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

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ABSTRACT

The crystal and molecular structures of two copper(II) dinuclear complexes bridged by the inorganic pyrophosphate tetraanion, namely, $[Cu(bipy)(cis-H_2P_2O_7)]_2 \cdot 3H_2O$ **1** and $[Cu_2(terpy)_2(HP_2O_7)] \cdot 2H_2O(OH)$ **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′ ↔ 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.

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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 $P_2O_7^{4-}$ to hydrolysis generates additional multidentate ligand anions such as $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$ and $H_3P_2O_7^{-}$ 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 $[Cu(H_2P_2O_7)(terpy)]_2 \cdot 4.5H_2O$ 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 π···π interactions.

Coinciding with publication [4] we were studying the structure of the dinuclear $[Cu(bipy)(cis-H_2P_2O_7)]_2 \cdot 3H_2O$, 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 $[Cu_2(terpy)_2(HP_2O_7)] \cdot 2H_2O(OH)$, 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**.

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a

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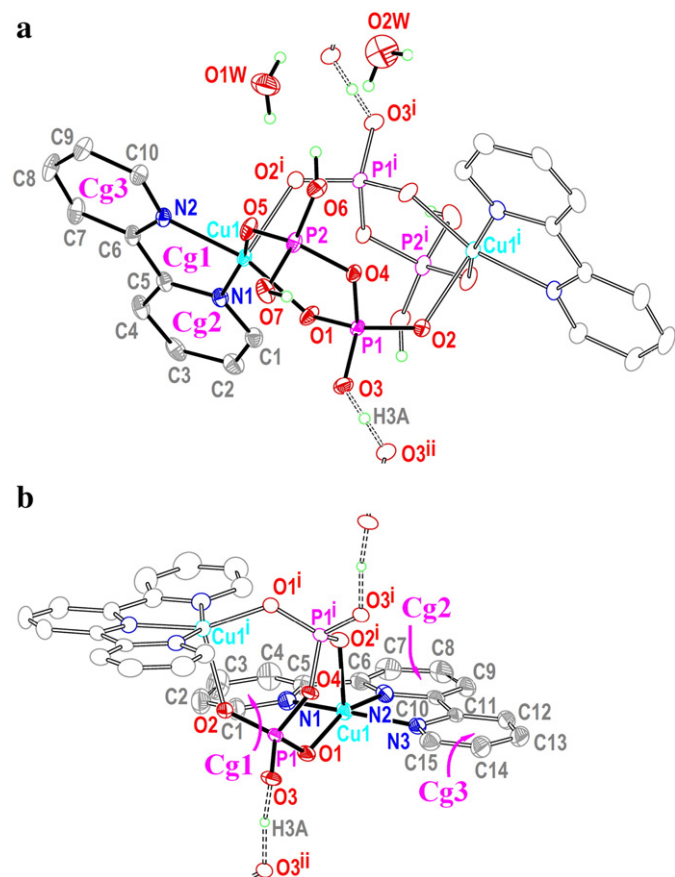
Fig. 1. Molecular views of dinuclear units **1** and **2**, in full 40% displacement ellipsoids. The symmetry independent parts shown in heavy bonds. The H-bond connecting dinuclear units into [100] chains suggested in double dashed lines. H atoms attached to carbon not shown, for clarity. (a) Structure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

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 CuN_2O_3 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 $O\cdots O$ 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 $O7-H7\cdots O6^{ii}$ (ii): $-x+1$, $-y+1$, $-z+2$, $O\cdots O$: 2.575(3) Å, and $O3-H3\cdots O1W^{vi}$ (vi): $x-1$, y, z, $O\cdots\cdots O$: 2.813(3) Å. Two further interoxygen interactions were reported, since H atoms in the solvates had not been found: $O1W\cdots O2W^{iv} = 2.360(6)$ Å, $O6\cdots O2W^{iv} = 2.482(6)$ Å, (iv): $-x+2$, $-y+1$, $-z+2$. However, the very short contact $O3\cdots O3^{iii} = 2.433(2)$ Å, (iii): $-x$, $-y+1$, $-z+1$, appears to our view overlooked by the authors [4].

Although examples of $P-O\cdots(O-P)^i$ 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

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

	1a $C_{20}H_{20}Cu_2N_4O_{14}P_4\cdot3(H_2O)$	**1** $Cu_2\cdot(C_{10}H_8N_2)_2\cdot(H_2O_7P_2)_2.3(H_2O)$	**2** $C_{15}H_{11}N_3)_2Cu_2\cdot HO_7P_2\cdot2(H_2O)\cdot(HO)$
M_r	845.41	845.41	821.60
System, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2/n$
a/Å	8.4735 (8)	8.4836 (16)	7.1407 (2)
b/Å	9.7033 (9)	9.7152 (18)	13.9750 (5)
c/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)	
V/Å^3	723.22 (12)	727.8 (2)	1898.24 (10)
Z	1	1	2
Rradiation, λ/Å	Mo K, 0.71073	Mo K, 0.71073	Mo K, 0.71073
μ/mm^{-1}	1.78	1.77	1.26
T/K	98	150	294
Crystal size/mm	$0.15\times0.10\times0.06$	$0.26\times0.20\times0.16$	$0.28\times0.18\times0.14$
Diffractometer	Bruker CCD area detector	Oxford Diffraction Gemini CCD S Ultra	Oxford Diffraction Gemini CCD S Ultra
Absorption correction	Multi-scan, *SADABS* [a]	Multi-scan, *CrysAlis PRO* [b]	Multi-scan, *CrysAlis PR* [b]
T_{min}, T_{max}	0.776, 0.901	0.98, 0.99	0.54, 0.73
Measured reflections	6795	6014	6942
Independent reflections	3295	3086	3743
Reflections with $I > 2\sigma(I)$	2994	2939	2504
Parameters	221	230	215
Restraints	2	3	0
R_{int}	0.017	0.011	0.037
$R[F^2 > 2\sigma(F^2)]$	0.032	0.027	0.036
$wR(F^2)$	0.087	0.075	0.109
S	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.