

# Magnetostructural Characterization of $\mu_4$ -Oxo-hexa- $\mu_2$ -chlorotetrakis(imidazole)copper(II)

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The  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  complex has been synthesized and its crystal structure and magnetic properties determined. The compound crystallizes as a dark green solid in the orthorhombic system, space group  $P2_12_12_1$ , with cell constants  $a = 11.469(2)$  Å,  $b = 13.933(2)$  Å,  $c = 16.778(3)$  Å and four formula units per cell. The complex has a tetrameric structure of four copper(II) ions connected to a central oxo group, in an approximately tetrahedral arrangement. Copper coordination is completed by three  $\mu_2$ -chloride ions and an imidazole nitrogen atom, defining a trigonal bipyramidal environment around each copper ion. A new Heisenberg exchange scheme has been developed, considering the experimentally observed distortion of the  $\text{Cu}_4$  tetrahedron. The magnetic susceptibilities measurements were interpreted by means of this model, in terms of three coupling constants,  $J = -7.65$  cm<sup>-1</sup>,  $J_S = 83.3$  cm<sup>-1</sup>, and  $J_L = -58.8$  cm<sup>-1</sup>, which show a linear correlation with the observed Cu–O–Cu angles.

## Introduction

Since higher nuclearity copper(II) complexes are of current interest as models of copper metalloenzymes and as inorganic materials, in this paper we present the syntheses, X-ray structure determination, and magnetic properties of a copper(II) tetramer with imidazole as the Lewis base ligand,  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$ .

The first example of clusters of the type  $[\text{Cu}_4\text{OX}_6\text{L}_4]$  was described by Bertrand and Kelly in 1966.<sup>1</sup> The clusters  $[\text{Cu}_4\text{OX}_6(\text{TPPO})_4]$  showed the metal ions to be in a tetrahedral arrangement, bridged over the edges by chloride ions and by an oxygen atom in the center of the tetrahedron, while the triphenylphosphine oxide ligands (TPPO) complete the distorted trigonal bipyramidal coordination around the copper atoms.<sup>2</sup> Since then similar clusters have been reported in the literature.<sup>3–8</sup> Several of these have been studied from a magnetostructural point of view, since a notable feature of the magnetic susceptibility data for some of these copper(II) tetramers has been the occurrence of a maximum in the temperature dependence of the magnetic moment.<sup>9</sup>

If one considers that the mathematical expression for six pairs of copper(II) ions, with the same value for the exchange constant, does not permit a maximum for the value of the magnetic moment, the experimental occurrence of this maximum is a relevant fact. To overcome this situation several models have been developed, in which the form of the curve of  $\mu$  versus  $T$  (including the maximum) were explained in terms of (a) orbital contribution to the magnetic moment<sup>10</sup> and (b) intermo-

lecular interactions between the  $\text{Cu}_4\text{O}$  clusters.<sup>3,7,11</sup> Even though both models can predict the existence of a maximum in the value of the magnetic moment, their application has been limited and/or discarded since the parameters obtained from the fit of the experimental data do not have a real physical meaning.<sup>12</sup>

A more successful scheme has been that to consider more than one value for the exchange constant  $J$  between the copper(II) ions within the  $\text{Cu}_4$  core. Several models of magnetic exchange have been developed on the basis of different symmetries.<sup>13</sup> These have been successfully used in the analysis of the existing experimental data.<sup>12,14</sup>

In the present work we analyze the magnetic behavior of the  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  cluster (IMIDH = imidazole) with the use of the existing models, and we propose a new scheme of interaction for the copper(II) ions within the  $\text{Cu}_4\text{O}$  core which is better related to the observed structure.

## Experimental Section

**Synthesis.** The  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  complex was prepared by the slow addition of 1 mmol of imidazole in methanol to a solution of 1 mmol of copper(II) chloride dihydrate in the same solvent. The resulting solution was refluxed for 30 min. Dark green crystals slowly deposited over a period of several days.

