



Two dinuclear pyrophosphate-bridged copper(II) complexes displaying unusually strong O–H–O interactions

Mireille Percec^{a,*}, Rosana P. Sartoris^b, Rafael Calvo^b, Ricardo Baggio^c

^a INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

^b Departamento de Física, Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral and INTEC (CONICET-UNL), Güemes 3450, 3000 Santa Fe, Argentina

^c Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Avda. Gral. Paz 1499, 1650 San Martín, Argentina

ARTICLE INFO

Article history:

Received 30 January 2012

Accepted 25 May 2012

Available online 1 June 2012

Keywords:

Crystal structure

Pyrophosphate-bridge

Binuclear copper(II) complex

H-bonds

π - π bonds

EPR

ABSTRACT

The crystal and molecular structures of two copper(II) dinuclear complexes bridged by the inorganic pyrophosphate tetraanion, namely, $[\text{Cu}(\text{bipy})(\text{cis-H}_2\text{P}_2\text{O}_7)]_2 \cdot 3\text{H}_2\text{O}$ **1** and $[\text{Cu}_2(\text{terpy})_2(\text{HP}_2\text{O}_7)] \cdot 2\text{H}_2\text{O}(\text{OH})$ **2**, are reported (bipy = 2,2'-pyridine; terpy = 2,2':6',2''-terpyridine). Both compounds are characterized by two very strong O–H–O interactions which play a fundamental role in their crystal structure building. Compound **1** is identical to the recently reported compound **1a** (Marino et al. *Inorg. Chem.* 50 (2011) 378–389), except for the supramolecular interaction which is revised in the present communication. Analysis of our data for **1** reveals the existence of a strong double well O–H–O' \leftrightarrow O'–(H–O) interaction around an inversion center (O–O: 2.433(2) Å), which binds dinuclear units together into [100] polymeric chains. Dinuclear compound **2** is monoclinic, halved by a twofold axis bisecting it through the central O atom of the bridge. The extreme disorder found in the solvates in **2** prevented an accurate description of the solvato content, and a detailed analysis of the H-bonding scheme. However, the extremely short O···O = 2.473(2) Å intermolecular distance points to a (quasi) symmetrical O–H–O interaction.

© 2012 Elsevier B.V. All rights reserved.

The study of Cu(II) pyrophosphate compounds is a subject of increasing interest because of its relevance in bioenergetics [1], and in materials science applications [2]. The susceptibility of the $\text{P}_2\text{O}_7^{4-}$ to hydrolysis generates additional multidentate ligand anions such as $\text{HP}_2\text{O}_7^{3-}$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$ and $\text{H}_3\text{P}_2\text{O}_7^-$ among others, difficulting the reproducible isolation of specific structures, even using similar ligands and conditions, owing to the many factors that can affect the structures of the final products. However the use of chelating ligands under precise control of the experimental conditions in the synthetic procedures allowed the isolation of a limited number of Cu(II) metallo-organic pyrophosphates and the investigation of their crystal structures, biological, magnetic and catalytic properties. Cu(II) mononuclear, dinuclear, tetranuclear and hexanuclear compounds with 2,2'-bipyridine, ethylenediammonium, 1,10-phenanthroline, 2-formyl-pyridine thiosemicarbazone, 2,2'-dipyridilamine and N,N'-biphenyl-pyridine have been reviewed [3]. More recently, three new Cu(II) pyrophosphate structures have been reported: a dinuclear with bipy, a tetranuclear with phen, and a 2D polymer with 1,10-phenanthroline-5-amine [4]. Also, we reported our results with the tridentate 2,2':6',2''-terpyridine ancillary ligand, and the characterization of the $[\text{Cu}(\text{H}_2\text{P}_2\text{O}_7)(\text{terpy})]_2 \cdot 4.5\text{H}_2\text{O}$ complex [5]. From the structural studies of the complexes it appeared that the H-bonding scheme is a crucial feature in determining the stability of

the dinuclear units, and also in the formation of the 3D supramolecular structure stabilized by a variety of H–bonds as well as $\pi \cdots \pi$ interactions.

