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Copper(II) Complexes with Bridging Diphosphinates – The Effect of the Elongation of the Aliphatic Chain on the Structural Arrangements Around the Metal Centres

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The reactivity in water solution of the two closely related *P,P′*-diphenylmethylenediphosphinic (H_2pcp) and *P,P′*-diphenylethylenediphosphinic (H_2pc$_2$p) acids towards copper(II) salts, in the presence of 2,2′-bipyridine, has been investigated. The reaction of H_2pc$_2$p with copper(II) acetate and 2,2′-bipy resulted in the dinuclear complex of formula [(2,2′-bipy)Cu(μ-pc$_2$p)$_2$Cu(2,2′-bipy)]·4.5H_2O (**2**), which contrasts the monomeric complex [(2,2′-bipy)Cu(pcp)(H_2O)] (**1**) previously obtained from H_2pcp. The reactions of H_2pcp and H_2pc$_2$p with copper(II) perchlorate and 2,2′-bipy resulted in the two different dinuclear complexes respectively of formulas [(2,2′-bipy)(H_2O)Cu(μ-pcp)(μ-ClO_4)Cu(2,2′-bipy)][ClO_4]·[(2,2′-bipy)(ClO_4)Cu(μ-pcp)(μ-ClO_4)Cu(2,2′-bipy)]·H_2O (**3**) and [(2,2′-bipy)Cu(μ-pc$_2$p)(μ-ClO_4)Cu(2,2′-bipy)(ClO_4)] (**4**). The structures of the new complexes and those of the solid diphosphinic acids H_2pcp and H_2pc$_2$p have been characterized by single-crystal X-ray diffraction analyses. In spite of their close similarity the two diphosphinate ligands adopt different conformations which in turn can remarkably influence the structural arrangements of the resulting copper complexes. The magnetic properties of complex **3**, which contains four metal centers, with three of them in different (even if similar) chemical environments, have been characterized by low-temperature measurements.
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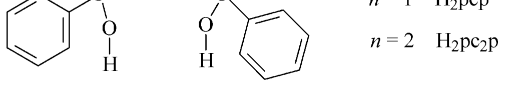
Introduction

Polymeric metal phosphinates were already known forty years ago to be used in the coating and grease thickeners industry.[1] They are also used commercially as replacement of the common brominated flame retardant in polymers that are banned in the electronic devices in the European Union.[2] These materials generally constructed from divalent metals and monofunctional phosphinates showed invariably one-dimensional frameworks with linear chains consisting of metal atoms linked by double bridging phosphinate groups. As a matter of fact the mode of coordination of the phosphinate group involved always the coordination of one oxygen to one metal.[3]

In recent years, we have found that the bifunctional anion of the *P,P′*-diphenylmethylenediphosphinic acid (H_2pcp), Scheme 1, is suitable to give coordination polymers displaying a remarkable array of different frameworks. Indeed pcp^{2-} contains four oxygen donor atoms, allowing the coordination of a single metal ion (either with one or two oxygens atoms) and/or bridging of multiple metal centers. As a result we have isolated a number of hybrid materials with 1D (ladders, sinusoidal ribbons, strands, tubelike etc.) or 2D layered structural arrangements.[4–12] In the presence of coordinated or solvated water molecules the architectures extend to higher dimensions through strong hydrogen bonding interactions. Moreover, to favour the formation of materials with potential porous behaviour we have reacted the pcp/metal system also in the presence of additional linkers such as 2,2′-bipy and 4,4′-bipy.[12–15] This strategy, very recently, allowed the synthesis of the noteworthy hybrid [$Cu_2(pcp)_2$(4,4′-bipy)]·5H_2O, featuring a mono-dimensional tubelike structure.[14]



Scheme 1.

In the light of the growing interest for porous materials containing nanochannels[16] a stimulating challenge is the understanding of how small systematic changes in the linker (skeleton, aromatic or aliphatic groups) can affect the con-

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formation of the resultant networks. Keeping this in mind, we are considering the ligand *P*,*P*′-diphenylethylenediphosphinate, $pc_2p^{2–}$, Scheme 1, with a longer carbon chain connecting the phosphinate moieties in comparison with $pcp^{2–}$.

The corresponding methylene- and ethylene-diphosphonates have been extensively used to construct hybrids materials of various structural arrangement. In general, alkyl and aryl diphosphonates allow chemists to vary the length of the carbon chain in order to manipulate the size of the pores of the solid state materials.[17]

In the present work, first we focus on the characteristics of the H_2pcp and H_2pc_2p acids both in solution and in the solid state, secondly we compare the structures of some corresponding 0D copper(II) complexes with $pcp^{2–}$ and $pc_2p^{2–}$ ligands, namely the already described [Cu(2,2′-bipy)(pcp)-(H_2O)] (**1**)[7] and the newly synthesized [(2,2′-bipy)Cu(μ-pc_2p)$_2$Cu(2,2′-bipy)]·4.5H_2O (**2**), [(2,2′-bipy)(H_2O)Cu(μ-pcp)(μ-ClO_4)Cu(2,2′-bipy)][ClO_4]·[(2,2′-bipy)(ClO_4)Cu(μ-pcp)(μ-ClO_4)Cu(2,2′-bipy)]·H_2O (**3**) and [(2,2′-bipy)Cu(μ-pc_2p)(μ-ClO_4)Cu(2,2′-bipy)(ClO_4)] (**4**). The hydrated complex **2** has been investigated by thermal analysis. The complex **3**, which contains four metal centers (with three of them in different chemical environments), has been characterized by low-temperature magnetic measurements. To the best of our knowledge no metal complexes of $pc_2p^{2–}$ have been reported previously.

Results and Discussion

Water Solution Equilibrium Constants and Solid State Structures of the Diphosphinic Acids H_2pcp and H_2pc_2p

The experimental potentiometric data of $pc_2p^{2–}$ are shown in Table 1, where the corresponding values previously obtained for $pcp^{2–}$ [7] are also reported.

Table 1. Decimal logarithm values of the equilibrium constants for the reactions of $pc_2p^{2–}$ and $pcp^{2–}$with H^+, in aqueous solution.[a]

		log *K*	
	reaction	L = $pc_2p^{2–}$	L = $pcp^{2–}$ [5]
log K_1	$H^+ + L^{2–} \leftrightarrows HL^–$	3.78(6)	3.33(1)
log K_2	$H^+ + HL^– \leftrightarrows H_2L$	2.29(8)	1.35(9)

[a] *T* = 298 K and *I* = 0.5 mol dm^{-3}, Me_4NCl. Values in parentheses are standard deviations on the last significant digit.

The two basicity constants of $pc_2p^{2–}$ are both slightly higher than the corresponding values obtained for the similar ligand $pcp^{2–}$ [7]: the increase is to be attributed to the lengthening of the aliphatic chain. No values of the basicity constants of organic phosphinates are available in literature, except for the report by Cook and Mason.[18] In this paper the basicity of the monoprotic ligand phenylmethylphosphinate $[PhMePO_2]^{2–}$ (log*K* = 3.7, from NMR spectroscopic data) was found to be close to that of the diphosphinates considered in this study. The value of Δlog*K* = logK_1 – logK_2 decreases passing from $pcp^{2–}$ to $pc_2p^{2–}$ (2.0 and 1.5, respectively), exceeding in both cases the value expected on purely statistical basis (log4 = 0.6) for the protonation of two independent equivalent basic centres. This means that the two phosphonate groups are significantly interacting, the extent of this interaction being stronger for the ligand with the shorter aliphatic spacer.