**Crystal Structure Determination.** A prismatic crystal of  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  was mounted on a glass fiber. Preliminary examination shows acceptable crystal quality. Cell parameters were calculated from least-squares fitting of 25 high-angle reflections ( $30 \geq 2\theta \geq 15^\circ$ ). Data collection was performed on a Siemens R3m diffractometer (oriented graphite monochromator, Mo  $K\alpha$  radiation) at room temperature. Data were collected for  $3.80^\circ - 50.10^\circ$  in  $2\theta$  angle. Two standards reflections collected every 98 reflections showed no significant decay. Lorentz and polarization corrections were applied to reflections. No absorption correction was applied. The structure was solved by direct methods,

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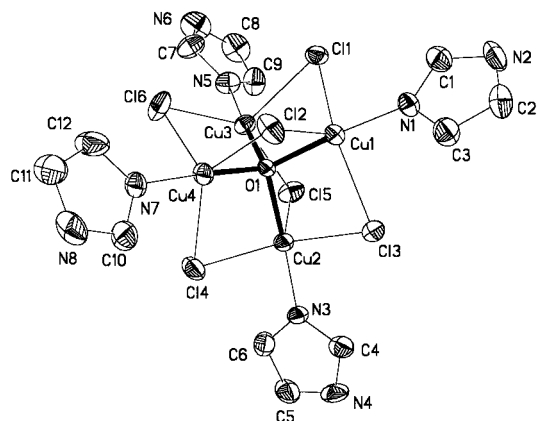
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**Table 1.** Crystal Data and Structure Refinement Details for  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4] \cdot 0.83\text{CH}_3\text{OH}$ 

empirical formula	$\text{C}_{12.83}\text{H}_{19.32}\text{Cl}_6\text{Cu}_4\text{N}_8\text{O}_{1.83}$
fw	787.23
cryst syst	orthorhombic
space group	$P2_12_12_1$
a/Å	11.469(2)
b/Å	13.933(2)
c/Å	16.778(3)
vol/Å <sup>3</sup>	2681.1(7)
Z	4
cryst size/mm	$0.1 \times 0.08 \times 0.05$
$D_c/\text{g cm}^{-3}$	1.950
$\mu/\text{mm}^{-1}$	3.76
$R^a$	0.0322
$R_w^b$	0.0695

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**Figure 1.** Molecular structure diagram of  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4] \cdot 0.83\text{CH}_3\text{OH}$ , showing atom numbering scheme and 33% displacement ellipsoids. Methanol solvate and hydrogen atoms are omitted for clarity.

completed by difference Fourier synthesis, and refined using full-matrix least-squares anisotropic refinement for all non-hydrogen atoms, using the SHELXTL PLUS package.<sup>15</sup> Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 1.2 or 1.5 times the value of the attached atom. The occupancy of the methanol molecule was refined in the last cycles of refinement and then was held constant at 0.83. Table 1 contains a summary of data collection and structural determination parameters.

**Magnetic Susceptibility Measurement.** The magnetic susceptibility of a powdered sample of the copper complex was measured in the 12–300 K temperature range using a SHE 906 susceptometer–magnetometer connected to a SQUID detector, using an applied field of 1 kG. The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms using Pascal's constants. A value of  $60 \times 10^{-6}$  cgs was assumed for the temperature independent paramagnetism (TIP) for each copper atom.

## Results and Discussion

The structure of the tetrameric molecule is shown in Figure 1. Selected bonds and angles are given in Table 2.

