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Magnetic Coupling between Copper(II) Ions Mediated by Hydrogen-Bonded (Neutral) Water Molecules

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A new hydrogen-bonded dinuclear copper(II) coordination compound has been synthesized from the Schiff-base ligand 6-(pyridine-2-ylhydrazonomethyl)phenol (**Hphp**). The molecular structure of $[Cu_2(\mathbf{php})_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ (**1**), determined by single-crystal X-ray diffraction, reveals the presence of two copper(II) centers held together by means of two strong hydrogen bonds, with O···O contacts of only 2.60−2.68 Å. Temperature-dependent magnetic susceptibility measurements down to 3 K show that the two metal ions are antiferromagnetically coupled ($J = -19.8(2)$ cm^{-1}). This exchange is most likely through two hydrogen-bonding pathways, where a coordinated water on the first Cu, donates a H bond to the O atoms of the coordinated **php** at the other Cu. This strong O···H (water) bonding interaction has been clearly evidenced by theoretical calculations. In the relatively few related cases from the literature, this exchange path, mediated by a (neutral) coordinated water molecule, was not recognized.

Introduction

Transition-metal coordination compounds in which the metallic centers are bridged by organic ligands are of great interest because of their potentially interesting magnetic properties.[1−10] Usually, the magnetic exchanges between the metal ions are realized through coordination bonds provided by at least dinucleating ligands.[11−19] Exchange interactions through a priori weak supramolecular interactions,[20,21] such as hydrogen-bond bridges

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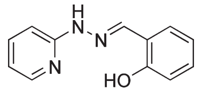
Scheme 1. Ligand 6-(Pyridine-2-ylhydrazonomethyl)phenol (**Hphp**)[28]



linking metal centers, have only been scarcely investigated.[22−27]

Recently, during investigations aimed at preparing polynuclear metal complexes with attractive magnetic properties, the potential tridentate ligand 6-(pyridine-2-ylhydrazonomethyl)phenol (**Hphp**, Scheme 1) has been used with copper (II) chloride to generate a chloride-bridged one-dimensional (1D) coordination polymer, which does not show any significant copper−copper magnetic interactions.[28] The reaction of **Hphp** with copper(II) perchlorate, using the experimental conditions described earlier with $CuCl_2$,[28] results in the formation of the hydrogen-bonded dinuclear compound $[Cu_2(\mathbf{php})_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ (**1**). Interestingly, the doubly $[Cu{-}O_{PhO}\cdots H{-}(O_{water}){-}Cu]$-bridged Cu···Cu unit exhibits significant antiferromagnetic interactions, which most likely must occur through these hydrogen bonds.

In the present article, the synthesis and single-crystal X-ray structure of **1** is reported together with its magnetic properties. Structural features and the magnetic interactions are compared with those of the few related examples found in the literature. The formation energy and stability of the hydrogen-bonded dinuclear species **1** have also been theoretically investigated using MP2/6-31+G(d,p) calculations combined with an AIM analysis.

Experimental Section

Materials. All chemicals purchased were reagent grade and used without further purification. Elemental analyses for C, H, and N were performed with a Perkin-Elmer 2400 analyzer. Fourier transform infrared (FTIR) spectra were recorded with a Perkin-Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000−300 cm^{-1}). The ligand 6-(pyridine-2-ylhydrazonomethyl)phenol (**Hphp**) was synthesized according to a procedure described earlier.[28,29] Variable−temperature magnetic susceptibilities were measured on a Quantum Design MPMS−XL−5 SQUID magnetometer (using a magnetic field of 0.1 T and applying a heating and cooling rate of ± 1 K min^{-1}; the magnetization was measured every 3 K). Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[30]