The solid-state structures of H_2pcp and H_2pc_2p are both characterized by strong hydrogen bonds as shown in Figure 1. Only half of H_2pc_2p molecule lays in the asymmetric unit. In H_2pcp the P–OH distances are 0.08 Å longer than the P=O distances [1.561(3) for P1–O2, 1.5494(18) for P2–

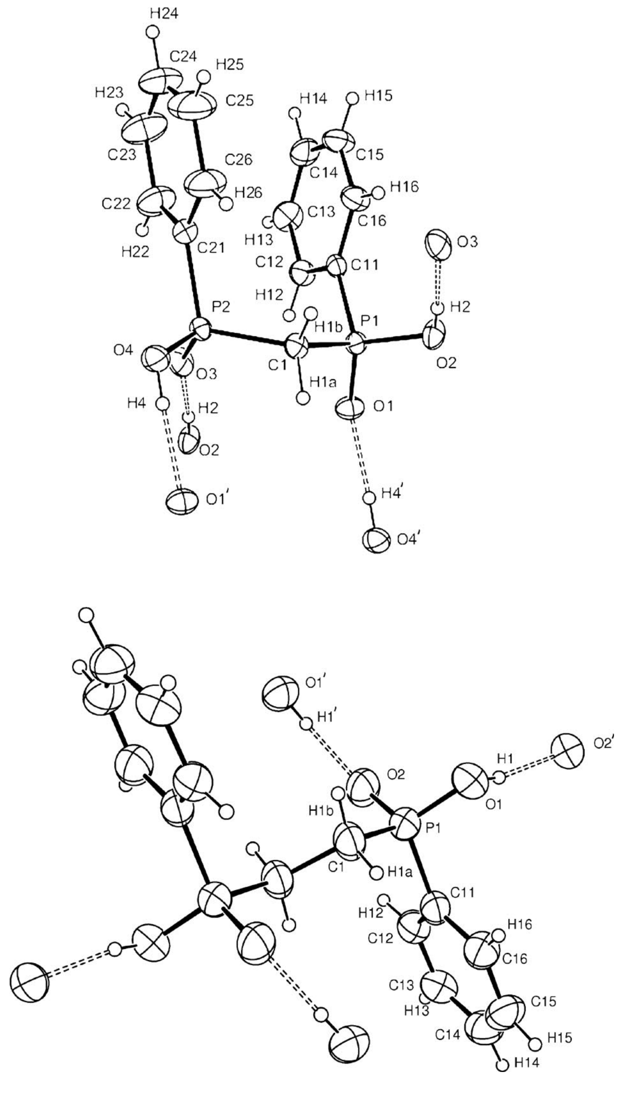


Figure 1. Fragments of the H_2pcp (left) and of the H_2pc_2p (right). ORTEP drawing with the 30% of probability. Hydrogen bonding interactions are highlighted as dashed lines. Selected distances [Å] and angles [°] for H_2pcp: P(1)–O(1) 1.4851(19), P(1)–O(2) 1.561(3), P(1)–C(11) 1.782(2), P(1)–C(1) 1.806(2), P(2)–O(3) 1.480(2), P(2)–O(4) 1.5494(18), P(2)–C(21) 1.778(2), P(2)–C(1) 1.804(3), O(2)···O(3)#1 2.554(3), O(4)···O(1)#2 2.533(3), O(1)–P(1)–O(2) 111.82(12), O(3)–P(2)–O(4) 114.91(11), P(1)–C(1)–P(2) 117.53(12) symmetry code: #1 –*x*, –*y* + 2, –*z* + 2; #2 *x* + 1, *y*, *z*; #3 –*x*, –*y* + 2, –*z* + 2. Selected distances [Å] and angles [°] for H_2pc_2p: P(1)–O(1) 1.5300(17), P(1)–O(2) 1.5186(18), P(1)–C(1) 1.773(3), P(1)–C(11) 1.808(3), C(1)–C(1)#1 1.531(4), O(1)···O(2)#2 2.441(3), O(2)–P(1)–O(1) 115.40(10), C(1)#1–C(1)–P(1) 113.4(2) (symmetry code: #1 –*x* + 2, –*y*, –*z* + 1; #2 *x* –0.5, –*y* – 0.5, *z*; #3 *x* + 0.5, –*y* – 0.5, *z*).

O4 against 1.4851(19) for P1–O1 and 1.480(2) for P2–O3]. In the H_2pc_2p molecule, the two distances are closer [1.5186(18) for P1–O1 and 1.5300(17) for P1–O2].

Each H_2pcp unit forms four strong hydrogen bonds with three other H_2pcp molecules. As shown in Figure 2, in the first step a kind of dimeric moiety is formed through the O1 and O4 atoms, then the O2, $O2^1$, O3 and $O3^1$ oxygen atoms in turn connect such a dimer with the neighbour dimers to form a 1D ribbon parallel to the *a* axis. The O4–$O1^2$ and O2–$O3^1$ distances are respectively 2.533(3) and 2.554(3) (symmetry code: #1 $-x + 1$, y, z; #2 $-x$, $-y + 2$, $-z + 2$). The ribbons are packed as shown in Figure 2. Considering in the counting also the hydrogen atoms, in the ribbon there are a 12-membered ring formed in the H_2pcp dimer and a 16-membered ring formed by the coupling of two dimers.

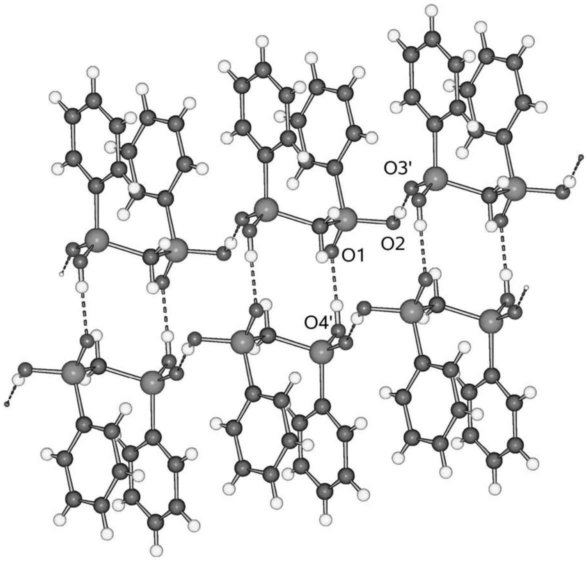


Figure 2. Propagation of the 1D ribbon of the H_2pcp dimer, parallel to the *a* axis. Hydrogen bonding interactions are highlighted as dashed lines.

Also each H_2pc_2p molecule forms four strong hydrogen bonds but with four different molecules. The O1–$O2^2$ distance is 2.441(3) (symmetry code: #$x - 0.5$, $-y - 0.5$, z). The result is a 2D layer perpendicular to the *c* axis, as shown in Figure 3. In this case there is only one type of ring and it is a 22-membered one, considering in the counting also the hydrogen atoms.

It is of interest to notice the relative position of the two phenyl rings in the two structures. In H_2pcp the phenyl rings of each molecule are in the same side of the 1D chain [C11–P1–P2–C21 torsion angle: 32.75(12)°] while in H_2pc_2p the phenyl rings of each unit are on opposite side of the slab (C11–P1–$P1^1$–$C11^1$ angle: 180°). As a result in H_2pc_2p the hydrophilic and the hydrophobic regions are separated, while in H_2pcp the hydrophilic part of the structure is inserted in a hydrophobic matrix.

