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# Synthesis, Characterization, and Magnetic Properties of Self-assembled Compounds Based on Discrete Homotrinuclear Complexes of Cu(II)

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Three new supramolecular entities of Cu(II) were synthesized and characterized: $[\{Cu(H_2O)(tmen)\}_2\{\mu\text{-}Cu(H_2O)(opba)\}]_2\{(ClO_4)_2\}_2\cdot 2H_2O$ (**1**), $[\{Cu(H_2O)(tmen)\}_2\{\mu\text{-}Cu(H_2O)(Me_2pba)\}]_2\{(ClO_4)_2\}_2$ (**2**), and $[\{Cu(H_2O)(tmen)\}\{Cu(tmen)\}\{\mu\text{-}Cu(OHpba)\}]_n\{(ClO_4)_2\}_n\cdot nH_2O$ (**3**), where opba = *o*-phenylenbis(oxamato), $Me_2pba$ = 2,2-dimethyl-1,3-propylenbis(oxamato), OHpba = 2-hydroxy-1,3-propylenbis(oxamato), and tmen = *N,N,N'N'*-tetramethylethylenediamine. The crystal structures of **1**, **2**, and **3** were solved. Complex **1** crystallizes in the monoclinic system, space group *C*2/*c* with $a = 20.572(4)$ Å, $b = 17.279(6)$ Å, $c = 22.023(19)$ Å, $\beta = 103.13(4)°$, and $Z = 8$. Complex **2** crystallizes in the monoclinic system, space group *P*2(1)/*c*, with $a = 16.7555(7)$ Å, $b = 13.5173(5)$ Å, $c = 17.1240(7)$ Å, $\beta = 104.9840(10)°$, and $Z = 4$. Complex **3** crystallizes in the orthorhombic system, space group *Pca*2(1) with $a = 21.2859(4)$ Å, $b = 12.8286(10)$ Å, $c = 12.6456(2)$ Å, and $Z = 4$. The three complexes are very similar in structure: a trinuclear Cu(II) complex with the two terminal Cu(II) ions blocked by *N,N,N′,N′*-tetramethylethylenediamine, but with a different environment in the Cu(II) central ion. In the case of complex **1**, two of these trinuclear entities are packed with a short distance between the central Cu(II) ions of two separate entities forming a hexanuclear-type compound. In the case of **2**, two of these trinuclear entities are linked by a hydrogen bond between a water molecule of one terminal Cu(II) and one oxygen atom of the oxamato ligand of the neighboring entity, also forming a hexanuclear complex. In the case of complex **3**, the intermolecular linkages give a one-dimensional system where the OH groups of the OHpba entities are linked to the terminal Cu(II) of the neighboring entities. The magnetic properties of the three complexes were studied by susceptibility measurements vs temperature. For complex **1**, an intramolecular $J$ value of $-312.1$ $cm^{-1}$ and a contact dipolar interaction of $-0.44$K were found. For complex **2** and **3** the fit was made by the irreducible tensor operator formalism (ITO). The values obtained were as follows: $J_1 = -333.9$ $cm^{-1}$ and $J_2 = 0.67$ $cm^{-1}$ for **2** and $J_1 = -335.9$ $cm^{-1}$ and $J_2 = 3.5$ $cm^{-1}$ for **3**.

## Introduction

The ability to control the construction of coordination supramolecular arrays based on covalent interactions or hydrogen bonding has been a major focus of research efforts in recent years for the rational design of functional materials.[1] Y. Journaux et al.[2] have recently indicated that the pathways used to obtain these species are based, essentially, on the following synthetic schemes: (i) the self-assembly method, (ii) the use of polynucleating ligands, and (iii) the use of complexes as ligands.

On the basis of these principles, a large variety of supramolecular architectures have been reported.[3−11] Focusing our interest on the coordination supramolecular self-assembly processes, we find that very few complexes starting from polynuclear building blocks have been reported to date. McAuley et al.[12] reported the synthesis of a chloro-bridged polymeric copper(II) complex, $[Cu_2Cl(L)]^{3+}$ (L = 6,6′-spiro-bi(cyclam) where cyclam = 1,4,8,11-tetraazacyclotetradecane), in which

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the ligand structure plays a crucial role in facilitating participation of the chloride ion in the self-assembly process. Very recently a rational design of homo and hetero hexanuclear coordination compounds such as $\{[Cu(tmen)(H_2O)_2][Cu(tmen)]_2[Cu_2L(H_2O)\}(ClO_4)_4 \cdot 2H_2O$ and analogues (L is the bis-tetradentate chelating ligand *N*,*N*′,*N*″,*N*‴-tetramethylenemethanetetrakis(oxamato) has been developed by Journaux et al.[2]

Continuing with this approach, we have attempted the synthesis and characterization of new supramolecular magnetic species, starting from ferrimagnetic molecules, such as trinuclear $Cu^{II}$ systems or dinuclear $Cu^{II}-Ni^{II}$ entities. Applying the strategy of a self-assembly process, we have demonstrated that trinuclear $Cu^{II}_3$ cation systems have a tendency to give one-dimensional systems using $XCN^-$ (X = S, Se) as a bridging ligand and by synthesizing the first architectures derived from $Cu^{II}_3$ trinuclear cations and $S(Se)CN^-$ anions.[13] With dinuclear $Cu^{II}-Ni^{II}$ entities we have reported some tetranuclear systems which can be considered as the first discrete supramolecular structures with the $SCN^-$ anion acting as ligand in a self-assembly process.[14] With nitrito ligand we have also prepared a new one-dimensional supramolecular system, in which the $NO_2$ ion is chelated to one metal through the two oxygen atoms and bridged to a second metal ion via one of these oxygen atoms.[15]

As a consequence, we can state that the trinuclear Cu−Cu−Cu complexes can be used as a building block for the synthesis of high nuclearity complexes or extended networks, following the strategy of "complexes as ligands" or self-assembly process.