$[Cu_2(php)_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ (1). Compound **1** was synthesized from $Cu(ClO_4)_2 \cdot 6H_2O$ (0.50 mmol, 185 mg) and **Hphp** (0.25 mmol, 53 mg) in methanol (15 mL). The resulting dark-green solution was left unperturbed to allow the slow evaporation of the solvent. Dark-green single crystals, suitable for X-ray diffraction analysis, were formed after several days. Yield: 61 mg, (61%, based on the ligand **Hphp**). Elemental analysis (%) calcd for $C_{24}H_{26}Cl_2Cu_2N_6O_{13}$: C 35.83, H 3.26, N 10.45; found: C 35.82, H 3.27, N 10.48. IR data for **1**: ν = 3229 (w), 1622 (vs), 1573 (s), 1531 (s), 1471 (s), 1427 (s), 1370 (w), 1331 (w), 1288 (s), 1206 (s), 1039 (vs), 927 (s), 761 (vs), 619 (vs), 565 (w), 477 (w), 415 (w), 323 (s) cm^{-1}.

Table 1. Selected Bond Distances (Angstroms) and Angles (Degrees) for $[Cu_2(\mathbf{php})_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ (**1**)

Cu1A−O1A	1.909(2)	Cu1B−O1B	1.888(2)
Cu1A−O2A	1.967(1)	Cu1B−O2B	1.956(1)
Cu1A−O12	2.444(2)	*Cu1B···O13*	*2.999(2)*
Cu1A−N1A	1.943(2)	Cu1B−N1B	1.942(2)
Cu1A−N3A	1.977(2)	Cu1B−N3B	1.975(2)
O1A−Cu1A−O2A	91.55(6)	O1B−Cu1B−O2B	92.90(6)
O2A−Cu1A−N3A	94.03(6)	O2B−Cu1B−N3B	94.05(7)
N3A−Cu1A−N1A	81.82(7)	N3B−Cu1B−N1B	81.95(8)
N1A−Cu1A−O1A	91.91(7)	N1B−Cu1B−O1B	92.50(7)
Hydrogen Bonds			
O2A−H22A···O1B	2.685(2)	O2A−H21A···O3	2.696(3)
O2B−H22B···O1A	2.601(2)	O2B−H22A···O21	2.877(4)
N2A−H2A···O23	2.913(3)	N2B−H2B···O14	2.996(3)

Structural Determination. X-ray crystallographic data for $[Cu_2(php)_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ were collected with a Nonius Kappa CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at room temperature. The data were processed by using DENZO.[31] The structures were solved by direct methods using SIR97[32] and refined by a full-matrix least-squares procedure based on *F* with XTAL3.6.[33] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms parameters were not refined. Their positions were obtained from difference Fourier map. Selected bond lengths (Å) and angles (deg) are listed in Table 1. Details of the crystal data, data collection and refinement parameters are summarized in Table 2.

Computational Details. All calculations were carried out using the Gaussian03 suite of programs.[34] First, structural optimization was performed in vacuo at the MP2/6-31+G(d,p) level to assess the structural stability of the complex: despite a slight rearrangement, the hydrogen bonding is mostly preserved and the metal−metal distance is hardly altered (see Supporting Information). Second, single-point calculations

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Table 2. Crystal Data and Structure Refinement for Compound **1**

	$[Cu_2(\mathbf{php})_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$
empirical formula	$C_{24}H_{26}Cl_2N_6O_{13}Cu_2$
formula weight	804.5
temperature, K	293
wavelength, Å	0.71073
crystal system	triclinic
space group	$P\bar{1}$
a, Å	8.1867(2)
b, Å	11.3618(2)
c, Å	17.3567(4)
α, deg	104.624(1)
β, deg	100.981(1)
γ, deg	93.776(1)
volume, $Å^3$	1522.47(6)
Z	2
density (calculated), mg m^{-3}	1.755
aborption coefficient, mm^{-1}	1.648
$F(000)$	816
θ range for data collection, °	2.55 to 27.48
limiting indices	h: −10 to 10 k: −14 to 13 l: −22 to 22
reflections collected	28805
unique reflections (R_{int})	6890 (0.051)
observed reflections [$I > 2\sigma(I)$]	5497
data/restraints/parameters	6397/0/424
goodness-of-fit on F^2	1.285
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.044$ $wR_2 = 0.034$
largest different peak and hole, e $Å^{-3}$	0.647, −0.903

at the MP2/6-31+G(d,p) level were carried out directly on the experimental structure to estimate the formation energy of compound **1**. The basis set superposition error (BSSE) was corrected using the Boys and Bernardi's counterpoise method.[35]

