)
O(3)–Cu(1)–N(3)	167.2(4)	O(2)–P(1)–C(11)	109.6(4)
O(1)–Cu(1)–N(3)	87.6(4)	C(1)–P(1)–C(11)	104.7(4)
O(3)–Cu(1)–N(1)	89.7(4)	O(3)–P(2)–O(4)	116.1(4)
O(1)–Cu(1)–N(1)	170.9(4)	O(3)–P(2)–C(21)	108.9(4)
N(3)–Cu(1)–N(1)	88.4(4)	O(4)–P(2)–C(21)	109.7(4)
O(3)–Cu(1)–O(5)	91.8(3)	O(3)–P(2)–C(1)	108.0(5)
O(1)–Cu(1)–O(5)	90.9(3)	O(4)–P(2)–C(1)	109.2(6)
N(3)–Cu(1)–O(5)	101.0(3)	C(21)–P(2)–C(1)	104.3(4)
N(1)–Cu(1)–O(5)	97.8(3)	P(1)–O(1)–Cu(1)	131.8(5)
O(1)–P(1)–O(2)	116.9(4)	P(2)–O(3)–Cu(1)	139.6(5)
O(1)–P(1)–C(1)	108.4(6)	P(1)–C(1)–P(2)	115.6(6)
O(2)–P(1)–C(1)	110.0(6)		

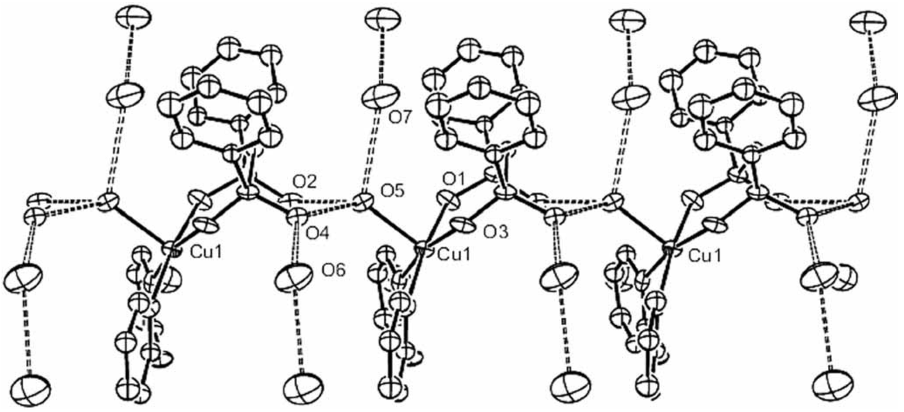

Figure 2. Fragment of the structure of **1** showing propagation of the polymer in the *z* direction.

Finally the complete packing diagram of **1** is reported in figure 4, with view normal to [001]. Here the head-to-tail π–π stacking of the dipyam ligands can be seen (the shortest contacts between the atoms of two adjacent dipyam moieties being 3.33 Å).

The propagation of the polymer of **1** in the *z* direction (see figure 2) resembles that of the related, recently reported [Cu(pcp)(2,2′bipyridine)(H_2O)] material [15], with very similar bond distances and angles in the coordination sphere. The only way the latter differs is the further extension of the building. As a matter of fact, whereas the bipy derivative, missing solvent water molecules, is a hydrogen-bonded, monodimensional polymer, complex **1** exploits the solvent water molecules and the protonated nitrogen donor of dipyam to construct a three-dimensional architecture.

The structure of **2** consists of [Cu(pcp)(terpy] units and solvent water molecules, held together by a network of hydrogen bonding interactions. Figure 5 shows the asymmetric unit of the structure, comprising two crystallographically independent