From a topological point of view, the network of the H_2pcp acid is a simple ladder, while the network of H_2pc_2p is one of the two possible conformations of a brick wall.

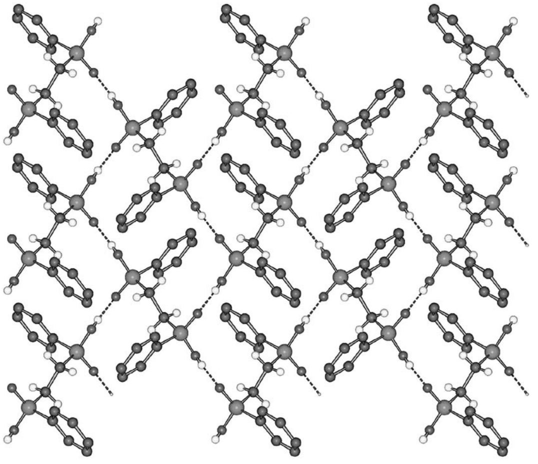
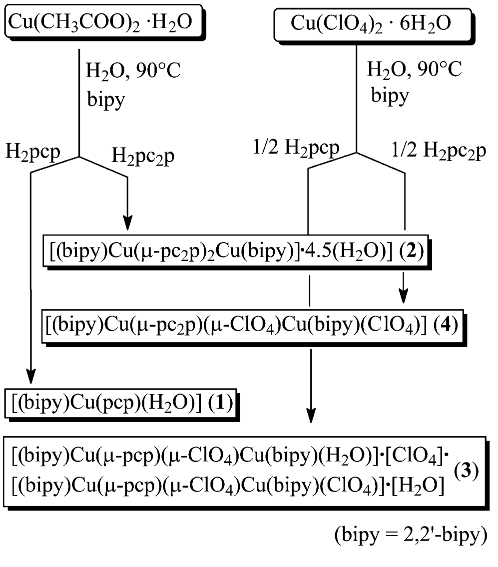


Figure 3. The hydrogen bonding 2D layer of H_2pc_2p. The hydrogen atoms of the phenyl rings are omitted. Hydrogen bonding interactions are highlighted as dashed lines.

The same net conformation was found in the structure of the related diphosphinic acid HO(O=)PH–CH_2CH_2–HP(=O)OH.[19] The only remarkable difference between the two structures is the inter-plane separation that correspond to the length of the *c* axes, 8.950(17) in case of H_2pc_2p while for diphosphinic acid the interplane distance is 3.66 Å. It is also noteworthy that the HO(O=)PH–CH_2–HP(=O)OH compound[20] has instead a different hydrogen bond network with respect the one found for H_2pcp.

Preparation of the Complexes

The reactions of the diphosphinic acids H_2pcp or H_2pc_2p, in the presence of 2,2′-bipy, with copper(II) acetate or perchlorate, in water solution, at ca. 90 °C, allow the formation of diphosphinate complexes (Scheme 2).



Scheme 2.

Whereas acetate is not contained in the isolated complexes, the perchlorate anion is always present either as a ligand (terminal and/or bridging) or as counter anion. Accordingly, to balance the charges, the reactions proceed with a molar ratio of Cu/diphosphinate equals 1 in the case of acetate and 2 in the case of perchlorate. The different nature of H_2pcp and H_2pc$_2$p remarkably affects the relative reactions: while for H_2pcp the yield of the complex is always high, in the case of H_2pc$_2$p the addition of a basis appears to be necessary to promote the coordination of copper ions in considerable yield. As a matter of fact for copper acetate just the acetate itself can act as a basis, whereas copper perchlorate reacts with H_2pc$_2$p to give only low amount of **4**, the major products recovered being unreacted diphosphinic acid and the previously reported complex [Cu(2,2′-bipy)$_2$(ClO$_4$)]·[ClO$_4$][21] (see Exp. Sect.). When the latter reaction is performed in the presence of equimolar amounts of a basis, **4** is obtained in high yield. Both the different acidities of the two acids and the different solubilities and/or stabilities of the complexes may account for these different reaction trends.

Structures of the Complexes

The structure of complex **1**[7] consists of monodimensional [(2,2′-bipy)Cu(pcp)(H_2O)] hydrogen-bonded polymers while the complex obtained by reaction of the Cu^{II} acetate with H_2pc$_2$p and 2,2′-bipy is dinuclear with formula [(2,2′-bipy)Cu(μ-pc$_2$p)$_2$Cu(2,2′-bipy)]·4.5H_2O (**2**). In complex **1**, the copper center is surrounded in a distorted square pyramidal geometry by two phosphinate oxygen donors, two bipy nitrogen atoms and one water molecule in the apical position. The ligand phenylphosphinate coordinates as bidentate only one metal center with two phenylphosphinate oxygen atoms remaining free and available for hydrogen-bonding interactions with the water molecule of one neighbouring moiety (see Figure S1 in the Supporting Information).

The asymmetric unit of **2** (see Figure 4) consists of two independent half dimer as well as five water solvent molecules with one of them with a refined occupancy factor 0.5. Each metal unit features a centre of inversion halfway the M–M vector.

In each metal unit, the two copper metals have a square-pyramidal coordination. The basal positions are occupied by the nitrogen atoms of the bipy and by two oxygen atom of a pc$_2$p^{2-} ligand. The oxygen atom in the axial position belongs to another pc$_2$p^{2-} group. The pc$_2$p^{2-} ligand acts as a tridentate one, coordinating two metal centres and with the forth oxygen atom (O4 and O8) involved in hydrogen bonding with solvent water molecules. The Cu–O bond length in the apical position are more than 0.20 Å longer than the Cu–O distance in the apical position [1.941(10) vs. 2.192(8) averaged values]. Also the P–O distances of the basal coordinated oxygen atom (O1, O3, O5, O7) are slightly longer than the others (O2, O4, O6, O8).

The unit 1 (see Figure 4) is connected with unit 2 by the water molecules O1w, O3w, O4w. The unit 2 is also connected with another unit 2 through the O2w water molecule. Figure 5 shows the 2D hydrogen bond slab formed by the rows of the units 2. Unit 1 connects two rows of unit 2. Finally the 3D dimension is reached by the π–π stacking of the bipy rings. The water molecules are removed from the structure heating the complex at more than 100 °C as shown by the thermal analysis (see below).