Here we report on the synthesis and characterization of $[\{Cu(H_2O)(tmen)\}_2\{\mu\text{-}Cu(H_2O)(opba)\}]_2\{(ClO_4)_2\}_2 \cdot 2H_2O$ (**1**), $[\{Cu(H_2O)(tmen)\}_2\{\mu\text{-}Cu(H_2O)(Me_2pba)\}]_2\ \{(ClO_4)_2\}_2$ (**2**), and $[\{Cu(H_2O)(tmen)\}\{Cu(tmen)\}\{\mu\text{-}Cu(OHpba)\}]_n\ \{(ClO_4)_2\}_n nH_2O$ (**3**), where opba = *o*-phenylenbis(oxamato), $Me_2pba$ = 2,2-dimethyl-1,3-propylenbis(oxamato), OHpba = 2-hydroxy-1,3-propylenbis(oxamato), and tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

The three complexes are very similar in structure: a trinuclear Cu(II) complex with the two terminal Cu(II) ions blocked by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, but with a different environment in the Cu(II) central ion. In the case of complex **1**, two of these trinuclear entities are packed with a short distance between the central Cu(II) ions of two separate entities forming a supramolecular hexanuclear-type compound. In the case of **2**, two of these trinuclear entities are linked by a hydrogen bond between a water molecule of one terminal Cu(II) and one oxygen atom of the oxamato ligand of the neighboring entity, also forming a supramolecular hexanuclear complex. In the case of complex **3**, the intermolecular linkages give a supramolecular one-dimensional system where the oxygen atoms of the OH group of the OHpba ligands are linked to the terminal Cu(II) of the neighboring entities.

The parent pba derivative[16] (pba = 1,3-propanediylbis(oxamato)) does not form any interesting assembly with the same terminal ligand (tmen). The one-dimensional Cu−Mn complex with pba is *simply* a ferrimagnetic chain, but with the OHpba, it is one of the first molecular-based magnets to have been reported in the literature.[17]

## Experimental Section

**Caution!** Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared and this should be handled with caution.

**Synthesis of the new complexes.** The copper(II) precursors were prepared as described elsewhere.[18]

**$[\{Cu(H_2O)(tmen)\}_2]_2[\{\mu\text{-}Cu(H_2O)(opba)]_2\{(ClO_4)_2\}_2.2H_2O$ (1).** An ethanolic solution (10 mL) of tmen (0.313 g, 2.69 mmol) was added to an ethanolic solution (25 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.00 g, 2.69 mmol). To this mixture, an aqueous solution (35 mL) of $(NBu_4)_2[Cu(opba)]$ (1.074 g, 1.35 mmol) was added. After filtration to remove any impurities, the solution was left undisturbed, and well-formed blue-green crystals of **1** were obtained after several days. The yield was ca. 65%.

**$[\{Cu(H_2O)(tmen)\}_2]_2[\{\mu\text{-}Cu(H_2O)(Me_2pba)]_2\{(ClO_4)_2\}_2$ (2).** An ethanolic solution (5 mL) of tmen (0.313 g, 2.69 mmol) was added to an ethanolic solution (25 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.00 g, 2.69 mmol). To this mixture, an aqueous solution (35 mL) of $Na_2[Cu(Me_2pba)] \cdot 3H_2O$ (0.547 g, 1.35 mmol) was added. After filtration to remove any impurities, the solution was left undisturbed, and well-formed blue-green crystals of **2** were obtained after several days. The yield was ca. 75%.

**$[\{Cu(H_2O)(tmen)\}\{Cu(tmen)\}\{\mu\text{-}Cu(OHpba)\}]_n\{(ClO_4)_2\}_n \cdot nH_2O$ (3).** An ethanolic solution (5 mL) of tmen (0.313 g, 2.69 mmol) was added to an ethanolic solution (30 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.00 g, 2.69 mmol). To this mixture, an aqueous solution (35 mL) of $Na_2[Cu(OHpba)] \cdot 3H_2O$ (0.553 g, 1.4 mmol) was added. After filtration to remove any impurities, the solution was left undisturbed, and well-formed blue-green crystals of **3** were obtained after several days. The yield was ca. 50%.

Elemental analyses (C, N, H, Cu, Cl) were consistent with the formulation.

**Crystal Structure Determination.** A prismatic crystal of **1** (prism, blue-green, dimensions 0.1 mm × 0.2 mm × 0.2 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($8° < \theta < 12°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation using $\omega/2\theta$ scan technique. A total of 11 421 reflections were measured in the range $2.03 < \theta < 29.98$, 11 094 of which were nonequivalent by symmetry ($R$(int) (on $I$) = 0.017). A total of 5885 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h to serve as orientation and intensity control; significant decay was not observed. Lorentz-polarization, but not absorption, corrections were made. The structure was

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solved by Direct methods, using the SHELXS computer program,[19] and refined by full-matrix least-squares method with the SHELX93 computer program,[20] using 11 040 reflections (highly negative intensities were not assumed). The function minimized was $\sum w\ ||F_0|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0815P)^2 + 0.1691P]^{-1}$, and $P = (|Fo|^2 + 2|Fc|^2)/3$, $f$, $f'$, and $f''$ were taken from the *International Tables of Crystallography*.[21] All the atoms of each perchlorate ion were refined with the same isotropic temperature coefficient. All H atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final $R$(on $F$) factor was 0.044, $wR$(on $|F|^2$) = 0.120 and goodness of fit = 1.089 for all observed reflections. The number of refined parameters was 430. Max. Shift/esd = 0.0. Mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0.065 and −0.629 e$Å^{-3}$, respectively.

Suitable crystals of **3** (prism, blue-green, dimensions 0.50 mm × 0.30 mm × 0.25 mm) and **2** (prism, blue-green, dimensions 0.50 mm × 0.35 mm × 0.15 mm) were used in the structure determination. X-ray data were collected using a Bruker SMART CCD area detector single-crystal diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) by the phi-omega scan method. A total of 1271 frames of intensity data were collected for each compound. The integration process yielded a total of 18 739 reflections for **3** and 24 360 for **2**, of which 7535 [$R$(int) = 0.0310] and 9211 [$R$(int) = 0.0533], respectively, were independent. Absorption corrections were applied using SADABS[22] program (maximum and minimum transmission coefficients, 1.000 and 0.853 for **3**, and 0.763 and 0.449 for **2**). The structures were solved using the Bruker SHELXTL-PC[23] software by direct methods and refined by full-matrix least-squares methods on $F^2$. Hydrogen atoms were included in calculated positions and refined in the riding mode, except those in the water molecules that were located on residual density maps, but then also refined in the riding mode. For **3**, convergence was reached at a final $R1 = 0.0439$ [for $I > 2\sigma(I)$], $wR2 = 0.1017$ [for all data], 451 parameters, with allowance for the thermal anisotropy for all non-hydrogen atoms. The weighting scheme employed was $w = [\sigma^2(F_0^2 + (0.0398\ P)^2 + 2.7928P]$ and $P = (|F_0|^2 + 2|F_c|^2)/3$ and the goodness of fit on $F^2$ was 1.080 for all observed reflections. For **2**, convergence was reached at a final $R1 = 0.0590$ [for $I > 2\sigma(I)$], $wR2 = 0.1951$ [for all data], 452 parameters, with allowance for the thermal anisotropy for all non-hydrogen atoms. The weighting scheme employed was $w = [\sigma^2(F_0^2 + (0.1119P)^2]$ and $P = (|F_0|^2 + 2|F_c|^2)/3$ and the goodness of fit on $F^2$ was 1.013 for all observed reflections. The perchlorate anions are disordered in the cell of the complexes. Crystal data and details on the data collection and refinement are summarized in Table 1.