The structure consists of a tetrahedral arrangement of cupric ions bonded to a single central oxo ion. The  $\text{Cu}_4$  tetrahedron is slightly distorted, the copper–copper distances can be classified in three groups: a short distance of 3.061(1) Å for  $\text{Cu}(2)\text{—Cu}(4)$ ; a medium distance group of 3.114(1) Å, 3.126(1) Å, 3.125(1) Å, and 3.124(1) Å for  $\text{Cu}(1)\text{—Cu}(2)$ ,  $\text{Cu}(1)\text{—Cu}(3)$ ,  $\text{Cu}(2)\text{—Cu}(3)$ , and  $\text{Cu}(3)\text{—Cu}(4)$ , respectively; and a large distance of 3.167(1) Å for  $\text{Cu}(1)\text{—Cu}(4)$ . Coincidentally, because all copper–oxygen distances are relatively similar, the  $\text{Cu—O—Cu}$  angle

**Table 2.** Selected Bond Lengths (Å), Angles (deg), and Hydrogen Bonds (Å) for  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4] \cdot 0.83\text{CH}_3\text{OH}$ 

$\text{Cu}(1)\text{—Cu}(2)$	3.114(1)	$\text{Cu}(2)\text{—Cu}(3)$	3.125(1)
$\text{Cu}(1)\text{—Cu}(3)$	3.126(1)	$\text{Cu}(2)\text{—Cu}(4)$	3.061(1)
$\text{Cu}(1)\text{—Cu}(4)$	3.167(1)	$\text{Cu}(3)\text{—Cu}(4)$	3.124(1)
$\text{Cu}(1)\text{—O}(1)$	1.924(4)	$\text{Cu}(2)\text{—O}(1)$	1.909(4)
$\text{Cu}(3)\text{—O}(1)$	1.906(4)	$\text{Cu}(4)\text{—O}(1)$	1.903(4)
$\text{Cu}(1)\text{—Cl}(1)$	2.372(2)	$\text{Cu}(1)\text{—Cl}(2)$	2.510(2)
$\text{Cu}(1)\text{—Cl}(3)$	2.415(2)	$\text{Cu}(2)\text{—Cl}(3)$	2.383(2)
$\text{Cu}(2)\text{—Cl}(4)$	2.367(2)	$\text{Cu}(2)\text{—Cl}(5)$	2.513(2)
$\text{Cu}(3)\text{—Cl}(1)$	2.564(2)	$\text{Cu}(3)\text{—Cl}(5)$	2.408(2)
$\text{Cu}(3)\text{—Cl}(6)$	2.374(2)	$\text{Cu}(4)\text{—Cl}(2)$	2.410(2)
$\text{Cu}(4)\text{—Cl}(4)$	2.404(2)	$\text{Cu}(4)\text{—Cl}(6)$	2.473(2)
$\text{Cu}(1)\text{—N}(1)$	1.938(6)	$\text{Cu}(2)\text{—N}(3)$	1.934(6)
$\text{Cu}(3)\text{—N}(5)$	1.943(6)	$\text{Cu}(4)\text{—N}(7)$	1.961(6)
$\text{Cu}(2)\text{—O}(1)\text{—Cu}(1)$	108.7(2)	$\text{Cu}(3)\text{—O}(1)\text{—Cu}(1)$	109.5(2)
$\text{Cu}(4)\text{—O}(1)\text{—Cu}(1)$	111.7(2)	$\text{Cu}(3)\text{—O}(1)\text{—Cu}(2)$	110.0(2)
$\text{Cu}(4)\text{—O}(1)\text{—Cu}(2)$	106.8(2)	$\text{Cu}(4)\text{—O}(1)\text{—Cu}(3)$	110.2(2)
$\text{Cl}(1)\text{—Cu}(1)\text{—Cl}(2)$	110.04(8)	$\text{Cl}(3)\text{—Cu}(1)\text{—Cl}(2)$	109.04(8)
$\text{Cl}(1)\text{—Cu}(1)\text{—Cl}(3)$	138.60(8)	$\text{Cl}(4)\text{—Cu}(2)\text{—Cl}(3)$	128.61(9)
$\text{Cl}(3)\text{—Cu}(2)\text{—Cl}(5)$	106.49(8)	$\text{Cl}(4)\text{—Cu}(2)\text{—Cl}(5)$	121.81(9)
$\text{Cl}(5)\text{—Cu}(3)\text{—Cl}(1)$	108.41(8)	$\text{Cl}(6)\text{—Cu}(3)\text{—Cl}(1)$	105.71(8)
$\text{Cl}(6)\text{—Cu}(3)\text{—Cl}(5)$	142.91(9)	$\text{Cl}(4)\text{—Cu}(4)\text{—Cl}(6)$	108.08(10)
$\text{Cl}(2)\text{—Cu}(4)\text{—Cl}(6)$	115.22(9)	$\text{Cl}(4)\text{—Cu}(4)\text{—Cl}(2)$	133.94(9)
$\text{Cu}(1)\text{—Cl}(1)\text{—Cu}(3)$	78.50(6)	$\text{Cu}(4)\text{—Cl}(2)\text{—Cu}(1)$	80.09(6)
$\text{Cu}(2)\text{—Cl}(3)\text{—Cu}(1)$	80.93(6)	$\text{Cu}(2)\text{—Cl}(4)\text{—Cu}(4)$	79.79(6)
$\text{Cu}(3)\text{—Cl}(5)\text{—Cu}(2)$	78.80(6)	$\text{Cu}(3)\text{—Cl}(6)\text{—Cu}(4)$	80.22(7)
$\text{O}(1)\text{—Cu}(1)\text{—Cl}(2)$	82.53(13)	$\text{O}(1)\text{—Cu}(3)\text{—Cl}(6)$	85.95(14)
$\text{O}(1)\text{—Cu}(3)\text{—Cl}(5)$	84.38(14)	$\text{O}(1)\text{—Cu}(2)\text{—Cl}(4)$	85.37(13)
$\text{O}(1)\text{—Cu}(4)\text{—Cl}(4)$	84.45(14)	$\text{O}(1)\text{—Cu}(2)\text{—Cl}(3)$	85.42(14)
$\text{O}(1)\text{—Cu}(4)\text{—Cl}(2)$	85.7(2)	$\text{O}(1)\text{—Cu}(2)\text{—Cl}(5)$	81.44(14)
$\text{O}(1)\text{—Cu}(4)\text{—Cl}(6)$	83.2(2)	$\text{O}(1)\text{—Cu}(3)\text{—Cl}(1)$	82.69(14)