To quantify the intermolecular interactions that may contribute to the stabilization of **1**, the electron density was analyzed using Bader's theory[36,37] of Atoms-In-Molecules (AIM) directly on experimental structure, as reported earlier.[38−40] In the present study, attention has been focused on the topological analysis of the density (ρ), by finding minima, maxima, and saddle points of ρ. The properties at such critical points (CPs), especially at (3, −1) or bond CPs (BCP), have found extensive use in characterizing bonding interactions. Notably, it has been shown that a metal−metal interaction is characterized by a bond critical point (BCP) with low electron density and a positive Laplacian.[41] More generally, the electron density evaluated at the BCPs correlates with the strength of covalent bonds, hydrogen bonding, and π-stacking interactions.[36−38,40,42,43]

Results and Discussion

Structural Description. The reaction of copper(II) perchlorate with 6-(pyridine-2-ylhydrazonomethyl)phenol (**Hphp**) in methanol produces the hydrogen-bonded dinuclear compound $[Cu_2(php)_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ (**1**), whose molecular structure determined by single-crystal X-ray diffraction is depicted in Figure 1. **1** crystallizes in the triclinic $P\bar{1}$ space group. Selected bond lengths and angles are given in Table 1, and crystal parameters are shown in Table 2. **1** consists of two different copper(II) centers that are doubly bridged through hydrogen bonds between coordinated water molecules and phenoxido ligands with twice the pathway: $[Cu-O_{PhO}\cdots H-(O_{water})-Cu]$ (Figure 1). Cu1A is in an almost perfect square-pyramidal coordination environment ($\tau_5 = 0.04$).[44] Cu1A is coordinated to two N atoms and one O atom from a deprotonated **php** unit which acts as a chelating, planar ligand. The plane of the square pyramid is completed by a water molecule. The Cu−N, $Cu-O_{PhO}$, and $Cu-O_{water}$ bond distances (Table 1) are in the range of those found for related coordination compounds.[45,46] The axial position of the square pyramid is occupied by a perchlorato ligand at a normal apical distance of 2.442(2) Å.[47] The basal angles, varying from 81.82(7) to 94.03(6)°, are indicative of a minor distortion of the square plane, most likely because of the bite angle of the pyridine/hydrazino chelating unit of the ligand **php** (the angle N3A−Cu1A−N1A is 81.82(7)°). The copper atom Cu1B exhibits a slightly distorted square-planar geometry ($\tau_4 = 0.16$).[48] However, it has to be mentioned that the perchlorate oxygen atom O13 is weakly interacting with Cu1B (Cu1B···O13 = 2.999(2) Å). The distortion of the square plane arises from the bite angle of the pyridine/hydrazino chelating donor group (N3B−Cu1B−N1B = 81.95(8)° and from the fact that the coordinated water molecule O2B is hydrogen bonded to an adjacent Cu unit. The Cu−N, $Cu-O_{PhO}$ (from the planar tridentate **php** ligand), and $Cu-O_{water}$ bond lengths (Table 1) can be considered as normal.[49,50]

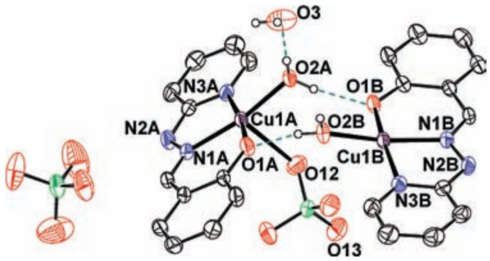

Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) representation at the 30% probability level of $[Cu_2(\mathbf{php})_2(H_2O)_2(ClO_4)](ClO_4)(H_2O)$ (**1**) whose crystal structure was determined at 293 K. Only the water hydrogen atoms are shown for clarity. The blue dashed lines illustrate hydrogen-bonding interactions.