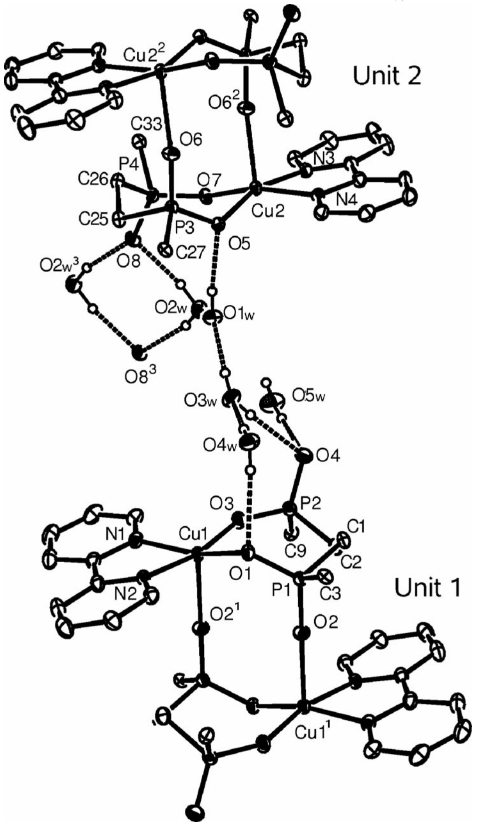


Figure 4. Molecular structure of **2** showing the asymmetric unit and the most important hydrogen bonding interactions (dashed lines). The hydrogen atoms of the bipy as well as the phenyl ring (except the C_{ipso} carbon) are omitted. Selected distances [Å] and angles [°] for **2**: Cu(1)–O(1) 1.9609(15), Cu(1)–O(2)#1, 2.1849(17), Cu(1)–O(3) 1.9161(16), Cu(1)–N(1) 2.0237(19), Cu(1)–N(2) 2.0195(18), P(1)–O(1) 1.5283(16), P(1)–O(2) 1.4911(16), P(2)–O(3) 1.5188(16), P(2)–O(4) 1.4940(17), Cu(2)–O(5) 1.9497(15), Cu(2)–O(6)#2, 2.2002(16), Cu(2)–O(7) 1.9358(15), Cu(2)–N(3) 2.0126(18), Cu(2)–N(4) 2.0159(18), P(3)–O(5) 1.5300(15), P(3)–O(6) 1.4898(16), P(4)–O(7) 1.5161(15), P(4)–O(8) 1.5008(16), O(1)–Cu(1)–O(2)#1 108.02(6), O(1)–Cu(1)–O(3) 95.05(7), O(2)#1–Cu(1)–O(3) 97.24(7), N(1)–Cu(1)–N(2) 79.86(8), O(5)–Cu(2)–O(6) #2 108.83(6), O(5)–Cu(2)–O(7) 93.18(6), O(6)#2–Cu(2)–O(7) 97.49(6), N(3)–Cu(2)–N(4) 80.29(7). Hydrogen bonds: O(1w)···O(5) 2.870(2), O(2w)···O(8) 2.762(3), O(3w)···O(4) 2.746(3), O(3w)···O(1w) 2.749(3), O(4w)···O(1) 2.914(2), O(1w)···O(2w) 2.798(3), O(2w)···O(8)#3 2.774(2), O(3w)···O(4w) 2.850(3), O(4)···O(5w) 3.100(6) (symmetry code: #1 $-x + 3$, $-y + 1$, $-z + 2$; #2 $x - 1$, $-y - 1$, $-z + 1$, #3 $-x + 2$, $-y + 1$, $-z + 1$).

The structures of **3** and **4** consist of copper dinuclear complexes containing the pc$_n$p ligand and the 2,2′-bipyridine, with perchlorate and, in the case of **3**, water molecules.

The asymmetric unit of **3**, reported in Figure 6, is constituted by four copper ions, two pcp^{2-} ligands, four 2,2′-bi-

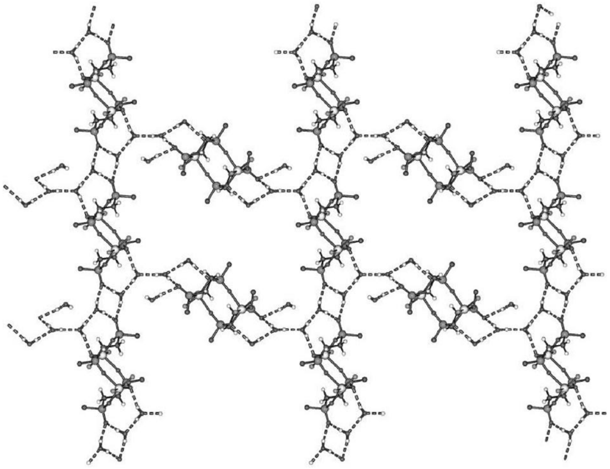


Figure 5. 2D Slab of **2**. The phenyl rings except for the C_{ipso} and the carbon atoms of the 2,2′-bipy are omitted. Hydrogen bonding interactions are highlighted as dashed lines.

pyridines, four perchlorate anions and two water molecules. In each crystallographically independent dinuclear complex (Cu1/Cu2 and Cu3/Cu4) the two copper centers are bridged by one pcp^{2-} ligand, acting as tetra donor.

Moreover, both copper ions are surrounded by the nitrogen atoms of the 2,2′-bipy ligand. In each dinuclear unit, while one copper (Cu2 or Cu4) reaches a five-coordination interacting with the oxygen donor of one perchlorate group, the second copper ion (Cu1 or Cu3) presents a pseudo octahedral geometry, with two long axial interactions, normal to the basal plane of the pcp^{2-} oxygen and 2,2′-bipy nitrogen atoms. Actually the two complexes differ just for the coordination of the two pseudo-octahedral metal ions: whereas Cu3 is linked to the same oxygen atoms of two perchlorate groups with contacts of 2.668(5) and 2.764(8) Å, the Cu1 ion is coordinated to the oxygen of one perchlorate and to one water molecule with distances of 2.751(5) and 2.423(5) Å, respectively.

The structure of **4** is shown in Figure 7. There are no water molecules in the crystal structure. As for one of the complexes of **3**, in **4** one copper atom is five-coordinate and

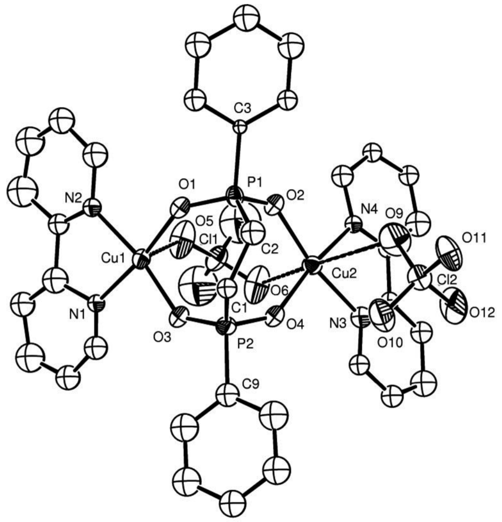


Figure 7. Asymmetric unit of **4**. Selected distances [Å] and angles [°] for **4**: Cu(1)–O(1) 1.904(18), Cu(1)–O(3) 1.911(16), Cu(1)–O(5) 2.39(2), Cu(1)–N(1) 1.960(18), Cu(1)–N(2) 1.920(19), Cu(2)–O(2) 1.979(18), Cu(2)–O(4) 1.960(19), Cu(2)–O(6) 2.57(2), Cu(2)–O(9) 2.81(2), Cu(2)–N(3) 1.99(2), Cu(2)–N(4) 2.03(2), O(1)–Cu(1)–O(3) 95.5(7), O(1)–Cu(1)–O(5) 91.5(9), O(3)–Cu(1)–O(5) 104.1(9), N(1)–Cu(1)–N(2) 82.8(8), O(2)–Cu(2)–O(4) 95.3(7), O(2)–Cu(2)–O(6) 98.3(8), N(3)–Cu(2)–N(4) 78.9(8), O(1)–P(1)–O(2) 116.1(12).