D—H	$d(\text{H} \cdots \text{A})$	atom
$\text{N}(8)\text{—H}(8\text{B})$	2.543	$\text{Cl}(1)^i$
$\text{N}(4)\text{—H}(4\text{B})$	2.777	$\text{Cl}(5)^{ii}$
$\text{N}(4)\text{—H}(4\text{B})$	2.911	$\text{Cl}(3)^{ii}$
$\text{N}(2)\text{—H}(2\text{B})$	2.054	$\text{O}(2)^{iii}$
$\text{N}(6)\text{—H}(6\text{B})$	2.485	$\text{Cl}(2)^{iv}$

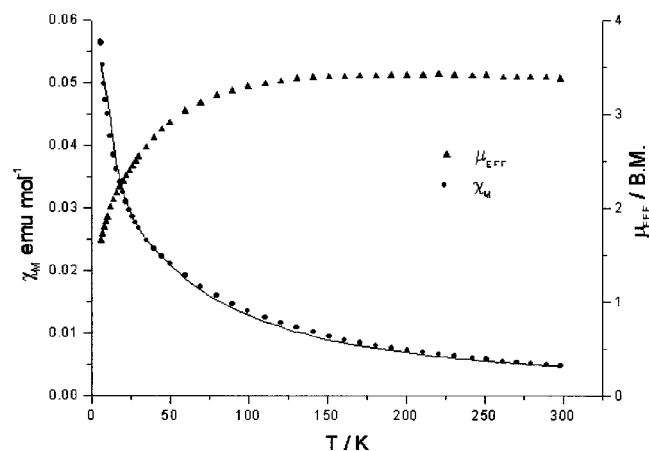
<sup>a</sup> Symmetry code of A: <sup>i</sup> $[x + 1/2, -y - 3/2, -z]$ , <sup>ii</sup> $[x + 1/2, -y - 1/2, -z]$ , <sup>iii</sup> $[-x - 2, y + 1/2, -z + 1/2]$ , <sup>iv</sup> $[-x - 5/2, -y - 1, z - 1/2]$ .