As mentioned above, two copper coordination entities are hydrogen bonded to form a dinuclear species. The corresponding hydrogen bonds O2A−H22A···O1B = 2.685(2) Å (angle O2A−H22A−O1B = 165°) and O2B−H22B···O1A = 2.601(2) Å (angle O2A−H22A−O1B = 168°)

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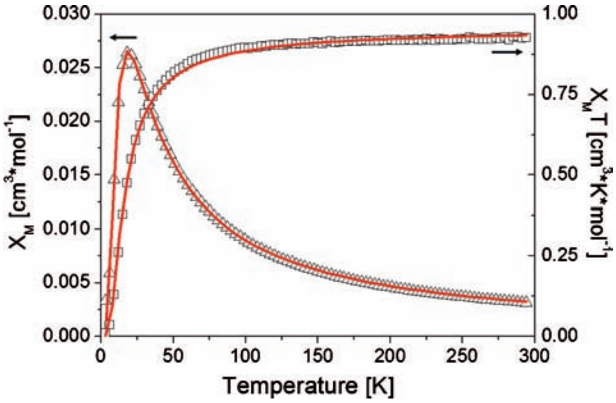
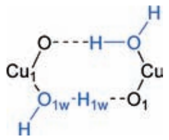


Figure 2. $\chi_M T$ vs T (□) and χ_M vs T (△) plots per mol of compound **1**. The red solid lines are fits to the experimental data (see text).

Scheme 2. Schematic Representation of the Doubly [O···H(water)]-Bridged Cu···Cu Unit



can be regarded as moderate to strong,[51] and apparently are responsible for the magnetic exchange interactions between the two copper(II) ions (see below). In addition, the coordinated water molecules O2A and O2B are hydrogen bonded to a lattice water molecule (O2A−H21A···O3 = 2.696(3) Å) and lattice perchlorate anion (O2B−H21B···O21 = 2.877(4) Å), respectively. The coordinated perchlorate accepts a hydrogen bond from a nearby N2A−H2A ligand group; N2A···O23 = 2.913(3) Å. Finally the lattice perchlorate is hydrogen bonded to the N2B−H2B group (N2B···O14 = 2.996(3) Å) of a neighboring **php** ligand. This hydrogen-bonding network gives rise to an intricate 3D framework as is evidenced in Supporting Information, Figure S1.

Magnetic Properties. The $\chi_M T$ and χ_M versus T plots for a crystalline sample of the dinuclear copper compound **1**, recorded under a constant magnetic field of 0.1 T in the temperature range 3−300 K, are shown in Figure 2 (χ_M being the molar magnetic susceptibility per Cu(II)Cu(II) pair). By decreasing the temperature, χ_M increases and reaches a maximum around 18 K and then smoothly decreases to reach a value close to zero (at very low temperature). At room temperature, the $\chi_M T$ product is 0.9 $cm^3 \cdot K \cdot mol^{-1}$, which is in fair agreement with the expected value for two uncoupled Cu(II) ions, with $S = 1/2$ and $g = 2$. When the sample is cooled, the $\chi_M T$ value decreases to reach a $S_T = 0$ value below 5 K, which is consistent with antiferromagnetic interactions between the Cu(II) centers (which are separated by a distance of 4.8896(3) Å). Thus, from a magnetic point of view, these results suggest that the single-crystal X-ray structure of **1** should be considered as an assembly of quasi-isolated dinuclear copper(II) species, where the metal centers interact through hydrogen bonds (Scheme 2). To estimate the magnitude of the antiferromagnetic coupling, the magnetic susceptibility data were fitted to the Bleaney−Bowers[52] equation (eq 1) for two interacting copper(II) ions using the Hamiltonian $H = -J\, S_1 \cdot S_2$.