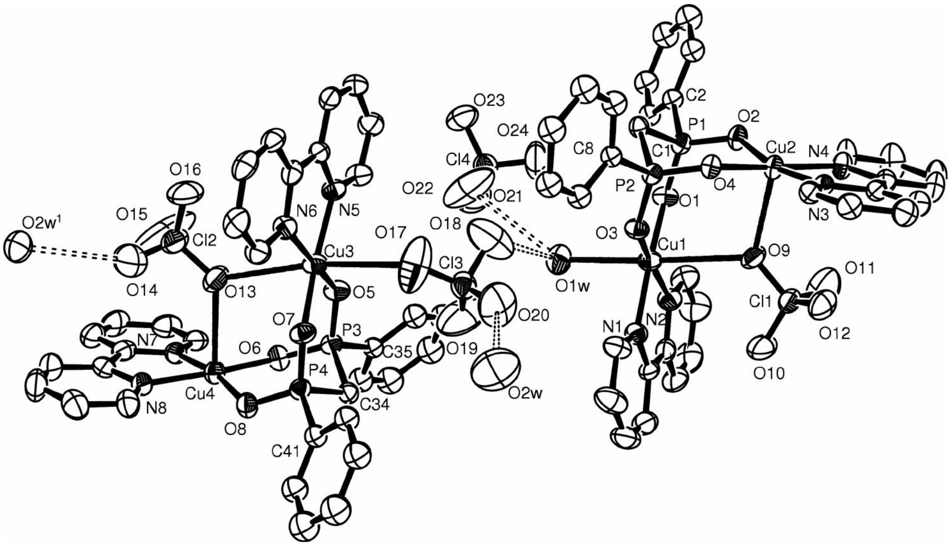


Figure 6. Asymmetric unit of **3** with the symmetry equivalent O2w^1 water, generated using the trasformation $-x + 1$, $y + 0.5$, $-z + 1.5$. Hydrogen bonding interactions are highlighted as dashed lines. Selected distances [Å] and angles [°] for **3**: Cu(1)–O(1) 1.937(4), Cu(1)–O(3) 1.967(4), Cu(1)–N(1) 1.997(6), Cu(1)–N(2) 1.997(6), Cu(1)–O(1w) 2.423(5), Cu(2)–O(2) 1.922(4), Cu(2)–O(4) 1.929(4), Cu(2)–N(3) 1.984(5), Cu(2)–N(4) 1.990(5), Cu(3)–O(7) 1.918(4), Cu(3)–O(5) 1.922(4), Cu(3)–N(5) 1.986(5), Cu(3)–N(6) 1.977(5), Cu(4)–O(6) 1.925(4), Cu(4)–O(8) 1.925(4), Cu(4)–N(7) 1.976(5), Cu(4)–N(8) 1.984(6), O(1)–Cu(1)–O(3) 96.07(17), N(1)–Cu(1)–N(2) 80.7(3), O(2)–Cu(2)–O(4) 94.73(17), N(3)–Cu(2)–N(4) 81.3(2), O(5)–Cu(3)–O(7) 96.34(18), N(5)–Cu(3)–N(6) 81.0(2), O(6)–Cu(4)–O(8) 95.16(18), N(7)–Cu(4)–N(8) 81.7(3). Hydrogen bonds: O(1w)···O(18) 3.234(10), O(1w)···O(22) 3.110(13), O(2w)···O(20) 2.898(14), O(2w)#1···O(14) 3.10(2).

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the second has a pseudo-octahedral coordination. Also pc_2p^{2-} is acting as tetra-donor ligand. The perchlorate anion in the bridging position is linked with the two copper metals using two different oxygen atoms. This is the most evident difference between **3** and **4**, which is a consequence of the different coordination capability of the two ligands. From a search in the Cambridge Structural Database[22] we have found that one oxygen atom bridging coordination of a perchlorate is less common (44 hits) in comparison with the perchlorate bridging through two different oxygen atoms (160 hits). The angle between the best planes calculated using the copper coordinated oxygen and nitrogen atoms are for the two dinuclear units in **3** 81.25(11)° and 84.42(12)° while for **4** the same angle is 72.7(5)°.

Other differences between **3** and **4** can be highlighted looking at the organization of the dinuclear complexes in the solid state. In **3** the two crystallographically independent complexes are moreover connected through a network of hydrogen bonding interactions between the perchlorate groups and the water molecules, both of coordination and of crystallization. It results a monodimensional polymeric array (see Figure 8), which extends to 3D dimension through the π–π interactions of the stacked 2,2′-bipy. For **4** the π–π interactions between the 2,2′-bipy and the phenyl ring are the only forces responsible for the packing (see Figure S2, Supporting Information).

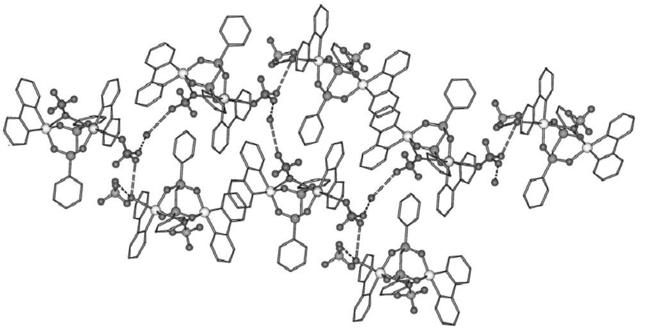


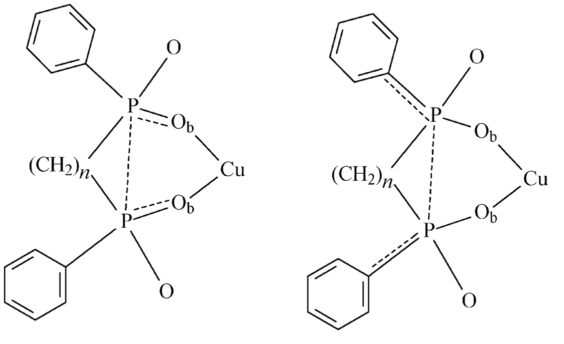
Figure 8. Propagation of the monodimensional hydrogen-bonded (dashed bonds) polymer **3** along the *y* direction. The phenyl rings and the carbon atoms of the bipyridine ligand are shown in stick style.

Comparison of the Structural Frameworks

In the complexes **1**–**4**, the coordination geometries around the metal ions are similar, with the copper atoms at the center of a square formed by two 2,2′-bipy nitrogen atoms and two phosphinate oxygen donors; the further coordination in apical positions of one or two oxygen atoms (from an other phosphinate, a water molecule, or a perclorate anion) allows to reach respectively final distorted square pyramidal or elongated octahedral coordinations. Accordingly the Cu–O distances are in the range 1.91–1.96 Å (see Tables S6, S8, S10), the longer distances corresponding to the oxygen atom bonded to the group involved in the bridge of two copper atoms (complex **2**). The equatorial O–Cu–O angles are in the limited range of 93.18–96.34°, which is a consequence of the constrain angle of the 2,2′-bipy.

However the different conformations of the two ligands pcp^{2-} and pc_2p^{2-} can remarkably affect the overall structure of the resulting complexes: for instance if we compare complexes **1** and **2**, it appears evident that the conformation of the anion pcp^{2-} with the two phenyl rings in the same side of the pcp^{2-} chain (just as in the structure of solid H_2pcp) does not allow the further coordination of a second copper atom and the formation of a dimeric unit as in **2**. Another differentiation factor is the formation of a six- or seven-membered chelate rings respectively in the case of pcp^{2-} or pc_2p^{2-}, the six-membered one being currently considered more stable.

The influence of the phosphinate conformation on the structures of the complexes can be suitably evaluated by considering the dihedral angles O_bPPO_b and CPPC as defined in Scheme 3. Table 2 reports the values of both angles for a selected series of pcp^{2-} and pc_2p^{2-} complexes. A more complete list is reported as supplementary material (Table S11). The O_bPPO_b angle should be equal to zero in basal plane of the square pyramid or in the equatorial positions of the elongated octahedral complexes as in the reported complexes. A value different from zero is indicating a stretching of the chelating group.