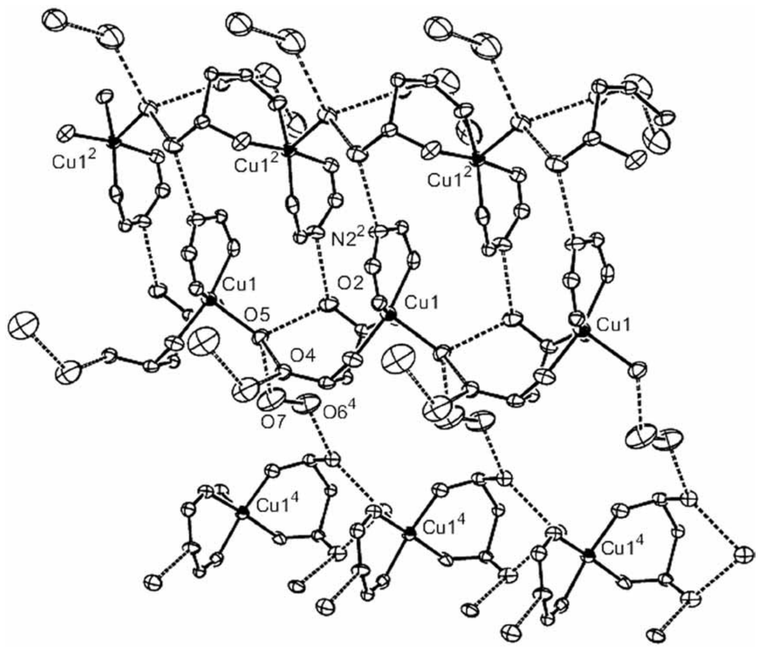

Figure 3. Portion of the packing of **1**, showing the most important hydrogen bonds. For clarity, the *pcp* phenyl rings are omitted and the *dipyam* has been schematized as NCNCN.

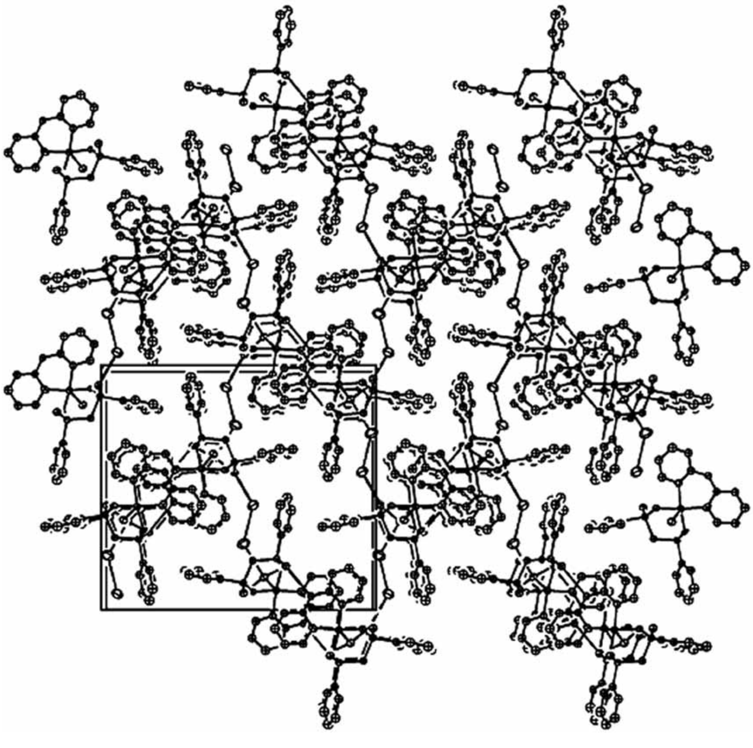

Figure 4. Complete packing diagram of **1**, viewed along the *z* axis.