Coinciding with publication [4] we were studying the structure of the dinuclear $[\text{Cu}(\text{bipy})(\text{cis-H}_2\text{P}_2\text{O}_7)]_2 \cdot 3\text{H}_2\text{O}$, hereafter **1**, Fig. 1a, (see preparation in Ref. [6]) which is basically identical to the compound reported by Marino et al. as **1a**, the first example of a Cu(II)-pyrophosphate with ferromagnetic intradinuclear exchange couplings [4]. In the present paper we discuss our structural results for **1** as compared to those reported for **1a**, in particular the role assigned to H-bonds in the building up of the supramolecular structure. In addition and based on the EPR spectrum of **1** we discuss the exchange coupling and the zero field splitting of the dinuclear units. We also present preliminary results of a new compound formulated as $[\text{Cu}_2(\text{terpy})_2(\text{HP}_2\text{O}_7)] \cdot 2\text{H}_2\text{O}(\text{OH})$, hereafter **2**, Fig. 1b, in which the solvate disorder prevents a detailed analysis of the crystal structure (see preparation in Ref. [7]). However, very short O···O distances have been found, allowing to assume the existence of strong H-bonds. The focus of this paper is to assess the role of strong H-bonding interactions on the intermolecular assembly, in the sense introduced by Gilli et al. [8]. Crystallographic data for **1a** and **1** and **2** are summarized in Table 1. A least squares fit of the refined models showed maximum deviations in the non-H positional parameters in the third decimal place, which are not distinguishable in an overlapping projection, thus allowing us to confirm that they correspond to the same structure. The small differences are attributable to thermal mismatch, 150(2) K for **1** and 98(2) K for **1a**.

* Corresponding author.

E-mail address: percec@q1.fcen.uba.ar (M. Percec).

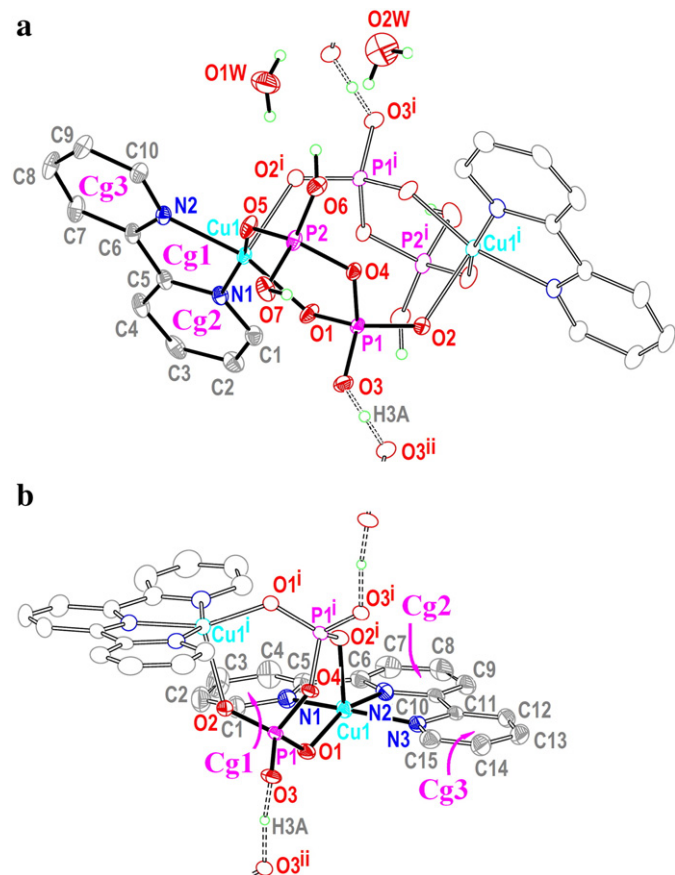


Fig. 1. Molecular views of dinuclear units **1** and **2**, in full 40% displacement ellipsoids. The symmetry independent parts shown in heavy bonds. The H-bond connecting dinuclear units into [100] chains suggested in double dashed lines. H atoms attached to carbon not shown, for clarity. (a) Structure **1**. Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$. (b) Structure **2**. Symmetry codes: (i) $-x+1/2, y, -z+1/2$, (ii) $-x+3/2, y, -z+1/2$.