$$\chi_M = 2Ng^2\beta^2[kT(3 + \exp(-J/kT))]^{-1} \tag{1}$$

The least-squares fitting of the data applying the eq 1 leads to $J = -19.8(2)$ cm^{-1}, $g = 2.25(1)$, TIP = 60×10^{-6} $cm^3 \cdot mol^{-1}$ per Cu^{II} and $R = 7 \cdot 10^{-5}$ ($R = \sum_i(\chi_{calcd} - \chi_{obs})^2/\sum_i(\chi_{obs})^2$). The solid line in Figure 2 corresponds to the theoretical curve obtained using the above parameters.

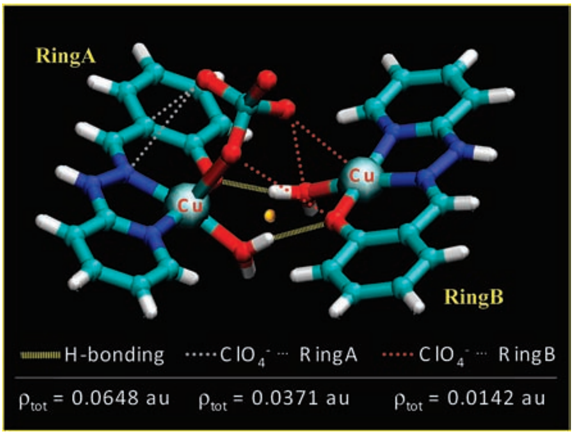


Figure 3. Schematic view of AIM topology calculated at MP2/6-31+G(d,p), showing intermolecular interactions and ring critical point (yellow ball) in compound **1**, as well as the total electron density (ρ_{tot}) collected at the BCPs for the hydrogen bonding and ClO_4^-···ring interactions. Note that ρ_{tot} of ClO_4^-···ring A includes the electron density at the BCP of the coordination bond Cu1A−O12, r = 0.0249 au (Supporting Information, Table S1).

Computational Studies. This unusual, hydrogen-bonded dinuclear copper(II) compound, exhibiting antiferromagnetic exchange interactions, has also been theoretically investigated. As experimentally assessed, the copper atoms Cu1A and Cu1B are separated by a distance of 4.8896(3) Å, which might allow weak metal−metal exchange interactions. The possibility to undergo such long-range interactions is being thoroughly studied by theoretical calculations for many years.[41,53−56] In this respect, the AIM theory represents a method of choice[41,53,57] because a bond between two atoms (hence the two metal centers in the present study) is unambiguously defined by the presence of a BCP in a topological analysis of the electron density.[41] Herein, MP2/6-31+G(d,p) calculations combined with an AIM analysis have been performed to characterize the bonding properties of compound **1** (in its triplet state). In the first instance, a critical point (stationary point) has been found between the metal centers, but the diagonalization of the Hessian of the electron density clearly shows that it characterizes a Ring Critical Point (RCP) rather than a BCP. This observation suggests that, as expected from the Cu−Cu

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Table 3. Hydrogen-Bonding Parameters and Magnetic Properties for **1** and Seven Compounds (with Their CSD Refcode) Described in the Literature (see Figure 4)