shows the same tendency, varying from a value of  $106.8^\circ$  for  $\text{Cu}(4)\text{—O}(1)\text{—Cu}(2)$ , passing by a medium value group,  $108.7(2)^\circ$  for  $\text{Cu}(2)\text{—O}(1)\text{—Cu}(1)$ ,  $109.5(2)^\circ$  for  $\text{Cu}(3)\text{—O}(1)\text{—Cu}(1)$ ,  $110.0(2)^\circ$  for  $\text{Cu}(3)\text{—O}(1)\text{—Cu}(2)$  and  $110.2(2)^\circ$  for  $\text{Cu}(4)\text{—O}(1)\text{—Cu}(1)$ , to a large value of  $111.7(2)^\circ$  for  $\text{Cu}(4)\text{—O}(1)\text{—Cu}(3)$ .

The coordination geometry around each metal center is an irregular trigonal bipyramid, where three bridged chloride atoms occupy the equatorial coordination sites. The apical coordination positions of each copper ion correspond to the central oxygen, and to the nitrogen of the imidazole group. The value for the  $\text{Cl—Cu—Cl}$  angles varies markedly around the value for the nondistorted equatorial angle in a trigonal bipyramid of  $120^\circ$ , ranging from  $106.49(8)^\circ$  to  $138.60(8)^\circ$ .

Each of the six edges of the copper tetrahedron is occupied by a bridging  $\mu_2$ -chloride ion so that each copper ion is linked to each of the others three metal ions through the central oxygen and through three separate chloride bridges. The six chloride ions comprise a fairly regular octahedron around the central oxygen atom. The values for the  $\text{Cu—Cl—Cu}$  angle do not show a great variation around the average value of  $80.25^\circ$ . A somewhat greater deviation is to be found in the relative location of three Cl atoms with respect to the  $\text{Cu—O}$  axis. The deviation from the ideal case ( $\text{O—Cu—Cl} = 90^\circ$ ) can be expressed in terms of the  $\text{O—Cu—Cl}$  angles which in this case are systematically lower than  $90^\circ$ . This same kind of distortion is found in similar tetrameric compounds with general formula  $\text{Cu}_4\text{OCl}_6\text{L}_4$

(15) SHELXTL PLUS, Release 4.1. Siemens Analytical X-ray Instruments, Madison, WI, 1990.



**Figure 2.** Temperature dependence of the (●) magnetic susceptibility and (▲) magnetic moment for  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4] \cdot 0.83\text{CH}_3\text{OH}$ . The full line corresponds to the calculated values.

reported in the literature; when L corresponds to (2-methylpyridine), the O—Cu—Cl angles vary from  $76.9^\circ$  to  $90.8^\circ$ . The authors suggested that the main reason for this distortion is the intramolecular steric effects of the methyl groups.<sup>2,4,5</sup> In the case of  $[\text{Cu}_4\text{OCl}_{10}][(\text{CH}_3)_4\text{N}]_4$ , the angles O—Cu—Cl show a slight distortion (from  $83.5^\circ$  to  $85.6^\circ$ ); it appears that intramolecular contacts between pyridine carbons and the chlorides are responsible for this distortion.<sup>5</sup>

In the crystal packing, the tetrameric nuclear unit  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  is interconnected by a number of intermolecular hydrogen bonds of the  $\text{Cl} \cdots \text{H} - \text{N}$  type to adjacent units (Table 2).