Table 1

Crystal data for compounds **1a** (Ref. [4]), **1** and **2** (this work).

	1a C ₂₀ H ₂₀ Cu ₂ N ₄ O ₁₄ P ₄ ·3(H ₂ O)	1 Cu ₂ ·(C ₁₀ H ₈ N ₂) ₂ ·(H ₂ O ₇ P ₂) ₂ ·3(H ₂ O)	2 C ₁₅ H ₁₁ N ₃) ₂ Cu ₂ ·HO ₇ P ₂ ·2(H ₂ O)·(HO)
<i>M_r</i>	845.41	845.41	821.60
System, space group	Triclinic, <i>P</i> 1	Triclinic, <i>P</i> 1	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.4735 (8)	8.4836 (16)	7.1407 (2)
<i>b</i> /Å	9.7033 (9)	9.7152 (18)	13.9750 (5)
<i>c</i> /Å	9.8403 (9)	9.8740 (18)	19.0775 (5)
α /°	93.399 (2)	93.326 (4)	
β /°	110.835 (2)	110.790 (3)	94.368 (3)
γ /°	104.247 (2)	104.275 (3)	
<i>V</i> /Å ³	723.22 (12)	727.8 (2)	1898.24 (10)
<i>Z</i>	1	1	2
Radiation, λ /Å	Mo K, 0.71073	Mo K, 0.71073	Mo K, 0.71073
μ /mm ⁻¹	1.78	1.77	1.26
<i>T</i> /K	98	150	294
Crystal size/mm	0.15 × 0.10 × 0.06	0.26 × 0.20 × 0.16	0.28 × 0.18 × 0.14
Diffractometer	Bruker CCD area detector	Oxford Diffraction Gemini CCD S Ultra	Oxford Diffraction Gemini CCD S Ultra
Absorption correction	Multi-scan, <i>SADABS</i> ^a	Multi-scan, <i>CrysAlis PRO</i> ^b	Multi-scan, <i>CrysAlis PR</i> ^b
<i>T_{min}</i> , <i>T_{max}</i>	0.776, 0.901	0.98, 0.99	0.54, 0.73
Measured reflections	6795	6014	6942
Independent reflections	3295	3086	3743
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2994	2939	2504
Parameters	221	230	215
Restraints	2	3	0
<i>R_{int}</i>	0.017	0.011	0.037
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.032	0.027	0.036
<i>wR</i> (<i>F</i> ²)	0.087	0.075	0.109
<i>S</i>	1.06	1.07	0.92
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ /e Å ⁻³	0.0, -0.37	0.78, -0.38	0.30, -0.41
Crystallographic software	SHELXS97, SHELXL97 ^a	SHELXS97, SHELXL97 ^a	SHELXS97, SHELXL97 ^a

^a G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.

^b Oxford Diffraction (2009). CrysAlis PRO. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Compound **1** consists of centrosymmetric dinuclear units, with a Cu(II) cation, a protonated pyrophosphate anion and a bipy ligand in the asymmetric unit, defining a fivefold CuN₂O₃ polyhedron. A useful discriminator parameter in fivefold coordination (τ) has been introduced by Addison et al. [9], where $\tau = 0.00$ characterizes a SP and 1.00 a TB. Thus, Cu1 can be described as being in a definite SP environment, with a τ value of 0.00. One water molecule with full occupancy (O1W), and a second one (O2W) disordered around an inversion center as two nearly overlapping images, complete the three formulated water solvates per dinuclear unit (Fig. 1a). Details on the molecular geometry have been thoroughly analyzed [4], disagreement arises, however, when the hydrogen bonding network responsible for the 3D supramolecular structure is examined. It should be mentioned that at the time of publication of Ref. [4] the structure factors were not publicly available, therefore our data for compound **1** were used in the calculations. Analysis of the structure revealed a very short O···O contact ($d < 2.45$ Å) between two centrosymmetrically related pyrophosphate oxygens which resulted in significant differences in the interpretation of the crystal network organization of the compound. We adopted for **1** the same atom labeling scheme used for **1a**, but in order to facilitate the comparative analysis we moved the positions of the solvates in **1a** to match those in **1**.