	Cu1−O1w (Å)	O1w···O1 (Å)	Cu1′−O1 (Å)	α (deg)	β (deg)	magnetic exchange
compound **1**	1.956	2.601	1.909	131.5	114.6	antiferromagnetic
	Cu1′−O1w′ (Å)	O1w′···O1′ (Å)	Cu1−O1′ (Å)	α′ (deg)	β′ (deg)	magnetic exchange
compound **1**	1.967	2.685	1.888	123.5	114.7	antiferromagnetic
CSD code	Cu1−O1w (Å)	O1w···O1 (Å)	Cu1−O1 (Å)	α (deg)	β (deg)	magnetic exchange
BEYRAY[78]	2.393	2.695	1.981	108.3	132.2	ferromagnetic
HULMOQ[79]	2.464	2.771	1.949	109.7	130.7	antiferromagnetic
MATLOJ[81]	2.196	2.722	1.984	116.3	135.5	antiferromagnetic
NUQKOZ01[82]	1.956	2.685	1.913	126.0	135.4	antiferromagnetic
FAHNAE[80]	1.995	2.709	1.952	111.9	122.4	antiferromagnetic
SAGLAC[83]	1.965	2.757	1.959	131.3	133.3	antiferromagnetic
KEDNIR[84]	1.980	2.629	1.870	110.6	109.3	antiferromagnetic
RAZJUX[62]	1.941	2.696	1.971	133.8	116.4	antiferromagnetic
RAZJOR[62]	2.485	2.710	1.907	116.6	110.3	ferromagnetic

separation distance, a direct metal−metal interaction is not occurring, since the main criterion for a bonding contact (namely the BCP) is actually lacking. However, the RCP implies that the formation of **1** is driven by other interactions (non metal−metal interactions), which contribute to the relatively large formation energy estimated to −38 kcal mol^{-1} (BSSE corrected, see computational details). The AIM analysis clearly reveals the origin of this strong stabilization of the dinuclear entity, which is illustrated in Figure 3 (and in Supporting Information, Table S1). Primarily, two (asymmetric) very strong H-bonds are observed (H···O = 1.73 and 1.91 Å), with electron densities of respectively, 0.0388 and 0.0260 au (ascribed to the hydrogen bonds H22B···O1A and H22A···O1B, respectively). Further BCPs were found between ClO_4^- and the aromatic rings, indicating the important role played by this group for the stabilization of the complex. In the intricate network of contacts revealed by the AIM analysis, lone pair···π[58] interactions (especially between a ClO_4^- anion and ring B, with an electron density of 0.0030 au), and a *secondary* $O_{perchlorate}$···Cu interaction (corresponding to Cu1A···O13; see Table 1) are of particular interest since they contribute to the formation energy of **1**.

In summary, no direct metal−metal interactions have been found, which is not surprising regarding the long Cu···Cu separation distance of about 4.9 Å. Moreover, the orbital topology at the Cu atoms does not allow for their direct overlap. Strong hydrogen bonding interactions are connecting the two copper(II) ions, which therefore may represent the main pathways for the magnetic exchange observed by magnetic susceptibility measurements.

[Cu−O_{PhO}···H−(O_{water})−Cu] Double Bridge. The occurrence of this unusual doubly [O···H(water)]-bridged Cu···Cu unit has been searched in the Cambridge Structural Database (CSD version 30; November 2008). As much as 125 molecular structures of copper coordination compounds exhibiting this dinuclear hydrogen-bonded motif are found in the CSD (see Supporting Information for all the corresponding CSD refcodes). From these 125 compounds, the magnetic properties of only 27 have been investigated in some detail.[59−82] From these 27 copper(II) compounds, the double hydrogen-bonded bridge, involving (neutral) coordinated **water** molecules, had been considered as a possible magnetic-exchange pathway for only seven of them (BEYRAY,[78] HULMOQ,[79] MATLOJ,[81] NUQKOZ01,[82] FAHNAE,[80] SAGLAC[83] and [84] see Table 3).