**Physical Measurements.** Magnetic measurements were carried out on polycrystalline samples with a SQUID Magnetometer. The magnetic field was 1000 G. The diamagnetic corrections were estimated from Pascal Tables.

## Results and Discussion

**Table 1.** Crystallographic Data for Complexes **1**, **2**, and **3**

| | **1** | **2** | **3** |
|---|---|---|---|
| empirical formula | $C_{22}H_{44}Cl_2$-$Cu_3N_6O_{18}$ | $C_{21}H_{48}Cl_2$-$Cu_3N_6O_{17}$ | $C_{19}H_{42}Cl_2$-$Cu_3N_6O_{17}$ |
| fw | 942.14 | 918.17 | 888.11 |
| space group | *C*2/*c* | *P*2(1)/*c* | *Pca*2(1) |
| temp (K) | 293 (2) | 298(2) | 298(2) |
| $\lambda$ (Mo Kα) (Å) | 0.71069 | 0.71073 | 0.71073 |
| *a* (Å) | 20.572(4) | 16.7555(7) | 21.2859(4) |
| *b* (Å) | 17.279(6) | 13.5173(5) | 12.82860(10) |
| *c* (Å) | 22.023(19) | 17.1240(7) | 12.6456(2) |
| α (deg) | 90.00 | 90.00 | 90.00 |
| $\beta$ (deg) | 103.13(4) | 104.9840(10) | 90.00 |
| $\gamma$ (deg) | 90.00 | 90.00 | 90.00 |
| $V$ ($Å^3$) | 7624(7) | 3746.5(3) | 3453.11(9) |
| $Z$ | 8 | 4 | 4 |
| $\rho_{calcd}$ (g $cm^{-3}$) | 1.640 | 1.628 | 1.708 |
| $\mu$ (Mo Kα) ($mm^{-1}$) | 1.872 | 1.904 | 2.063 |
| $R^a$ | 0.0441 | 0.0590 | 0.0439 |
| $wR^b$ | 0.1187 | 0.1691 | 0.0931 |

[a] $R$(on $F$) = $\sum|F_0| - |F_c||/\sum|F_0|$. [b] $wR$(on $F^2$) = $[\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

**Description of the structures [{Cu($H_2O$)(tmen)}$_2$][{*μ*-Cu($H_2O$)(opba)]$_2${($ClO_4$)$_2$}$_2$·2$H_2O$ (1), [{Cu($H_2O$)(tmen)}$_2${*μ*-Cu($H_2O$)($Me_2$pba)}]$_2${($ClO_4$)$_2$}$_2$ (2), and [{Cu($H_2O$)(tmen)}{Cu(tmen)}{*μ*-Cu(OHpba)}]$_n${($ClO_4$)$_2$}$_n$·*n*$H_2O$ (3).** A drawing of the cationic part with atom labeling scheme is given in Figures 1, 3, and 5. The main bond distances and angles are given in Tables 2, 3, and 4 for complexes **1**, **2**, and **3**, respectively. The terminal copper(II) ions, Cu(1) and Cu(3), have 4 + 1 coordination. Their basal planes are formed by two nitrogen atoms from the tmen ligand and two oxygen atoms from the oxamate. The pentacoordination in **1** and **2** is provided by an oxygen atom from a water molecule. In the case of complex **3**, the pentacoordination for Cu(1) is also achieved by an oxygen from a water molecule but the Cu(3) atom completes its coordination with the O of the OH group of OHpba from the neighboring entity instead a water molecule. Thus, the coordination polyhedron of Cu(1) and Cu(3) can be considered as a square pyramid with a $\tau$ factor value of 0.03 for Cu(1) and 0.01 for Cu(3) in **1**, 0.07 for Cu(1) and 0.08 for Cu(3) in **2**, and 0.02 for Cu(1) and 0.2 for Cu(3) in **3** ($\tau = 0$ for a square pyramid and $\tau = 1$ for trigonal bipyramid). The distances of copper(II) atoms to the basal plane are 0.202 Å for Cu(1) and 0.207 Å for Cu(3) in **1**, −0.145 Å for Cu(1) and 0.186 Å for Cu(3) in **2**, and −0.221 Å for Cu(1) and 0.246 Å for Cu(3) in **3**. At the central Cu(2) atom the basal plane is formed by two oxygen atoms and two nitrogen atoms from the oxamato ligand. Compounds **1** and **2** have 4 + 1 coordination and the fifth ligand is a water molecule: their coordination polyhedron can be considered as a square pyramid with a $\tau$ factor value of 0.02 for **1** and 0.07 for **2**. Complex **3** shows four-coordination (square-planar) geometry. The distance of the copper(II) atom to the basal plane is −0.110 Å in **1**, 0.075 Å in **2**, and 0.024 Å in **3**. The Cu···Cu separations within the trinuclear unit are as follows: Cu(1)−Cu(2) = 5.176 Å and Cu(2)−Cu(3) = 5.193 Å for **1**, Cu(1)−Cu(2) = 5.173 Å and Cu(2)−Cu(3) = 5.155 Å for **2**, and Cu(1)−Cu(2) = 5.179 Å and Cu(2)−Cu(3) = 5.163 Å for **3**. The Cu(1)−Cu(2)−Cu(3) angles are 165.15°, 169.14°, and 173.90° and the angle formed by the two mean oxamato-like planes (which contain the copper(II) ions) are 158.4°, 164.9°, and 164.0° for **1**, **2**, and **3**, respectively.