Fig. 2a presents a schematic view of the explanation given for the protonation of the pyrophosphate anion **1a**, [4]. Fully occupied H's were included at O3 and O7, accounting for charge balance and giving rise to H-bonding interactions of the type O7–H7···O6ⁱⁱ (ii): $-x+1, -y+1, -z+2$, O···O: 2.575(3) Å, and O3–H3···O1W^{vi} (vi): $x-1, y, z$, O···O: 2.813(3) Å. Two further interoxygen interactions were reported, since H atoms in the solvates had not been found: O1W···O2W^{iv} = 2.360(6) Å, O6···O2W^{iv} = 2.482(6) Å, (iv): $-x+2, -y+1, -z+2$. However, the very short contact O3···O3ⁱⁱⁱ = 2.433(2) Å, (iii): $-x, -y+1, -z+1$, appears to our view overlooked by the authors [4].

Although examples of P–O···(O–P)ⁱ short contacts can be found in the CSD [10] (*i* = standing for an inversion, a two-fold rotation or a mirror plane), the usual rationale for their existence is the presence

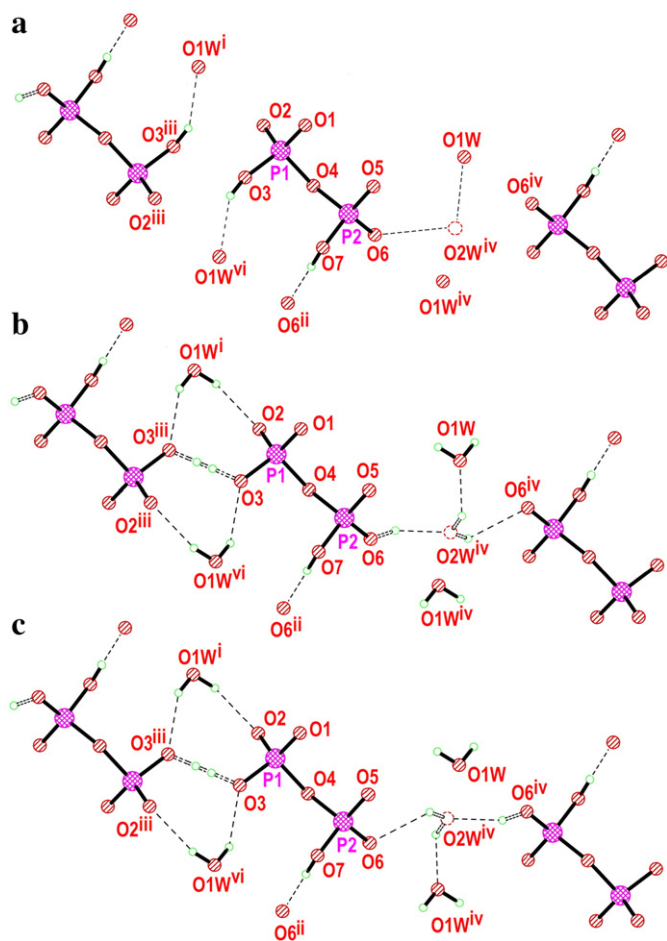


Fig. 2. Interaction schemes for structures **1a** (a) and **1** (b and c). H bonds in broken lines. Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x, -y+1, -z+1$; (iv) $-x+2, -y+1, -z+2$; (vi) $x-1, y, z$.

of a hydrogen atom, either (a) shared between the two symmetry related O moieties, or (b) disordered in two symmetry related halves at both sites of the symmetry element [11,12].