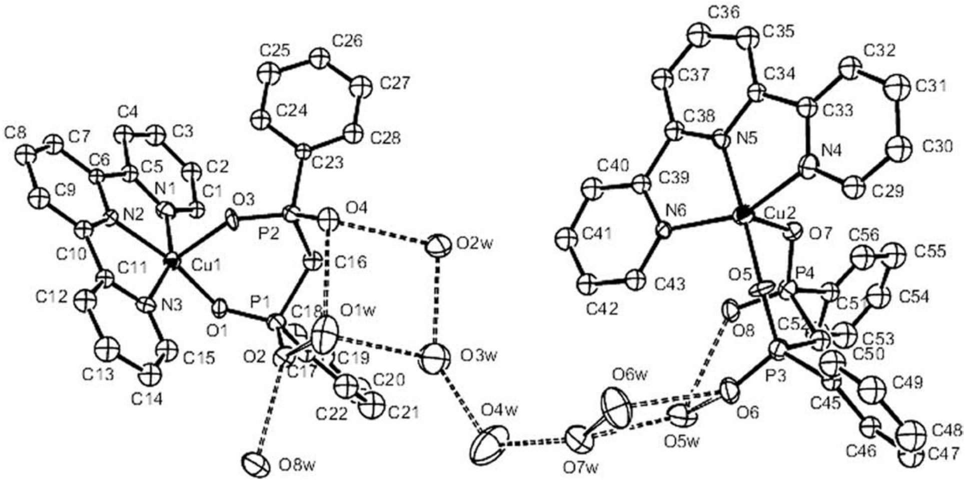

Figure 5. Perspective view of the asymmetric unit of **2**. Ortep drawing with 30% probability ellipsoids.

Table 3. Important hydrogen bonding interactions (Å) for [Cu(terpy)(pcp)] $\cdot 4H_2O$.

O2 ··· O1w	2.62	O1w ··· O4w^{II}	2.98
O2 ··· O8w	2.80	O2w ··· O3w	2.80
O4 ··· O2w	2.79	O3w ··· O4w	2.91
O4 ··· O1w	2.95	O3w ··· O8w^{II}	2.94
O6 ··· O6w	2.77	O4w ··· O7w	2.73
O6 ··· O5w	3.21	O5w ··· O7w	2.87
O7 ··· O2w^{I}	2.88	O6w ··· O7w	2.73
O8 ··· O5w	2.77	O6w ··· O8w^{III}	2.83
O1w ··· O3w	2.82		

Superscripts refer to the following symmetry operations: I $1-x$, $-1-y$, $1-z$; II $1-x$, y, $0.5-z$; III $1-x$, $-1+y$, $0.5-z$.

[Cu(pcp)(terpy)] molecules and eight water molecules. In each independent unit the metal center displays a distorted square-pyramidal coordination, being linked to three nitrogen donors from terpy ligand and to two oxygen donors from *pcp* phosphinate groups, one of the latter in an apical site.

The structural building is characterized by a close net of hydrogen bonding interactions, involving the phosphinate oxygen donors and the numerous solvent water molecules. Not only the free oxygens (O2 and O4) of pcp, but also one metal-coordinated oxygen (O7) is significantly involved in the hydrogen bonding network, resulting in a very intricated architecture, which propagates in three dimensions. The most important hydrogen bonds are reported in table 3.

Figure 6 shows a portion of the packing of **2**, demonstrating the hydrogen bonding framework and figure 7 reports the complete packing with view normal to [010]. As for **1** an additional stabilizing factor is the π–π stacking of the terpyridine rings, which features head-to-tail overlaps (shortest contacts 3.42 Å).

In the coordination sphere of both **1** and **2** the bond distances and angles appear normal (see tables 2 and 4) and fall in the range of values reported [15, 29]. Both present a distortion from idealized geometry, as evidenced by the *trans* basal angles,