The study of the magnetic properties of  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  is based on magnetic susceptibilities measurements. The susceptibility was determined as a function of temperature in the range 12–300 K. The plot of  $\chi_M^{-1}$  vs  $T$  has a negative intercept, where data between  $140 \text{ K} < T < 289 \text{ K}$  were considered in the fit. This permitted us to obtain the value for the Weiss constant,  $\theta = -0.133 \text{ K}$ . The slope of the curve corresponds to a Curie constant of  $C = 0.3591$ , from which a magnetic moment of  $1.7 \mu_B$  per copper atom was calculated. In the title compound,  $\mu_{\text{eff}}$  remains practically constant in the temperature range of 140–289 K and then falls rapidly with further decrease in temperature (Figure 2), showing paramagnetic behavior in the first zone and weak antiferromagnetic interactions at lower temperatures, in contrast to the ferromagnetic and antiferromagnetic behavior shown by the previously reported complexes.<sup>11,16</sup>

The tetrameric copper complexes have been classified in three classes in relation to the existence of a maximum in the temperature dependence of the effective magnetic moment.<sup>3,17</sup> In class I, the magnetic moments decrease monotonically with decreasing temperature, and in class II and class III, the magnetic moment passes through a maximum and then decreases at lower temperatures. (Class II complexes have a strong maximum, while class III complexes have a slight maximum in the  $\mu$  vs  $T$  curve.) To explain the observed magnetic behavior, these compounds have been modeled by assuming idealized symmetries such as  $T_d$ ,  $C_{2v}$ ,  $D_{2d}$ , and  $C_{3v}$ .<sup>9,13</sup> The  $C_{2v}$  coupling scheme is shown in Figure 3a.

The susceptibility data of  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  was adjusted to the  $C_{2v}$  model, developed by Jotham and Kettle.<sup>13</sup> The calculated values obtained from the analytical expression were  $g = 1.98$ ,  $J = -19 \text{ cm}^{-1}$ ,  $J_S = 77.97 \text{ cm}^{-1}$ ,  $J_L = 8.7 \text{ cm}^{-1}$ , with  $\sum(\chi_{\text{calc}} - \chi_{\text{obs}})^2 / \chi_{\text{obs}}^2 = 7 \times 10^{-3}$ . However, the applicability of this model to the  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  complex is low. In the imidazole compound described in this paper, the distortion from the idealized tetrahedral geometry permits us to describe the cluster in the  $C_1$  symmetry group. In this cluster the shortest distance is Cu(4)—Cu(2) and the longest distance is Cu(4)—Cu(1). In the  $C_{2v}$  model, a distortion for noncontiguous copper pairs involving the Cu(1)—Cu(2) as the short distance and Cu(3)—Cu(4) as the long distance is considered.

Considering the  $C_1$  symmetry (Figure 3b), theoretical calculations using an isotropic spin exchange Hamiltonian:  $H = -\sum J_{ij} S_i S_j$  were done. The spin Hamiltonian appropriate for the exchange interaction of the four atoms with spin  $S = 1/2$  in  $C_1$  symmetry can be written as

$$H = -J(S_1 S_2 + S_1 S_3 + S_2 S_3 + S_3 S_4) - J_S S_2 S_4 - J_L S_1 S_4 \quad (1)$$

where  $J_S = J_{24}$ ,  $J_L = J_{14}$ ,  $J = J_{12} = J_{13} = J_{23} = J_{34}$ .

Considering  $S = S_1 + S_2 + S_3 + S_4$ ,  $S_L = S_1 + S_4$  and  $S_S = S_2 + S_4$ , eq 1 reduces to

$$H = -\frac{1}{2}J(S^2 - 3) - \frac{1}{2}(J_S - J)(S_S^2 - \frac{3}{2}) - \frac{1}{2}(J_L^2 - J)(S_L^2 - \frac{3}{2}) \quad (2)$$