Fig. S1 (Supplementary material) shows a section of the difference electron density map of **1**, calculated through O3, O3ⁱⁱⁱ, O1Wⁱ, O1W^{vi} (with H3A, H1WA and H1WB removed from the calculation but included in the graph), with a high density central zone between O3, O3ⁱⁱⁱ with a clear double maxima, favoring (b), namely, a split disordered model for H3A. With this result the linkage we propose between the two oxygen atoms is confirmed. It also (though slightly blurred because being out of plane) shows the presence of two well defined H's in the fully occupied O1W solvate. But, with H3A placed on the center of symmetry, the pyrophosphate group would lack half a proton to achieve neutrality. A careful analysis of the difference map section through O2w, O6 and their (iv): $-x+2, -y+1, -z+2$ centrosymmetric counterparts (Fig S2, Supplementary material) shows peaks around O2W and O6 suggesting the hypothesis of a half occupied H6A atom attached to O6, conditioned by the presence of the centrosymmetric images of the O2W solvate. This interplay leads to two possible atomic distributions shown in Fig. 2b and c. The presence of H6A can only be compatible with one of the two disordered moieties of O2W, viz., the one with its H atoms pointing "outwards", hence introducing some order in the rather disordered structural arrangement. No evidence of this eventual "ordering" in the form of extra peaks could be observed in the x-ray diffraction patterns since it is a second order phenomenon involving only H atoms.

Table 2
Hydrogen-bond geometry (Å, °) for **1**.

D–H···A	D–H	H···A	D···A	D–H···A
O7–H7A···O6 ⁱⁱ	0.85 (1)	1.73 (1)	2.579 (2)	178 (3)
O3–H3A···O3 ⁱⁱⁱ	0.92	1.52	2.443 (3)	180
O2W–H2WA···O1W ^{iv}	0.85	1.73	2.359 (7)	129
O2W–H2WB···O6	0.85	2.29	2.958 (6)	136
O6–H6A···O2W ^{iv}	0.85	1.74	2.514 (6)	151
O1W–H1WA···O3 ^v	0.85 (1)	2.05 (2)	2.822 (3)	150 (4)
O1W–H1WB···O2 ⁱ	0.85 (1)	1.98 (1)	2.802 (3)	162 (4)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x, -y+1, -z+1$; (iv) $-x+2, -y+1, -z+2$; (v) $x+1, y, z$.

This problem did not arise in the model proposed in Ref. [4], but with the present analysis it is shown to be in error.

Table 2 presents the possible H-bonds, supporting the description of the structure in terms of H-bonded polymeric units running along [100] (as shown in Fig. 3a), where dinuclear units are solidly linked to each other by three strong H-bonds, viz., those mediated by the bridging O1W, (entries 6 and 7 at Table 2), and the one involving the disordered O3–H3A group, (entry 2 of the same table).

These [100] chains, in turn, interact with each other along [001] via an H-bond involving O7–H7 (first entry in Table 2), and along the [010] direction through the π - π interactions shown in Fig. 3b (Cg1...Cg2ⁱ, intercentroid distance: 3.5244(15) Å, $i = 1-x, 2-y, 1-z$).

Compound **2** is a new copper pyrophosphate complex of estimated formula Cu₂(terpy)₂(HP₂O₇)(OH)·2H₂O (see refinement section for details) obtained from a mixture of Cu₂P₂O₇ with terpy in a 1:1 water alcohol solution [5]. The compound is also dinuclear and centrosymmetric (Fig. 1b), but now halved by a twofold axis bisecting