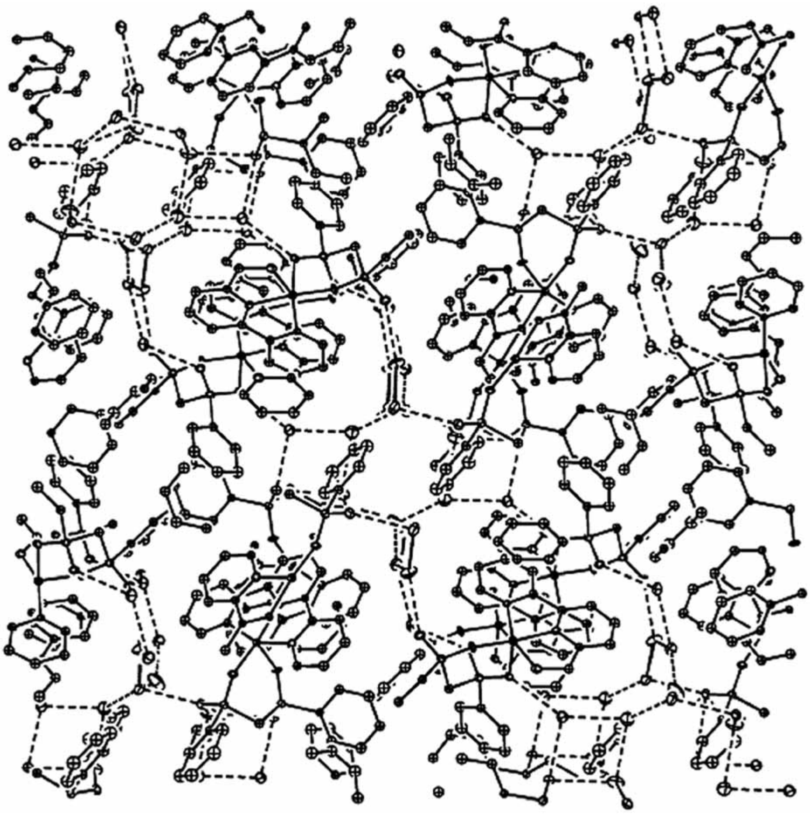

Figure 6. Portion of the packing of **2**, showing the hydrogen bonding network.

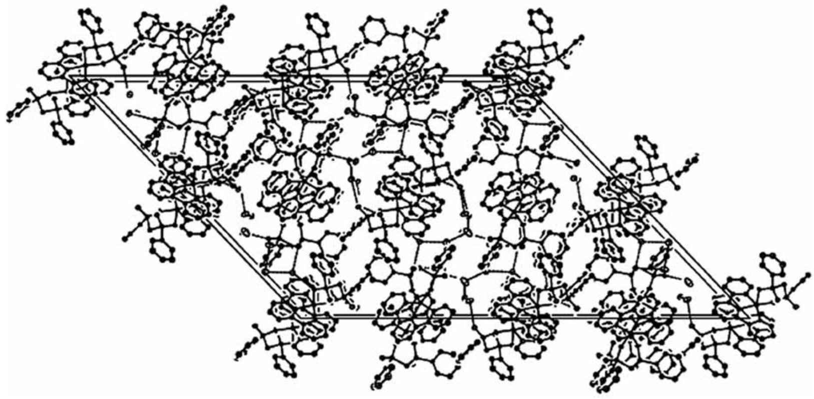

Figure 7. Complete packing diagram of **2**, with view normal to [010].

which in **1** are 167.2(4) (N1–Cu1–O1) and 170.9(4)° (N3–Cu1–O3), and in **2** are 164.9(2) (O1–Cu1–N2), 156.8(2) (N1–Cu1–N3), 169.3(2) (O5–Cu2–N5) and 155.9(2) (N6–Cu2–N4). In both compounds elongation of the apical bond is noticeable [30]. In **1** the Cu1–O5 (2.234(8) Å) is significantly longer than the basal bonds (Cu–O_{av} 1.950(2) and Cu–N_{av} 1.998(11) Å). Similarly, in **2** the apical Cu1–O3 (2.138(4) Å) and Cu2–O7

Table 4. Selected bond lengths (Å) and angles (°) for [Cu(terpy)(pcp)] · $4H_2O$.