In complex **1**, two of the trinuclear entities are self-assembled with a short distance (4.047 Å) between the central Cu(II) ions of two different entities giving a hexanuclear-type compound (Figure 2). The phenylene group remains on the main plane of each trinuclear entity, with the water molecules linked to the central Cu(II) ions in the opposite direction to the Cu···Cu interaction. These structural features permit packing of the trinuclear entities with a short distance between the central Cu(II) ions of two different entities. In complex **2**, two of the trinuclear entities are self-assembled by a hydrogen bond between a water molecule of one terminal Cu(II) and one oxygen atom of the oxamato ligand of the neighboring entity, also forming a hexanuclear complex (Figure 4). In Cu(1) the water molecule acts as a terminal ligand, while in Cu(3) it bridges

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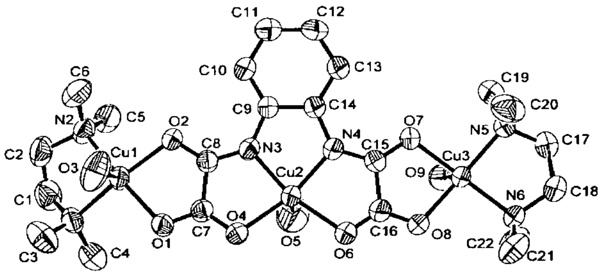


**Figure 1.** Drawing of the cationic part of [{Cu($H_2O$)(tmen)}$_2${$\mu$-Cu($H_2O$)(opba)}]$_2$ {($ClO_4$)$_2$}$_2$·$H_2O$ (**1**) with the atom labeling scheme. Ellipsoids at the 50% probability level.

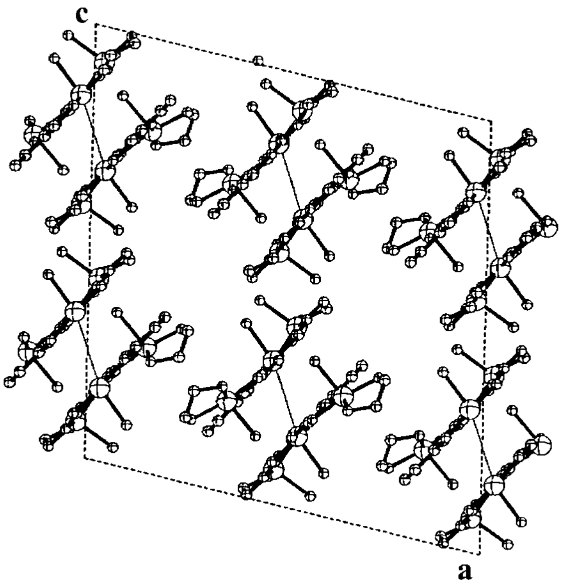


**Figure 2.** Projection down the *ac*-plane of the unit cell of [{Cu($H_2O$)(tmen)}$_2${$\mu$-Cu($H_2O$)(opba)}]$_2$ {($ClO_4$)$_2$}$_2$·2$H_2O$ (**1**), showing the best view of the hexanuclear entities. The perchlorate anions are omitted for clarity.

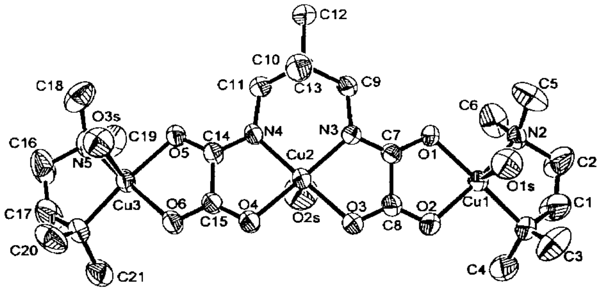


**Figure 3.** Drawing of the cationic part of [{Cu($H_2O$)(tmen)}$_2${$\mu$-Cu($H_2O$)($Me_2$pba)}]$_2${($ClO_4$)$_2$}$_2$ (**2**) with the atom labeling scheme. Ellipsoids at the 50% probability level.

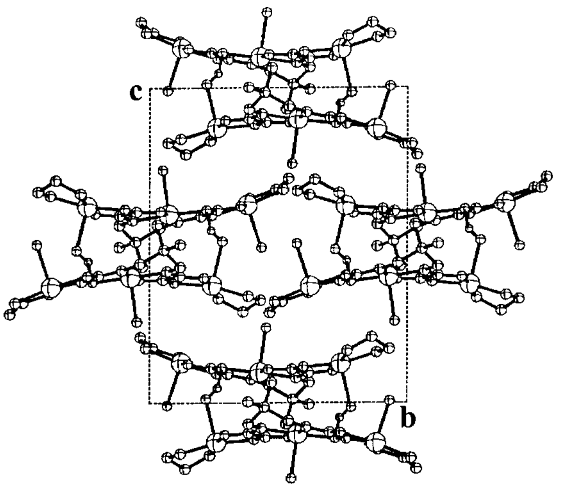


**Figure 4.** Projection down the *bc*-plane of the unit cell of [{Cu($H_2O$)(tmen)}$_2${$\mu$-Cu($H_2O$) ($Me_2$pba)}]$_2${($ClO_4$)$_2$}$_2$ (**2**), showing the best view of the hexanuclear entities. The perchlorate anions are omitted for clarity.

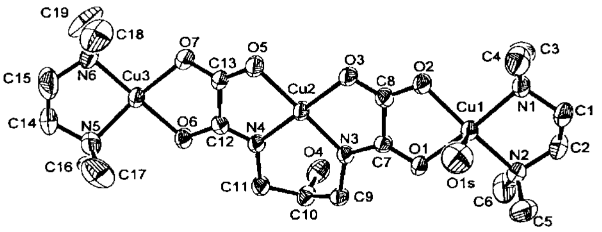


**Figure 5.** Drawing of the trinuclear cationic part of [{Cu($H_2O$)(tmen)}{Cu(tmen)}{$\mu$-Cu(OHpba)}]$_n${($ClO_4$)$_2$}$_n$($H_2O$)$_n$·$n$$H_2O$ (**3**) with the atom labeling scheme. Ellipsoids at the 50% probability level.