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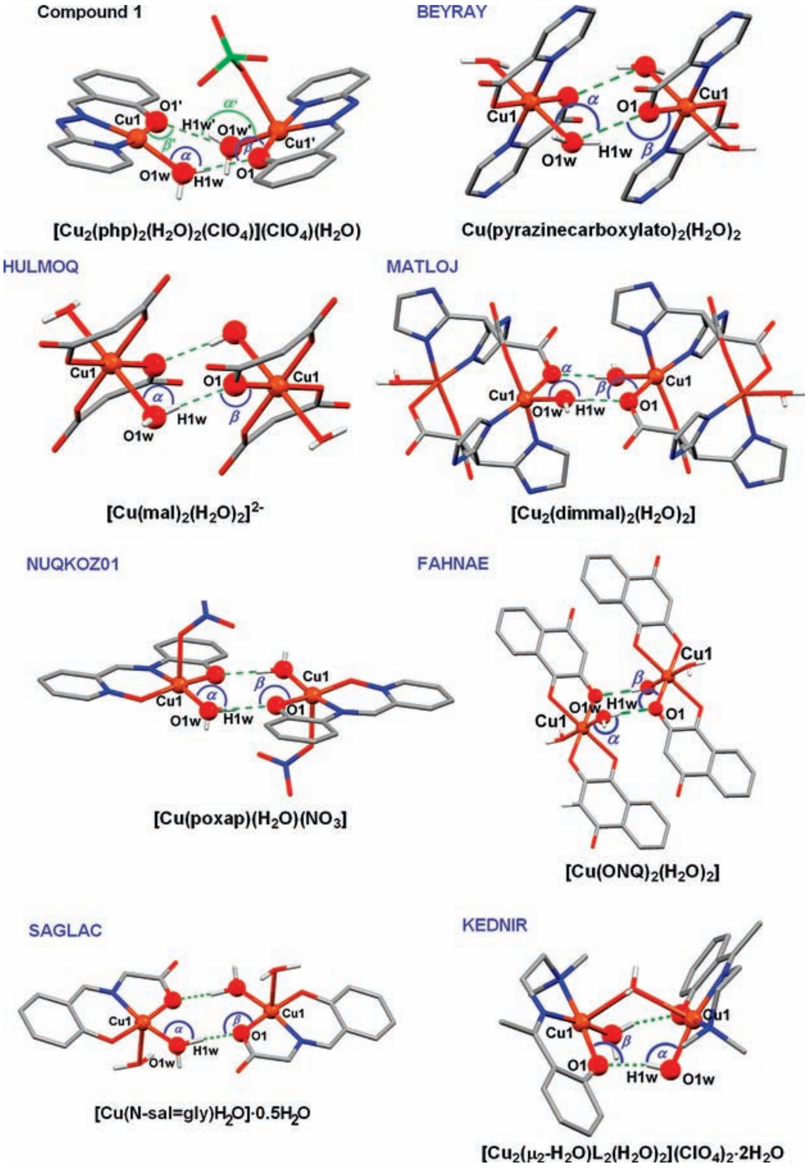

Figure 4. Molecular structures of dinuclear copper(II) units whose magnetic exchange interactions have been explained by the double [O···H(water)] bridge (see Table 3).

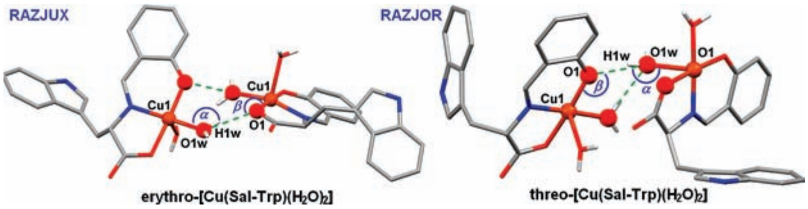

Figure 5. Molecular structures of two related copper(II) coordination compounds obtained from two different ligand stereoisomers.[62]