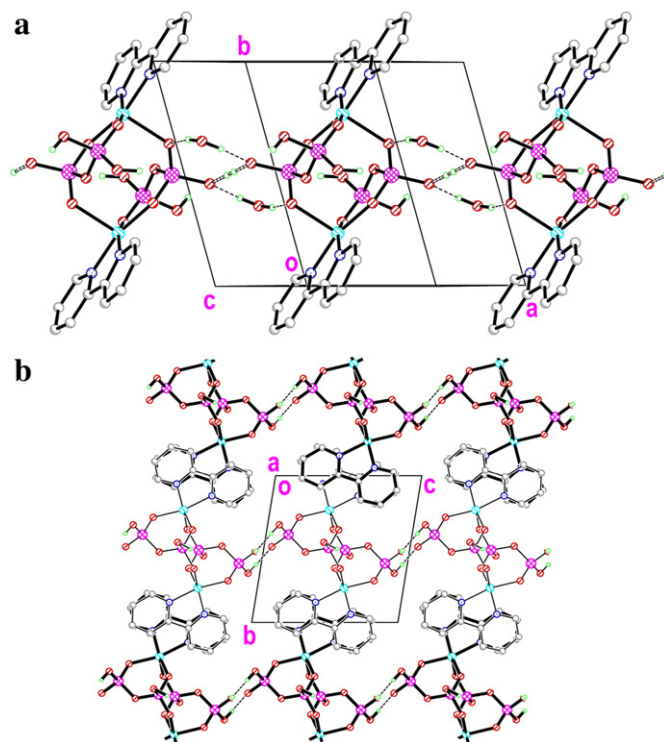


Fig. 3. Packing views for **1**. (a) Projection perpendicular to (001) showing the [100] chain, and in broken lines the H-bonds. (b) Projection down [100] showing chains coming upwards and the two types of lateral interactions: H-bonds linking chains horizontally, and π - π bonds connecting them vertically.

Table 3
Hydrogen-bond geometry (Å, °) for **2**.

D–H···A	D–H	H···A	D···A	D–H···A
O3–H3A···O3 ⁱⁱ	1.26 (1)	1.26 (1)	2.482 (3)	162 (4)
C1–H1···O2	0.93	2.43	3.262 (5)	149
C9–H9···O3 ⁱⁱⁱ	0.93	2.43	3.184 (4)	138
C12–H12···O2 ⁱⁱⁱ	0.93	2.56	3.426 (4)	155

Symmetry codes: (ii) $-x + 3/2, y, -z + 1/2$; (iii) $x - 1/2, -y, z + 1/2$.

the group through the central O atom of the $\text{HP}_2\text{O}_7^{3-}$ unit, chelating two copper(II) cations at both sides of an inversion center (Cu–Cu': 4.8475(6) Å). Two external terpy's complete the metal coordination via their triple N,N',N'' bite.

The copper cation is fivefold coordinated as in **1**, but within a CuN_3O_2 environment (the N's coming from terpy and O's from one single $\text{HP}_2\text{O}_7^{3-}$ anion). The environment around the cation can also be described as an almost perfect SP, with $\tau = 0.01$. A very short $\text{O3}\cdots\text{O3}^{\text{ii}}$, (ii): $-x + 3/2, y, -z + 1/2$) contact exists in the structure (d: 2.482(3) Å), much resembling the former compound. In the present structure, however, we can only claim an indirect evidence supporting the existence of an H atom linking the two symmetry related O's, in the form of a slightly positive region in the electron density map, along the two-fold axis relating both oxygens. Due to the generalized disorder we shouldn't expect to find a differentiated peak in the map attributable to H (see experimental section for details). However, when refining its position on the twofold axis, midway both O's, the free coordinate along the axis is displaced slightly, ending up in a O–H–O angle of 162 (4)°. Table 3 gives the complete information on the relevant H-bonds for this structure. With this information, the dinuclear unit in **2** can be formulated as a cationic $[\text{Cu}_2(\text{terpy})_2\text{HP}_2\text{O}_7]^+$ group, assuming that charge balance is achieved through the presence of an OH^- anion in the cloud of solvents. Fig. 4a shows the chains along [100]; linked by this "hidden" H-bond.

The protruding terpy groups in contiguous chains, in turn, interdigitate giving raise to π - π interactions linking chains into undulated 2D structures parallel to (010), at $y \sim 0.00, 1.00$ (Fig. 4b). The empty zone between layers, in the form of planar voids at $y \sim 0.5$, corresponds to the disordered solvate zone, excluded from the model, with its effects taken account for by means of the SQUEEZE algorithm implemented in PLATON [13].