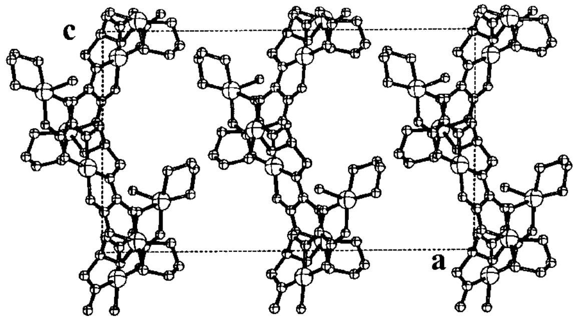


**Figure 6.** Projection down the *ac*-plane of the unit cell of [{Cu($H_2O$)(tmen)}{Cu(tmen)}{$\mu$-Cu(OHpba)}]$_n$ {($ClO_4$)$_2$}$_n$($H_2O$)$_n$·$n$$H_2O$ (**3**), showing the best view of the one-dimensional entities. The perchlorate anions are omitted for clarity.

through the hydrogen atom. In the hexanuclear entity the distance between H(3SB)−O(3) is 2.283 Å. The shortest intermolecular Cu···Cu distance is Cu(3)(terminal)−Cu(2)(central) = 5.064 Å. The methyl groups of the 2,2-dimethyl-1,3-propylenbis(oxamato) ligand are situated opposite each other in the center of the main plane of the hexanuclear entity. In this structural feature the proximity of the Cu(II) ions of the two trinuclear entities is impossible. In complex **3**, where the starting building block has the OHpba ligand, the presence of the oxygen atom of the OH group gives rise to 1D system as expected due to the possibility of Cu(II)−OH coordination. The oxygen atoms of the OH groups of the OHpba ligands are linked to the terminal Cu(3) of the neighbors (Figure 6). The shortest intermolecular Cu···Cu distance is via the bridge OH group, Cu(3)(terminal)−Cu(2)(central) = 5.913 Å.

We thus corroborate that the strategies for the construction of molecular architectures through the self-assembly process is consequence of several structural factors and numerous subtle intermolecular forces: van der Waals, hydrogen-bonding, electrostatic interactions and metal−ligand coordination. In this way, the polymerization of analogous trinuclear complexes by changing only the central part of the oxamato ligand, opba [*o*-phenylenbis(oxamato)], $Me_2$pba [2,2-dimethyl-1,3-propylenbis(oxamato)], and OHpba [2-hydroxi-1,3-propylenbis(oxamato)], gives three new polynuclear architectures.

**Magnetic Studies.** Susceptibility measurements for complex **1** are shown in Figure 7 as $\chi_M T$ vs $T$. From room temperature down to 75 K there is a clear fall in $\chi_M T$ values, followed by a plateau close to 0.41 cm$^3$ mol$^{-1}$ K, a typical value for an isolated

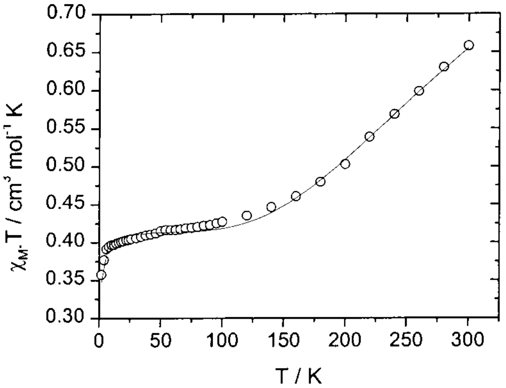
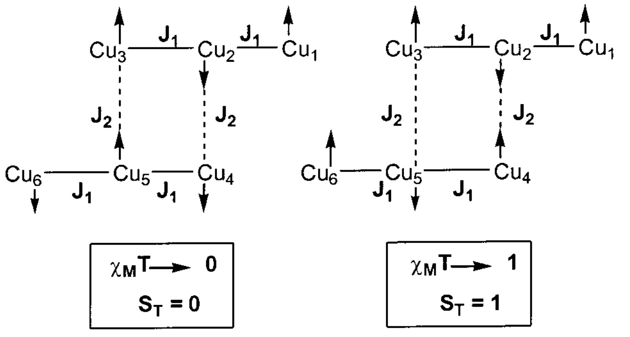


**Figure 7.** Experimental and calculated variations of the product $\chi_M T$ versus temperature for $[\{Cu(H_2O)(tmen)\}_2\{\mu\text{-}Cu(H_2O)(opba)\}]_2\{(ClO_4)_2\}_2\cdot 2H_2O$ (**1**).



(a) (b)

**Figure 8.** Scheme of the spin topology assuming intermolecular ferro (a) or antiferromagnetic (b) coupling between the two trinuclear [Cu−Cu−Cu] entities.

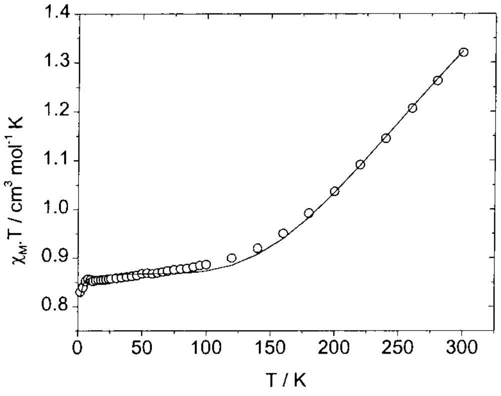


**Figure 9.** Experimental and calculated variations of the product $\chi_M T$ versus temperature for $[\{Cu(H_2O)(tmen)\}_2\{\mu\text{-}Cu(H_2O)(Me_2pba)\}]_2\{(ClO_4)_2\}_2$ (**2**).

$Cu^{II}$ trimer ($S = {}^1/_2$), assuming antiferromagnetic coupling between the $Cu^{II}$ ions. In the low-temperature zone, below 40 K, there is a clear fall in the $\chi_M T$ values, toward zero. This decrease can be explained by dipolar interactions between the two central copper(II) ions. According to the Hamiltonian and mathematical formula reported in the literature,[16] the best fit parameters are $J = -312.1$ cm$^{-1}$, $\theta = -0.44$ K, $g_t = 2.10$, and $g_c = 2.07$. $R = 3 \times 10^{-5}$ ($R = \sum_i(\chi_{Mcalc} - \chi_{Mobsd})^2/\sum_i(\chi_{Mcalc})^2$.