O_bPPO_b

CPPC

Scheme 3.

The O_b–P–P–O_b angles in the pcp^{2-} complexes **1** and **3** are all close to zero indicating that four atoms are coplanar. In the pc_2p^{2-} complexes the same angle is significantly different from 0°. The deviation from the coplanarity is evident also for complex **4** [15.4(3)° and 12.3(4)° for O1–P1–P2–O3 and O3–P1–P2–O4, respectively] where the pc_2p^{2-} has the same conformation of pcp^{2-} in **3**.

The CPPC dihedral angle is the measure of the relative orientation of the phenyl rings. For a CPPC angle around 0°, the phenyl rings are on the same side respect the coordination plane defined by the phosphorus and the copper atoms. For an angle of 120° the phenyl rings lie one on one side and the other on the opposite side of coordination plane. For the copper-pcp^{2-} complexes, the CPPC angle is ever less than 35°. This finding suggests that the pcp^{2-}-metal conformation found in complex **1** should be favoured.

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Table 2. Values of the dihedral angles defined in Scheme 3 for some copper(II) pcp^{2-} and pc_2p^{2-} complexes. The CPPC dihedral angle for the free ligands is also reported for comparison.

	O_bPPO_b	CPPC	Reference
H_2pcp		32.8	this work
$[Cu(pcp)]_n$	0.5	15.7	[6]
$[Cu(pcp)(H_2O)_2]_n$	7.9	7.5	[7]
$[Cu(pcp)(4,4'\text{-bipy})(H_2O)]_n$	14.7[a]	27.4[a]	[14]
$Cu(pcp)(2,2'\text{-bipy})(H_2O)$ (**1**)	2.2	3.0	[7]
$Cu(pcp)(2,2'\text{-bipy})_2(ClO_4)(H_2O)$ of (**3**)	3.1 3.0	10.8	this work
$Cu(pcp)(2,2'\text{-bipy})_2(ClO_4)_2$ of (**3**)	0.6 0.5	0.1	this work
H_2pc_2p		180.0	this work
unit 1 of $Cu_2(pc_2p)_2(2,2'\text{-bipy})_2$ (**2**)	24.0	144.0	this work
unit 2	20.0	149.5	
$Cu_2(pc_2p)(2,2\text{-bipy})_2(ClO_4)_2$ (**4**)	15.4 12.3	15.3	this work

[a] Average value.

Noteworthy this latter is an important brick for building the tubelike polymer $[Cu_2(pcp)_2(4,4'\text{-bipy})]_n$.[14] In the case of pc_2p^{2-} the structures of the complexes **2** and **4** indicate the formation of metal–ligand units featuring different arrangements. The preference of one or the other conformations may be in turn influenced by other species present in the structural unit: for instance the perchlorate anion favours the butterfly bimetallic coordination of the copper metals in **4**.

Thermal Behaviour of Complex 2

Coupled TG-DTA curve for compound **2** is shown in Figure 9. The first weight loss (obsd. 7%) is compatible with the complete dehydration process up to about 100 °C of the $4.5\,H_2O$ per formula unit (calcd. 6.9%). Then a plateau is observed up to about 210 °C suggesting the presence of a stable anhydrous phase. Above this temperature three bad-resolved weight losses can be observed and ascribed to the combustion of the organic parts of the molecule: the first one (obsd. 20%) can be ascribed to the combustion of the two bipy ligands per formula unit (calcd. 22%).

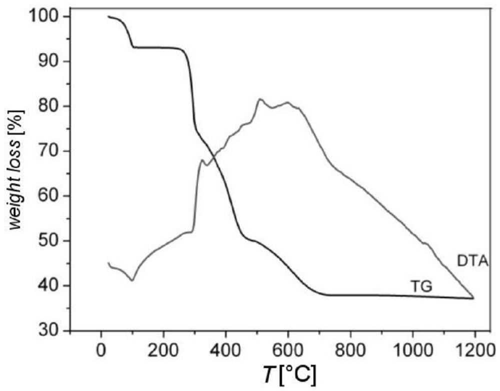

Figure 9. Coupled TG-DTA curve for complex **2**.

The remaining weight losses up to 700 °C are due to the final combustion of the C atoms belonging to the pc_2p^{2-} ligands of the structure (calcd. 40%). At the end of the analysis only a mixture of $Cu_2P_2O_7$ and CuO was found.

Magnetic Properties of Complex 3

The magnetic properties of complex **3**, between 2 and 100 K, in the form of χT vs. T curve are reported in Figure 10. The observed value of $1.8\ cm^3\,K\,mol^{-1}$ at 100 K is in the expected range for four uncoupled $S = 1/2$ spin with g> 2.00 as expected for Cu^{II} ions. On lowering temperature it is evident a clear increase in χT value, which reaches a maximum of $2.05\ cm^3\,K\,mol^{-1}$ at 3 K and then decreases on further lowering temperature. The observed behaviour is indicative of the presence of moderate intramolecular ferromagnetic interactions, which are presumably transmitted by the O–P–O bridge. Indeed, the exchange coupling path through the perchlorate anion has to be discarded, as it involves d_{z^2} orbitals of the copper centers which in the elongated symmetry observed by X-ray structure are not expected to bear any significant electron density. The decrease of χT observed at low temperature might on the other hand be attributed to weak intermolecular interactions, presumably transmitted by the hydrogen bonds involving adjacent molecular units.

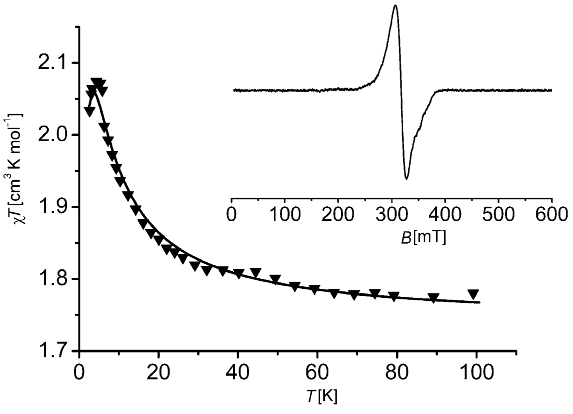

Figure 10. χT vs. T experimental data (full triangles) for **3** and best fit curve obtained by using parameters reported in the text. In the inset the X-band EPR spectrum recorded at 4 K is reported.

On these basis the χT vs. T data were fitted to Equation (1)

$$\chi = \frac{\chi_C}{1+\theta\chi_C} \tag{1}$$

with θ accounting for the intermolecular interactions and Equation (2)

$$\chi_c = \frac{Ng^2\beta^2}{k}\left(\frac{4}{3+\exp(J/kT)}\right) \tag{2}$$

where J is the exchange coupling constant of the Heisenberg–Dirac–van Vleck Hamiltonian, $\mathbf{H} = J(\mathbf{S_1S_2} + \mathbf{S_3S_4})$.[23]

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In this framework we considered the two crystallographically independent molecules to show the same exchange coupling interaction even if some subtle difference between corresponding J and g values might in principle exist as a consequence of small differences between their structures. The best-fit curve (R^2 = 0.987) was obtained with J = -5.2 ± 0.1 cm^{-1} (ferromagnetic) and θ = 0.13 K (antiferromagnetic), in agreement with the qualitative interpretation sketched above; the g value obtained from the graph is 2.15, in agreement with the value obtained by EPR data recorded at low temperature, g = 2.13 (see inset of Figure 10). Quite interestingly the latter spectrum exhibits a single quasi-isotropic g value, which arises as a consequence of the anisotropy averaging induced by exchange coupling between almost orthogonal copper centers.[24] It should be noted here that the mean-field correction implied by Equation (1) is a simple phenomenological one and the observed behaviour may in principle be caused by Zero Field Splitting effects of the resulting S = 1 ground state of each dinuclear unit. However, this would contrast with the quasi-isotropic EPR spectrum observed at low temperature, with no signature of a fine structure.