Cu(1)–O(1)	1.912(4)	P(1)–C(16)	1.820(5)
Cu(1)–N(2)	1.948(5)	P(2)–O(3)	1.510(4)
Cu(1)–N(1)	2.067(6)	P(2)–O(4)	1.513(5)
Cu(1)–N(3)	2.081(5)	P(2)–C(23)	1.795(6)
Cu(1)–O(3)	2.138(4)	P(2)–C(16)	1.829(5)
Cu(2)–O(5)	1.893(4)	P(3)–O(6)	1.477(5)
Cu(2)–N(5)	1.929(5)	P(3)–O(5)	1.522(4)
Cu(2)–N(6)	2.033(5)	P(3)–C(44)	1.801(6)
Cu(2)–N(4)	2.059(6)	P(3)–C(45)	1.807(7)
Cu(2)–O(7)	2.191(5)	P(4)–O(8)	1.488(4)
P(1)–O(2)	1.493(4)	P(4)–O(7)	1.495(4)
P(1)–O(1)	1.544(4)	P(4)–C(51)	1.806(7)
P(1)–C(17)	1.804(7)	P(4)–C(44)	1.837(6)
O(1)–Cu(1)–N(2)	164.9(2)	C(17)–P(1)–C(16)	102.6(3)
O(1)–Cu(1)–N(1)	94.8(2)	O(3)–P(2)–O(4)	117.4(3)
N(2)–Cu(1)–N(1)	78.4(2)	O(3)–P(2)–C(23)	107.6(3)
O(1)–Cu(1)–N(3)	103.9(2)	O(4)–P(2)–C(23)	110.7(3)
N(2)–Cu(1)–N(3)	80.1(2)	O(3)–P(2)–C(16)	109.1(2)
N(1)–Cu(1)–N(3)	156.8(2)	O(4)–P(2)–C(16)	109.0(2)
O(1)–Cu(1)–O(3)	96.73(17)	C(23)–P(2)–C(16)	102.1(3)
N(2)–Cu(1)–O(3)	97.63(19)	O(6)–P(3)–O(5)	116.1(3)
N(1)–Cu(1)–O(3)	99.45(19)	O(6)–P(3)–C(44)	110.5(3)
N(3)–Cu(1)–O(3)	92.00(19)	O(5)–P(3)–C(44)	108.5(3)
O(5)–Cu(2)–N(5)	169.3(2)	O(6)–P(3)–C(45)	109.9(3)
O(5)–Cu(2)–N(6)	101.8(2)	O(5)–P(3)–C(45)	106.2(3)
N(5)–Cu(2)–N(6)	79.8(2)	C(44)–P(3)–C(45)	104.9(3)
O(5)–Cu(2)–N(4)	96.4(2)	O(8)–P(4)–O(7))	118.4(3)
N(5)–Cu(2)–N(4)	79.4(2)	O(8)–P(4)–C(51)	106.7(3)
N(6)–Cu(2)–N(4)	155.9(2)	O(7)–P(4)–C(51)	109.2(3)
O(5)–Cu(2)–O(7)	94.94(18)	O(8)–P(4)–C(44)	107.9(3)
N(5)–Cu(2)–O(7)	95.28(19)	O(7)–P(4)–C(44)	107.0(3)
N(6)–Cu(2)–O(7)	97.58(19)	C(51)–P(4)–C(44)	107.2(3)
N(4)–Cu(2)–O(7)	96.4(2)	P(1)–O(1)–Cu(1)	126.6(3)
O(2)–P(1)–O(1)	117.8(3)	P(2)–O(3)–Cu(1)	132.4(3)
O(2)–P(1)–C(17)	109.1(3)	P(3)–O(5)–Cu(2)	137.1(3)
O(1)–P(1)–C(17)	107.8(3)	P(4)–O(7)–Cu(2)	116.6(3)
O(2)–P(1)–C(16)	111.3(3)	P(1)–C(16)–P(2)	116.6(3)
O(1)–P(1)–C(16)	107.0(2)	P(3)–C(44)–P(4)	113.8(3)

(2.191(5) Å) are longer than the basal bonds (Cu–O 1.893–1.912(4) Å, Cu–N 1.929(5)–2.081(5) Å). Finally, as concerns the Cu–N bond distances in **2**, the shortest value found for the central pyridyl donor is not surprising, taking into account the steric constraints in formation of two five-membered chelate rings.

3.2. *IR spectra*

The IR spectra of the compounds are quite complex containing a very large number of absorption bands. In the region 3400–3000 cm^{-1}, complex **1** shows a series of weak absorptions at 3295, 3247, 3194, 3136, 3075 and 3040 cm^{-1}attributable to OH and NH stretching vibrations. In complex **2** the same region has a strong broad band centered at 3300 cm^{-1} due to OH stretching of H_2O. This finding appears to be consistent with the presence, in complex **2**, of a very thick hydrogen bonding network, involving four similar, non-coordinated, water molecules. Conversely in complex **1** the hydrogen bonding network involves different water molecules (coordinated and non coordinated) and NH groups giving rise to a resolved system of weaker bands.

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