For complex **2**, as shown in the crystallographic part (Figure 4), the hexanuclear complexes are formed by two trinuclear entities linked by a hydrogen bond between a water molecule of one terminal copper(II) and one oxygen atom of the oxamato ligand of the neighboring entity. The two cases represented in Figure 8 are two extremes used for analyzing experimental magnetic measurements and the treatment of data. If the magnetic interaction between these two entities were weakly ferromagnetic, the resulting $S_T$ value would tend to zero at low temperatures, so the $\chi_M T$ curve would decrease and tend to zero at these temperatures. In contrast, if the coupling was weakly antiferromagnetic the resulting $S_T$ values would tend to 1 and the $\chi_M T$ curve would increase and tend to a value greater than 1 (taking into account that $g > 2.00$). The susceptibility measurements for complex **2** are shown in Figure 9 as $\chi_M T$ vs $T$. The fit of experimental data, was performed according to the following Hamiltonian:

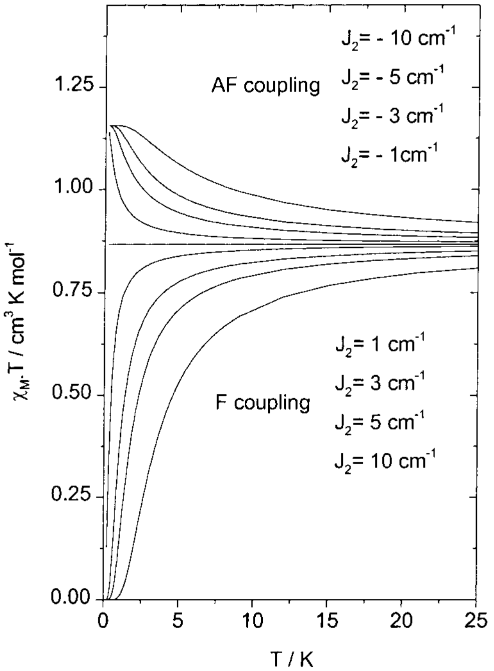


**Figure 10.** Theoretical curves obtained by CLUMAG program (see text) for different $J_2$ values. In all cases, $J_1$ and $g$ were constant: $J_1 = -334$ cm$^{-1}$ and $g = 2.15$.

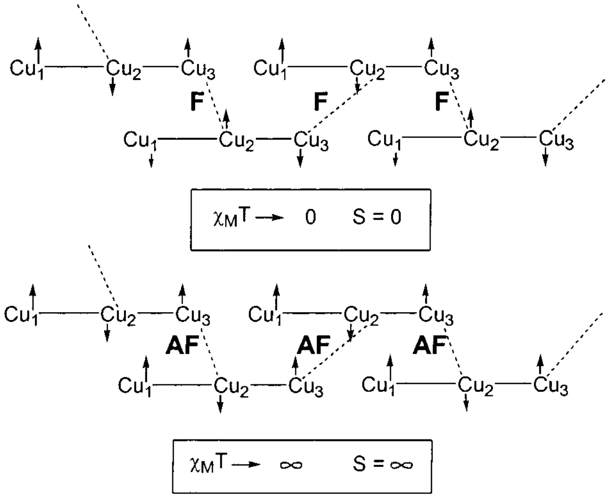


**Figure 11.** Scheme of the spin topology assuming ferro or antiferromagnetic coupling between the trinuclear [Cu−Cu−Cu] entities in the one-dimensional complex.

$$H = -J_1(S_1S_2 + S_2S_3 + S_4S_5 + S_5S_6) - J_2(S_2S_4 + S_3S_5) \quad (1)$$

where $J_1$ corresponds to the coupling through the oxamato bridge and $J_2$ to the coupling through the hydrogen bonding between trinuclear entities. The free parameters were $J_1$, $J_2$, and $g$

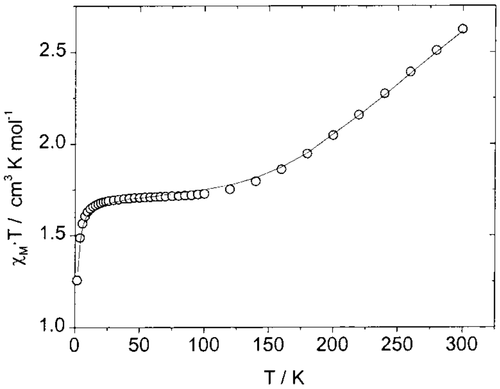


**Figure 12.** Experimental and calculated variations of the product $\chi_M T$ versus temperature for $[\{Cu(H_2O)(tmen)\}\{Cu(tmen)\}\{\mu\text{-}Cu(OHpba)\}]_n\text{-}\{(ClO_4)_2\}_n(H_2O)_n \cdot nH_2O$ (**3**).

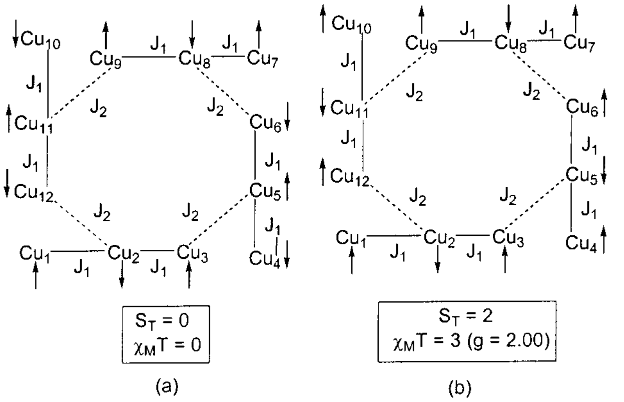


**Figure 13.** Scheme of the spin topology assuming intermolecular ferro (a) or antiferromagnetic (b) coupling for a ring of twelve copper(II) atoms.

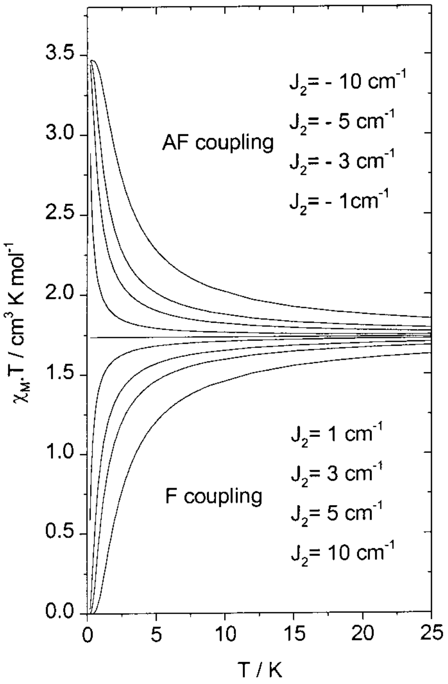


**Figure 14.** Theoretical curves obtained by CLUMAG program (see text) for different $J_2$ values. In all cases, $J_1$ and $g$ were constant: $J_1 = -336$ cm$^{-1}$ and $g = 2.14$.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**