On the basis of a survey analysis of the literature the occurrence of ferromagnetic coupling between Cu^{II} centers through O–P–O bridge appears to be quite uncommon, the only structurally characterized examples so far being a couple of tetranuclear hydrogen phosphate-bridged cluster of Reedijk's[18] group. The observed ferromagnetic interaction can be attributed to the almost orthogonal arrangement of the two Cu^{II} centers. On these basis, the smaller magnitude of the interaction observed in **3** compared to what reported[25] might be tentatively attributed to a difference in the dihedral angles between the $d_{x^2-y^2}$ orbitals of the Cu^{II} centers, resulting in an increased antiferromagnetic contribution to the coupling constant.

Conclusions

We have analyzed the effect of a longer carbon chain connecting the two phosphinate moieties in the pc_np^{2-} (n = 1, 2) both in the free acids and in a series of Cu^{II}/2,2′-bipyridine derivatives. The structures of H_2pcp and H_2pc_2p show that these two closely related molecules form in the solid state quite different structural networks, both characterized by strong hydrogen bonds. The resulting network of H_2pcp molecules actually is a single ladder with the phenyl rings of each molecule located on the same side of the 1D chain whereas H_2pc_2p forms 2D network with a brick-wall conformation with the phenyl groups of each unit located on the opposite side of the slab.

The reactions of H_2pcp and H_2pc_2p, with copper(II) salts, in aqueous solution, in the presence of 2,2′-bipyridine, allows the isolation of different species. The complexes with the stoichiometric ratio Cu:bipy:diphosphinate = 1:1:1 are mononuclear or dinuclear in the cases of pcp^{2-} (**1**) and pc_2p^{2-} (**2**), respectively. In **1**, the pcp^{2-} anion coordinates as bidentate only one metal centre while in **2**, pc_2p^{2-} acts as tridentate ligand, bridging two metal centres. Noteworthy the conformation of the pcp^{2-}, with two phenyl rings on the same side of the P–C–P chain, as found in the solid H_2pcp, does not allow the further coordination of the second copper atom as it occurs for pc_2p^{2-} in complex **2**.

The complexes of stechiometry Cu/bipy/diphosphinate = 1:1:0.5 (**3** and **4**) consist of dinuclear units with the diphosphinate anions, bridging two metal centre as tetradentate ligands, and a perchlorate anion, connecting the two metal centre through one or two oxygen atoms in **3** and **4** respectively. Two different dinuclear units are present in **3** which are further connected by hydrogen bonds forming a monodimensional chain. The conformation of pcp^{2-} and pc_2p^{2-} in **3** and **4** is similar. Nevertheless, the longer aliphatic chain of pc_2p^{2-} allow the perchlorate to bridge the copper(II) metal with two oxygen atoms. As a consequence the two dimeric complexes presents an overall different structural arrangement.

The preferred coordination mode of pcp^{2-} is the one found in complex **1**, while for pc_2p^{2-} the conformation preference is determined by other factors as for instance the presence of the perchlorate anion in **4**.

Experimental Section

Materials and Methods: All reagents were commercial products of analytical-grade quality and were used without further purification. The *P,P′*-diphenylmethylenediphosphinic (H_2pcp) and *P,P′*-diphenylethylenediphosphinic (H_2pc_2p) acids were prepared as described previously;[26] suitable crystals of the two diphosphinic acids for X-ray diffraction were obtained by crystallization from ethanol.

Elemental analyses (C,H,N) were performed with an EA 1108 CHNS-O automatic analyzer. IR spectra were recorded on a Perkin–Elmer BX FT-IR spectrometer, in the 4000–400 cm^{-1} region (KBr pellets). Coupled thermogravimetry (TG) and differential thermal analysis (DTA) was performed with a Netzsch STA490C thermoanalyser under a 20 mL min^{-1} air flux with a heating rate of 5 °C min^{-1}.

Potentiometric Measurements: The experimental data used for the determination of equilibrium constants were obtained by means of potentiometric titrations as described previously,[27] at a temperature of 298 K and an ionic strength of 0.5 mol dm^{-3} in Me_4NCl. The electrode system was calibrated in terms of hydrogen ion concentration, [H^+], using the method of Gran[28] and the computer program GLEE.[29] The equilibrium constants were derived from the experimental data with the use of the computer program HYPERQUAD.[30] Two titrations were performed by adding 0.1 mol dm^{-3} solution of Me_4NOH to a solution of the diphosphinic acid containing an equivalent amount of HCl. The concentration of H_2pc_2p was limited by solubility to 1 mmol dm^{-3} or below.

When similar titrations were performed in the presence of $CuCl_2$, precipitation of insoluble species occurred almost immediately. It was therefore not possible to collect sufficient experimental data to determine formation constants of any complexes between Cu^{2+} and the diphosphinate.

Magnetic Measurements: Magnetic measurements were performed with a Cryogenic SQUID S600 magnetometer operating between 2 and 300 K. Raw data were corrected for diamagnetic contribution of the sample holder and the intrinsic diamagnetism of the sample estimated by Pascal's constants. EPR spectrum at variable temperature has been measured with a Bruker Elexsys E500 spectrometer equipped with a continuous-flow ^{4}He cryostat.

Synthesis of [(2,2′-bipy)Cu(μ-pc$_2$p)$_2$Cu(2,2′-bipy)] 4.5H$_2$O (2): H_2pc_2p (40 mg, 0.13 mmol) and 2,2′-bipy (20.3 mg, 0.13 mmol) were dissolved in boiling water (50 mL) and then a solution of copper(II) acetate monohydrate (26 mg, 0.13 mmol) in water (10 mL) was added. The resulting solution was concentrated to a volume of 20 mL, in air, at ca. 80 °C, then slow evaporation at room temperature allowed the precipitation of large blue crystals. These were filtered, washed with a small amount of cold water and dried in the air; yield 53 mg (87%). $C_{48}H_{53}Cu_2N_4O_{12.5}P_4$ (1136.90): calcd. C 50.70, H 4.70, N 4.92; found C 50.58, H 4.82, N 4.90. IR (KBr): $\tilde{\nu}$ = 3401 (s), 3109 (m), 3077 (m), 3058 (m), 1437 (w), 1629 (w), 1618 (w), 1607 (m), 1600 (m), 1574 (w), 1493 (w), 1472 (m), 1446 (s), 1437 (s), 1310 (w), 1286 (w), 1252 (w), 1198 (m), 1175 (s), 1158 (s), 1142 (s), 1099 (m), 1062 (s), 1041 (m), 1030 (s), 1020 (s), 777 (s), 768 (s), 727 (s), 718 (s), 701 (s), 661 (w), 636 (w), 567 (s), 514 (m), 496 (w), 438 (w), 415 (w) cm^{-1}.