Information about the spin-spin couplings in compounds **1** and **2** was obtained from electron paramagnetic resonance (EPR) spectra of powder samples observed at 9.875 GHz and room temperature with a Bruker EMX Plus spectrometer, Fig. 5. The observed spectra do not display fine or hyperfine structure and are well fitted with a spin Hamiltonian for 1/2 spins using Easyspin [14] to obtain the axially symmetric g -matrices with principal values given in the figure. The absence of fine structure indicates that the zero-field splitting parameter is $D \sim 0$ for both compounds, which we ascribe to the long distances between Cu^{II} ions in the dinuclear units **1** and **2**. This result is different from the value $|D| = 0.65 \text{ cm}^{-1}$ obtained by Marino et al. from magnetic susceptibility measurements in compound **1a**. Such a large value of D would produce line splittings of several hundred mT, thus confirming that EPR is the most appropriate technique to evaluate D . Meanwhile, we do not obtain information on the exchange coupling J within dinuclear units. The hyperfine couplings of the Cu^{II} ions are probably averaged out by the small couplings between dinuclear units. The different g -matrices for **1** and **2** should be related to differences in the local coordinations of Cu^{II} , and for further search in this direction, we are planning EPR measurements in single crystal samples.

From our structural analysis, we conclude that O···O distances shorter than 2.45 Å in coordination complexes should be taken as an indication of strong hydrogen bonding. The association of H-bonds, in occasions comparable in strength to covalent interactions, may play a

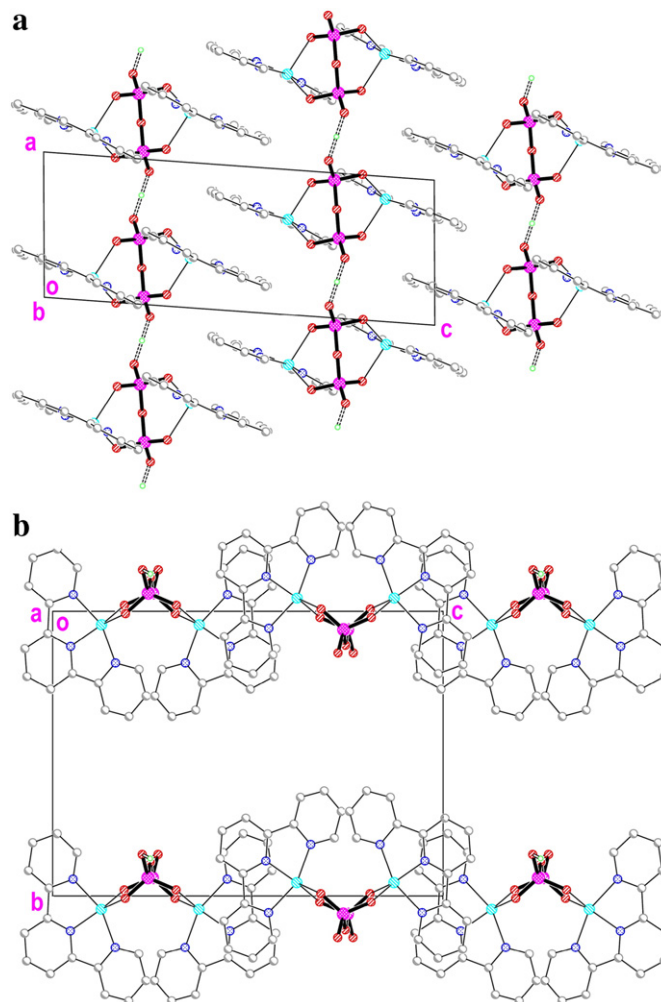


Fig. 4. Packing views for **2**. (a) A projection down [010], with the H-bonded [100] chains running vertically along [100], and showing the lateral 1:1 interdigitation. (b) A projection down [100] (at 90° from the latter orientation) showing the undulated planes formed. The empty space between planes is occupied by the disordered solvates/counterions, disregarded from the model.

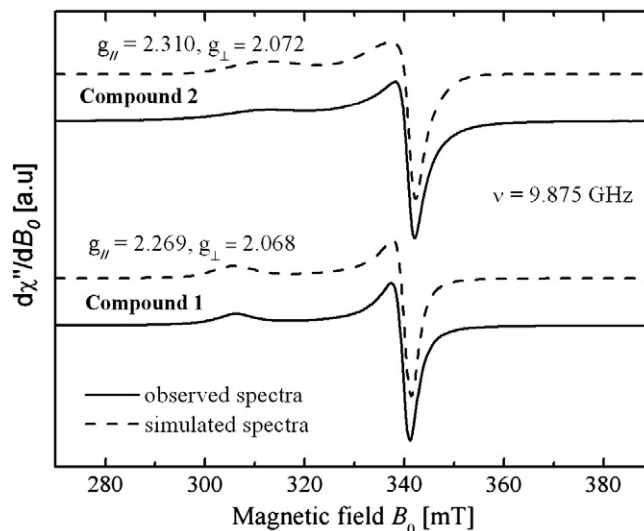


Fig. 5. EPR spectra of powder samples of **1** and **2**, experimental and simulated. The g -matrices obtained from a fit of an $S = 1/2$ spin Hamiltonian, have axial symmetry and are included in the Figure.