| | | | |
|---|---|---|---|
| Cu(3)−O(7) | 1.980(3) | Cu(2)−O(4) | 2.000(3) |
| Cu(3)−O(8) | 1.984(3) | Cu(2)−O(5) | 2.327(4) |
| Cu(3)−N(5) | 2.011(3) | Cu(1)−O(2) | 1.968(3) |
| Cu(3)−N(6) | 2.01(5) | Cu(1)−O(1) | 1.991(3) |
| Cu(3)−O(9) | 2.297(3) | Cu(1)−N(2) | 2.022(3) |
| Cu(2)−N(3) | 1.918(3) | Cu(1)−N(1) | 2.036(3) |
| Cu(2)−N(4) | 1.918(3) | Cu(1)−O(3) | 2.343(3) |
| Cu(2)−O(6) | 1.998(3) | | |
| O(1)−Cu(1)−N(1) | 93.53(13) | O(4)−Cu(2)−O(5) | 91.45(14) |
| N(2)−Cu(1)−N(1) | 87.80(14) | N(3)−Cu(2)−N(4) | 81.96(12) |
| O(2)−Cu(1)−O(3) | 92.62(13) | N(4)−Cu(2)−O(6) | 84.12(12) |
| O(1)−Cu(1)−O(3) | 89.74(12) | N(3)−Cu(2)−O(4) | 84.18(11) |
| N(2)−Cu(1)−O(3) | 100.65(14) | O(7)−Cu(3)−O(8) | 84.33(10) |
| N(1)−Cu(1)−O(3) | 99.8(2) | O(7)−Cu(3)−N(5) | 92.26(12) |
| O(2)−Cu(1)−O(1) | 84.17(10) | O(8)−Cu(3)−N(6) | 93.21(12) |
| O(2)−Cu(1)−N(2) | 92.18(12) | N(5)−Cu(3)−N(6) | 87.75(13) |
| O(6)−Cu(2)−O(4) | 109.04(10) | O(7)−Cu(3)−O(9) | 90.72(13) |
| N(3)−Cu(2)−O(5) | 103.1(2) | O(8)−Cu(3)−O(9) | 92.02(12) |
| N(4)−Cu(2)−O(5) | 98.5(7) | N(5)−Cu(3)−O(9) | 99.74(13) |
| O(6)−Cu(2)−O(5) | 83.2(2) | N(6)−Cu(3)−O(9) | 100.96(14) |

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **2**

| | | | |
|---|---|---|---|
| Cu(1)−O(1) | 1.947(3) | Cu(2)−O(2S) | 2.400(5) |
| Cu(1)−O(2) | 2.021(3) | Cu(2)−O(3) | 2.004(3) |
| Cu(1)−N(1) | 2.031(4) | Cu(3)−O(5) | 1.965(3) |
| Cu(1)−N(2) | 2.045(4) | Cu(3)−O(6) | 1.996(3) |
| Cu(1)−O(1S) | 2.351(4) | Cu(3)−N(6) | 2.020(4) |
| Cu(2)−N(4) | 1.936(4) | Cu(3)−N(5) | 2.034(4) |
| Cu(2)−N(3) | 1.937(4) | Cu(3)−O(3S) | 2.376(4) |
| Cu(2)−O(4) | 1.989(3) | | |
| O(1)−Cu(1)−O(2) | 84.71(13) | N(4)−Cu(2)−O(2S) | 89.64(19) |
| O(2)−Cu(1)−N(1) | 96.13(15) | N(3)−Cu(2)−O(2S) | 93.04(18) |
| O(1)−Cu(1)−N(2) | 90.38(15) | O(4)−Cu(2)−O(2S) | 93.58(17) |
| N(1)−Cu(1)−N(2) | 87.63(16) | O(3)−Cu(2)−O(2S) | 92.46(18) |
| O(1)−Cu(1)−O(1S) | 91.48(15) | O(5)−Cu(3)−O(6) | 85.48(13) |
| O(2)−Cu(1)−O(1S) | 90.68(16) | O(6)−Cu(3)−N(6) | 92.72(15) |
| N(1)−Cu(1)−O(1S) | 95.21(17) | O(5)−Cu(3)−N(5) | 92.52(16) |
| N(2)−Cu(1)−O(1S) | 99.14(16) | N(6)−Cu(3)−N(5) | 87.39(18) |
| N(4)−Cu(2)−N(3) | 94.81(15) | O(5)−Cu(3)−O(3S) | 85.51(15) |
| N(4)−Cu(2)−O(4) | 84.62(14) | O(6)−Cu(3)−O(3S) | 98.20(15) |
| N(3)−Cu(2)−O(3) | 84.34(14) | N(6)−Cu(3)−O(3S) | 102.88(16) |
| O(4)−Cu(2)−O(3) | 95.99(13) | N(5)−Cu(3)−O(3S) | 94.45(18) |

**Table 4.** Selected Bond Lengths, (Å) and Angles (deg) for **3**

| | | | |
|---|---|---|---|
| Cu(1)−O(1) | 1.967(3) | Cu(2)−O(3) | 1.969(3) |
| Cu(1)−O(2) | 1.989(3) | Cu(2)−O(5) | 1.986(4) |
| Cu(1)−N(1) | 2.024(4) | Cu(3)−O(6) | 1.969(3) |
| Cu(1)−N(2) | 2.027(4) | Cu(3)−O(7) | 1.989(4) |
| Cu(1)−O(1S) | 2.270(4) | Cu(3)−N(5) | 2.012(4) |
| Cu(2)−N(3) | 1.930(4) | Cu(3)−N(6) | 2.015(4) |
| Cu(2)−N(4) | 1.934(4) | | |
| O(1)−Cu(1)−O(2) | 84.31(13) | N(3)−Cu(2)−O(3) | 85.12(14) |
| O(2)−Cu(1)−N(1) | 92.42(14) | N(3)−Cu(2)−N(4) | 94.88(15) |
| O(1)−Cu(1)−N(2) | 93.05(15) | N(4)−Cu(2)−O(5) | 85.30(14) |
| N(1)−Cu(1)−N(2) | 87.43(16) | O(3)−Cu(2)−O(5) | 94.69(13) |
| O(1)−Cu(1)−O(1S) | 91.73(16) | O(6)−Cu(3)−O(7) | 84.22(14) |
| O(2)−Cu(1)−O(1S) | 91.89(17) | O(6)−Cu(3)−N(5) | 92.37(17) |
| N(1)−Cu(1)−O(1S) | 100.14(17) | O(7)−Cu(3)−N(6) | 92.52(16) |
| N(2)−Cu(1)−O(1S) | 101.29(19) | | |