Synthesis of [(2,2′-bipy)(H$_2$O)Cu(μ-pcp)(μ-ClO$_4$)Cu(2,2′-bipy)]-[ClO$_4$]·[(2,2′-bipy)(ClO$_4$)Cu (μ-pcp)(μ-ClO$_4$)Cu(2,2′-bipy)]·H$_2$O (3): H_2pcp (40 mg, 0.135 mmol) and 2,2′-bipy (42 mg, 0.27 mmol) were dissolved in boiling water (50 mL) and then a solution of copper(II) perchlorate hexahydrate (100 mg, 0.27 mmol) in water (10 mL) was added. The resulting solution was concentrated by evaporation in the air, at ca. 80 °C, until turquoise crystals precipitated. These were filtered, washed with water and dried in air, at room temperature; yield 86 mg (82%). $C_{66}H_{60}Cl_4Cu_4N_8O_{26}P_4$ (1901.06): calcd. C 41.70, H 3.18, N 5.89; found C 41.62, H 3.26, N 5.85. IR (KBr): $\tilde{\nu}$ = 3462 (m), 3115 (w), 3087 (w), 2921 (w), 2009 (w), 1611 (m), 1604 (m), 1576 (w), 1490 (w), 1472 (m), 1448 (s), 1437 (m), 1374 (w), 1313 (m), 1252 (m), 1164 (s), 1137 (s), 1098 (s), 1033 (s), 996 (m), 929 (w), 770 (s), 729 (s), 695 (m), 664 (w), 651 (w), 641 (w), 623 (s), 534 (m), 489 (w), 418 (w) cm^{-1}.

Synthesis of [(2,2′-bipy)Cu(μ-pc$_2$p)(μ-ClO$_4$)Cu(2,2′-bipy)(ClO$_4$)] (4): The reaction was carried out as in the above synthesis by using H_2pc_2p in the place of H_2pcp. Evaporation in air at ca. 80 °C allowed the precipitation of blue crystals of **4** together colourless crystals of H_2pc_2p. The mixture was filtered, washed with water and dried in the air. Further slow evaporation of the blue mother liquor, in the air, at room temperature, afforded dark blue crystals of the known complex [Cu(2,2′-bipy)$_2$(ClO$_4$)]·[ClO$_4$],[21] the structure of which was verified by X-ray diffraction analysis.

Pure complex **4** could be prepared by the following method: H_2pc_2p (30 mg, 0.097 mmol) and Cs(OH)·H$_2$O (32.5 mg, 0.194 mmol)[31] were dissolved in water (30 mL) at room temperature; 2,2′-bipy (30.2 mg, 0.194 mmol) was dissolved in this solution at 90 °C and then $Cu(ClO_4)_2·6H_2O$ (71.7 mg, 0.194 mmol) was added; concentration in air of the resulting solution, at room temperature, afforded blue crystals of **4** which were filtered, washed with cold water and dried in air; yield 66 mg (72%). $C_{34}H_{30}Cl_2Cu_2N_4O_{12}P_4$ (946.54): calcd. C 43.14, H 3.19, N 5.92; found C 43.03, H 3.26, N 5.88. IR (KBr): $\tilde{\nu}$ = 3115 (w), 3086 (w), 3058 (w), 2913 (w), 1981 (w), 1436 (w), 1612 (m), 1604 (m), 1575 (w), 1497 (w), 1473 (m), 1448 (s), 1438 (m), 1417 (w), 1313 (m), 1251 (m), 1171 (s), 1184 (s), 1132 (s), 1097 (s), 1076 (s), 1033 (s), 997 (m), 929 (w), 767 (m), 731 (s), 702 (m), 686 (w), 665 (w), 651 (w), 622 (s), 580 (s), 499 (w), 439 (w), 418 (w) cm^{-1}.

X-ray Structure Determinations: Data collections were performed on a Philips PW 1100 automatic diffractometer for H_2pc_2p, on a Nonius CAD4 automatic diffractometer for H_2pcp and **4** and for complexes **2** and **3** on an Oxford Diffraction Excalibur 3 diffractometer equipped with CCD area detector. All data collections were recorded at room temperature, with the exception of **2** for which the temperature was 150 K. Some crystal data and data collection details are given in Table 3. More details are reported in Tables S1, S3, S5, S7 and S9. Atomic scattering factors for neutral atoms are those reported by Cromer and Waber.[32] Both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[33] The structures were solved by direct methods and refined by full-matrix F^2 refinement, with anisotropic thermal parameters assigned to all non-hydrogen atoms except for the carbon atoms of the phenyl groups in the structure **3** and **4** in order to have a better ratio between the number of the parameters and the observed data. All the calculations were performed using the package WINGX[34] (SIR97,[35] SHELX97[36]). Molecular drawings

Table 3. Crystal data and structure refinement details for H_2pcp, H_2pc_2p, **2**, **3** and **4**.

	H_2pcp	H_2pc_2p	**2**	**3**	**4**
Empirical formula	$C_{13}H_{14}O_4P_2$	$C_{14}H_{16}O_4P_2$	$C_{48}H_{53}Cu_2N_4O_{12.50}P_4$	$C_{66}H_{60}Cl_4Cu_4N_8O_{26}P_4$	$C_{34}H_{30}Cl_2Cu_2N_4O_{12}P_2$
Formula weight	296.18	310.21	1136.90	1901.06	946.54
Temperature [K]	293(2)	293(2)	150(2)	293(2)	293(2)
Wavelength [Å]	0.71073	1.54180	1.54180	1.54180	0.71073
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/a$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
Unit cell dimensions					
a [Å]	5.839(9)	7.6330(10)	10.2860(16)	19.154(4)	8.630(4)
b [Å]	17.771(5)	10.6480(10)	12.403(3)	19.702(2)	14.686(8)
c [Å]	13.326(4)	8.950(17)	20.744(4)	22.014(4)	30.809(12)
α [°]	90	90	100.61(2)	90	90
β [°]	93.94(6)	91.91(8)	94.404(15)	113.07(2)	90
γ [°]	90	90	104.85(2)	90	90
V [Å^3]	1380(2)	727.0(14)	2492.9(9)	7643(2)	3905(3)
Z, calculated density [Mg/m^3]	4, 1.426	2, 1.417	2, 1.515	4, 1.652	4, 1.610
Absorption coefficient [mm^{-1}]	0.321	2.818	2.832	4.062	1.374
F(000)	616	324	1174	3856	1920
Reflections collected/unique	2412/2412	1160/1077	24631/9163	29336/8271	2898/2898
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0335	R_1 = 0.0416	R_1 = 0.0303	R_1 = 0.0550	R_1 = 0.0919
	wR_2 = 0.0776	wR_2 = 0.1059	wR_2 = 0.0795	wR_2 = 0.1591	wR_2 = 0.1638
R indices (all data)	R_1 = 0.0600	R_1 = 0.0591	R_1 = 0.0444	R_1 = 0.0781	R_1 = 0.2640
	wR_2 = 0.0859	wR_2 = 0.1120	wR_2 = 0.0852	wR_2 = 0.1788	wR_2 = 0.2039

were made using the ORTEP-III program for Windows[37] and with SCHAKAL97[38]

CCDC-677337 (for H_2pcp), -677334 (for H_2pc_2p), -677336 (for **2**), -646348 (for **3**) and -677335 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Packing diagrams of **1** and **4**. Crystal data, data collection details and selected bond lengths and angles are given in Tables S1–S10 for H_2pcp, H_2pc_2p, **2**, **3** and **4**. Table S11 reports the values of PCCP and O_bPPO_b angles for a series of pcp^{2-} and pc_2p^{2-} complexes.

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