significant role in determining the supramolecular assembly, and thus influence many of their physical chemical properties.

Acknowledgments

The authors acknowledge ANPCyT (project PME 2006-01113) for the purchase of the Oxford Gemini CCD diffractometer and the Spanish Research Council (CSIC) for provision of a free-of-charge license to the Cambridge Structural Database [10]. We acknowledge partial support from CAI + D (UNL) and PIP (CONICET) 112-200801-02533. MP and RC are members of CONICET.

Appendix A. Supplementary material

CCDC for **1** 864787 and 864788 for **2** 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. Supplementary data containing special sections of the difference electron density map in **1** (Fig. S1) and in **2** (Fig. S2) can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2012.05.045>.

Appendix B. Supplementary material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2012.05.045>.

References

- [1] I.S. Kulaev, V. Vagabov, T. Kulakovskaya, *The Biochemistry of Inorganic Polyphosphates*, second ed. John Wiley and Sons, NY, 2004.
- [2] T. Kasuga, M. Terrada, M. Nogami, M. Niinomi, *J. Mat. Res* 16 (2001) 876–880.
- [3] O.F. Ikotun, N. Marino, P.E. Kruger, M. Julve, R.P. Doyle, *Coord. Chem. Rev.* 254 (2010) 890–915.
- [4] N. Marino, O.F. Ikotun, M. Julve, F. Lloret, J. Cano, R.P. Doyle, *Inorg. Chem.* 50 (2011) 378–389.
- [5] M. Perec, R. Baggio, *Acta Cryst. C67* (2011) m140–m144.
- [6] Preparation of **1**. Copper (II) nitrate hemipentahydrate (0.25 g, 1 mmol) and 2, 2'-bipyridine (0.15 g, 1 mmol) were added to 40 mL of water and heated under stirring until complete dissolution. Sodium pyrophosphate (0.30 g, 1 mmol) dissolved in 10 mL of water was slowly added and the solution maintained at pH ~3. After filtering, the solution was left to evaporate at 38 °C over several hours, and pale blue crystals of **1** suitable for X-ray diffraction were isolate.
- [7] Preparation of **2**. Copper pyrophosphate (0.25 g, 1 mmol) and terpy (0.25 g, 1 mmol) was added to an alcohol–water (100 ml, 1:1, v:v) solution and the resulting suspension stirred for one week at room temperature. Perchloric acid was added to keep the pH around 1.5. The suspension was filtered and the filtrate left standing for a month, and light green crystals of **2** of poor quality but suitable for X-ray diffraction were obtained as the unique product.
- [8] (a) P. Gilli, V. Bertolasi, V. Ferretti, G.J. Gilli, *J. Am. Chem. Soc.* 116 (1994) 909–915;
(b) P. Gilli, G. Gilli, *J. Mol. Struct.* 972 (2010) 2–10.
- [9] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc. Dalton Trans.* (1984) 1349–1356.
- [10] F.H. Allen, *Acta Cryst. B58* (2002) 380–388.
- [11] Y. Wang, P. Chen, J. Li, J. Yu, J. Xu, Q. Pan, R. Xu, *Inorg. Chem.* 45 (2006) 4764–4768.
- [12] I. Němec, Z. Macháčková, K. Teubner, I. Čiřařova, P. Vaněk, Z. Mička, *J. Solid State Chem.* 177 (2004) 4655–4664.
- [13] A.L. Spek, *J. Appl. Cryst.* 36 (2003) 7–13.
- [14] S. Stoll, A. Schweiger, *J. Magn. Reson.* 178 (2006) 42–55.