(average). The fit made by the irreducible tensor operator formalism (ITO), using the CLUMAG program,[24] gave the following results $J_1 = -333.9$ cm$^{-1}$, $J_2 = 0.67$ cm$^{-1}$, $g = 2.15$, and $R = 2 \times 10^{-4}$. Finally, to compare the theoretical magnetic behavior for the two extreme cases represented in Figure 8, a simulation of the $\chi_M T$ vs $T$, using the same formalism, was performed, fixing the $J_1$ value as $-334$ cm$^{-1}$ and the $g$ value as 2.15 and varying the values of $J_2$ (coupling through the hydrogen bond) between $-10$ and 10 cm$^{-1}$. As expected, with these small $J_2$ values the variation of $\chi_M T$ vs $T$ is manifested only at low temperatures (Figure 10). When the $J_2$ coupling is

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[24] Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

**Table 5.** Main Molecular Parameters Affecting the Intramolecular Antiferromagnetic Coupling for the Three Similar Complexes **1**, **2**, and **3**

| | $J$ (cm$^{-1}$) | CuCuCu/ deg | planes angle[a]/ deg | deviation[b]/Å | | | $\tau$ descriptor for five coordination[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Cu1 | Cu2 | Cu3 | Cu1 | Cu2 | Cu3 |
| (1) | −312.1 | 165.15 | 158.38 | 0.202 | −0.110 | 0.207 | 0.03 | 0.02 | 0.01 |
| (2) | −333.9 | 169.14 | 164.90 | −0.145 | 0.075 | 0.186 | 0.07 | 0.07 | 0.08 |
| (3) | −335.9 | 173.90 | 164.00 | −0.221 | 0.024 | 0.246 | 0.02 | *d* | 0.20 |

[a] Formed by the two mean oxamato-like planes which contain the copper(II) ions. [b] Deviation of the copper(II) ions from the mean plane created by the four basal atoms. [c] $\tau$ is 0 for square-pyramid and 1 for trigonal bipyramid. [d] The environment for Cu(II) is square planar.

antiferromagnetic, $\chi_M T$ increased at lower temperatures tending to a finite value greater than 1 because $g = 2.15$; when $J_2$ coupling is ferromagnetic, $\chi_M T$ decreased with lower temperature, tending to zero.

For complex **3**, as can be seen from the crystal structure, the chain is formed by trinuclear entities linked by the oxygen atom of the OH group of OHpba ligand (Figure 6). Such a ligand can transmit an additional interaction between the trinuclear entities, giving rise to two different forms of the ground state at low temperature. These two forms are shown in Figure 11. If the magnetic interaction between these two entities were weakly ferromagnetic, the resulting total spin value would tend to zero at low temperatures, so the $\chi_M T$ curve would decrease and also tend to zero at these temperatures. In contrast, if the coupling were weakly antiferromagnetic, $\chi_M T$ would tend to infinity at low temperatures. The susceptibility measurements for complex **3** are shown in Figure 12 as $\chi_M T$ vs $T$. To fit the experimental data we have assumed a ring of 12 copper(II) atoms, which should describe the behavior of the infinite chain with negligible uncertainty (Figure 13). The fit of experimental data was performed according to the following Hamiltonian:

$$H = -J_1(S_1S_2 + S_2S_3 + S_4S_5 + S_5S_6 + S_7S_8 + S_8S_9 + S_{10}S_{11} + S_{11}S_{12}) - J_2(S_3S_5 + S_6S_8 + S_9S_{11} + S_{12}S_2) \quad (2)$$

where $J_1$ corresponds to the coupling through the oxamato bridges and $J_2$ through the oxygen bridged atom. The free parameters were $J_1$, $J_2$, and $g$ (average). The fit made by the irreducible tensor operator formalism (ITO) using the CLUMAG program[24] gave the following results: $J_1 = -335.9$ cm$^{-1}$, $J_2 = 3.5$ cm$^{-1}$, $g = 2.14$, and $R = 2.15 \times 10^{-4}$.

To compare the theoretical magnetic behavior of the two extreme cases shown in Figure 13, a simulation of $\chi_M T$ vs $T$ for the ring of twelve copper(II) atoms was calculated using the same method as that described above. The $J_1$ (coupling through the oxamato bridge) value was fixed as $-336$ cm$^{-1}$ and $g$ was set at 2.14. The value of $J_2$ was simulated between $-10$ and 10 cm$^{-1}$. As expected, with these small $J_2$ values, the variation of $\chi_M T$ vs $T$ is observed only at low temperatures. The theoretical $\chi_M T$ vs $T$ curves are shown in Figure 14. When the $J_2$ coupling is antiferromagnetic, $\chi_M T$ increases with decreasing temperature tending to $S = 2$ (4 electrons; $\chi_M T = 3.44$ cm$^3$mol$^{-1}$K, assuming $g = 2.14$)) value; when the $J_2$ coupling is ferromagnetic $\chi_M T$ decreases with decreasing temperature, tending to zero.

**Magneto-structural Correlations.** As previously reported[16] the most antiferromagnetic coupling occurs when the trinuclear entity is completely planar assuming that all copper(II) ions are in the center of the square-planar coordination: this is an ideal case. In Table 5 we have gathered some structural differences between the three complexes. The most important one lies in the angles formed by the three copper(II) ions, but the different values for complexes **2** and **3** do not justify the similar $J$ values. The small deviation from 180° for complex **3** is undoubtedly compensated by the deviation from square-pyramidal to trigonal bipyramid of Cu3 (0.2, Table 5). The magnetic orbital in a bpt distortion reduces the overlap between them and, consequently, the $J$ value. The explanation of the $J$ values gradation, $1 < 2 \approx 3$, lies in the variation formed by the two mean oxamato-like planes (which contains de copper(II) ions). These angles create a deviation from the planarity in the order $1 > 2 \approx 3$. This is the main factor that diminishes the antiferromagnetic coupling because it reduces the overlap between magnetic orbitals. The experimental $J$ values are consistent with this explanation.

With regard to the intermolecular Cu···Cu interactions is not possible to perform magneto-structural studies since there are three kinds of bonds: dipolar, hydrogen, and metal−ligand. For complexes **1** and **2** we cannot predict the sign of $\theta$ or $J$. Experimentally, **1** is antiferromagnetic and **2** is ferromagnetic. On the contrary, for **3** it is possible to predict the sign of $J_2$, due to the orthogonality of the magnetic orbitals because the OH group of the OHpba is almost perpendicular to the $xy$ plane of Cu(II).

**Acknowledgment.** This study was financially supported by the Dirección General de Investigación Científica y Técnica (Spanish Government, Grant No. PB96/0163).

**Supporting Information Available:** Three X-ray crystalographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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