The hydrogen-bonding parameters for **1** and these seven compounds, illustrated in Figure 4, are listed in Table 3. As is evidenced in Table 3, no clear relationship is visible between the hydrogen-bonding features (bond distances, angles α and β, Figure 4) and the magnetic properties, which can be antiferromagnetic or ferromagnetic. It has to be mentioned that, as stated by Alvarez and co-workers,[24] the nature of the magnetic exchange interaction depends on the orbital overlap, associated to the strength of the hydrogen bonds (characterized by the bond distances and angles). Moreover, H-bond-mediated exchange coupling in copper(II) coordination compounds requires the hydrogen-bonding interaction to involve donor atoms in the xy plane. For instance, the six-membered, hydrogen-bonded ring in **1** exhibits a boat conformation. For six out of the seven compounds described earlier, this ring has a chair conformation (see Figure 4). Similarly to **1**, whose boat conformation is apparently imposed by the bridging perchlorate anion, the conformation observed for $[Cu_2(\mu_2\text{-}H_2O)L_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (CSD code KEDNIR,[84] Figure 4) is obviously due to the μ_2-H_2O ligand (which is not involved in the magnetic exchange coupling;

see Talukder and co-workers[84]), linking the two copper atoms. Thus, a satisfactory magneto-structural correlation for such hydrogen-bonded systems involving coordinated water molecules would require a careful analysis of a significant number of representative examples found in the CSD together with advanced ab initio calculations.

Concluding Remarks

In summary, a supramolecular dinuclear-based copper(II) compound has been synthesized and characterized, whose antiferromagnetic exchange coupling is attributable to hydrogen-bonding interactions. Surprisingly, such hydrogen-bonded dinuclear copper(II) compounds have been barely studied. However, it appears that this type of [Cu$-$O$_{PhO}\cdots$H$-$(O$_{water}$)$-$Cu] bridge may be worth investigating in some more detail because it may significantly contribute to the magnetic behavior of a coordination compound. In that context, a beautiful case of a drastic effect of O$\cdots$H(water) bridge on the magnetic properties of two stereoisomers has been reported by García-Raso and co-workers.[62] Indeed, the reaction of copper(II) acetate with the ligands *erythro*-(Sal Trp) and *threo*-(Sal Trp) leads to two structurally different compounds, whose molecular structures have been redrawn in Figure 5. Amazingly, the *erythro* isomer exhibits antiferromagnetic interactions, whereas the *threo* isomer is ferromagnetic (Table 3). As is evidenced in Figure 5, the two systems exhibit different hydrogen-bonding interactions connecting the metal centers. As the result of the different steric constraints of the two stereoisomeric ligands, the *erythro* compound displays two O$\cdots$H(water) bridges while the *threo* one exhibits only one O$\cdots$H(water) bridge (Figure 5). For *erythro*-[Cu(Sal-Trp)(H$_2$O)$_2$] (CSD code RAZJUX), the hydrogen bonds involve equatorially coordinated oxygen atoms; such condition has been shown to be crucial for the system to exhibit antiferromagnetic interactions.[24] In contrast, the other isomer, namely *threo*-[Cu(Sal-Trp)(H$_2$O)$_2$] (CSD code RAZJOR), is characterized by hydrogen bonding interactions between equatorial and axial donor atoms, which cannot lead to antiferromagnetism.

This last example obviously demonstrates that this type of exchange pathway, mediated by *neutral*, coordinated **water** molecules should be considered for study in detail by the scientific community, when analyzing the magnetic properties of coordination compounds containing such hydrogen bonds.

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Supporting Information Available: Crystallographic data for **1** in CIF format. Figure S1 illustrating the hydrogen-bonding network observed in the crystal packing of **1**, MP2 Optimization of **1**, Table S1 listing the electronic densities calculated for **1** at the MP2/6-31 + G(d,p) level, and CSD refcodes (with the corresponding references) for the molecular structures deposited in the CSD exhibiting the hydrogen-bonded, dinuclear motif [Cu$-$(O$_{PhO}$)$\cdots$H$-$(O$_{water}$)$-$Cu]. This material is available free of charge via the Internet at http://pubs.acs.org.