On the basis of 16 spin functions, a  $16 \times 16$  secular determinant (nonsymmetry reducible) was formed. The determinant was partially diagonalized, resulting in two  $1 \times 1$  blocks, two  $4 \times 4$  blocks, and one  $6 \times 6$  blocks, generating six spin energies states:

$$E_Q = -J - \frac{1}{4}(J_L + J_S) \quad (3)$$

$$E_{T_3} = J - \frac{1}{4}(J_L + J_S) \quad (4)$$

$$E_{T_2} = \frac{1}{4}(J_L + J_S) + \frac{1}{2}r \quad (5)$$

$$E_{T_1} = \frac{1}{4}(J_L + J_S) - \frac{1}{2}r \quad (6)$$

$$E_{S_2} = J + \frac{1}{4}(J_L + J_S) + \frac{1}{2}r \quad (7)$$

$$E_{S_1} = J + \frac{1}{4}(J_L + J_S) - \frac{1}{2}r \quad (8)$$

where

$$r = [(J_S - J_L)^2 + (J_S - J)(J_L - J)]^{1/2} \quad (9)$$

These energies were substituted into the Van Vleck equation obtaining the following expression for the molar magnetic susceptibility:

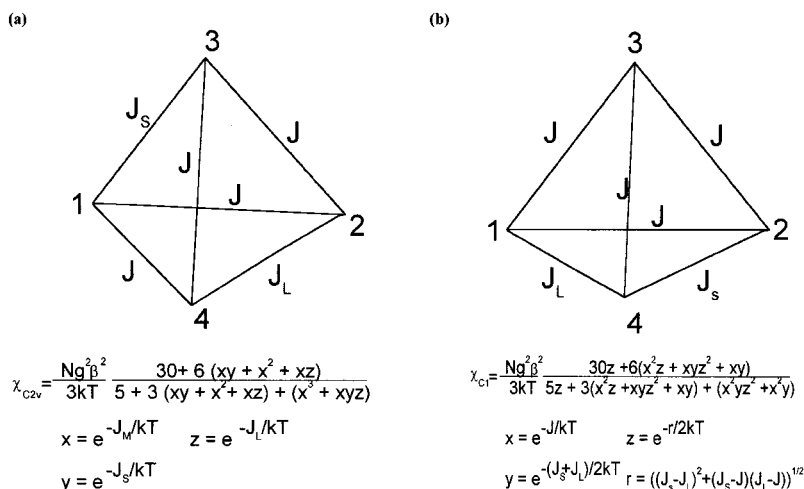
$$\chi_{\text{TET}} = \frac{Ng^2\mu_B^2}{kT} \frac{10z + 2(xyz^2 + xy + x^2z)}{5z + 3(xyz^2 + xy + x^2z) + (x^2yz^2 + x^2y)} \quad (10)$$

where  $x = \exp(-J/kT)$ ,  $y = \exp(-(J_S + J_L)/2kT)$ , and  $z = \exp(-r/2kT)$ .

The experimental susceptibility data were fitted to the susceptibility expression

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**Figure 3.** Coupling schemes for the distorted tetrahedral arrangement of copper ions in (a)  $C_{2v}$  and (b)  $C_1$  symmetries.

$$\chi = \chi_{\text{TET}}(1 - \rho) + \chi_{\text{im}}\rho + 4N\alpha \quad (11)$$

where  $\rho$  is the fractional amount of monomeric impurity which obeys the Curie law, and  $\chi_{\text{im}} = C_{\text{im}}/T$

The best fit for the magnetic data of the tetrameric complex was for  $g = 1.98$ ,  $J = -7.65 \text{ cm}^{-1}$ ,  $J_S = 83.3 \text{ cm}^{-1}$ ,  $J_L = -58.8 \text{ cm}^{-1}$ ,  $\rho = 0.057$ ,  $C_{\text{im}} = 0.34$ , with  $\sum(\chi_{\text{calc}} - \chi_{\text{obs}})^2/\chi_{\text{obs}}^2 = 1.8 \times 10^{-3}$ . These  $J$  values permit us to obtain the energies of the singlet, triplet, and quintet states described in eqs 3–8. The developed model predicts a singlet state as the ground state followed in energy by two triplet states. The calculated energy values indicate that near room temperature these states are all populated (Table 3). This scheme explains the fact that the tetrameric complex is paramagnetic at room temperature and starts to present a decrease in the magnetic moment, as the temperature is lowered and the triplet states become depopulated.

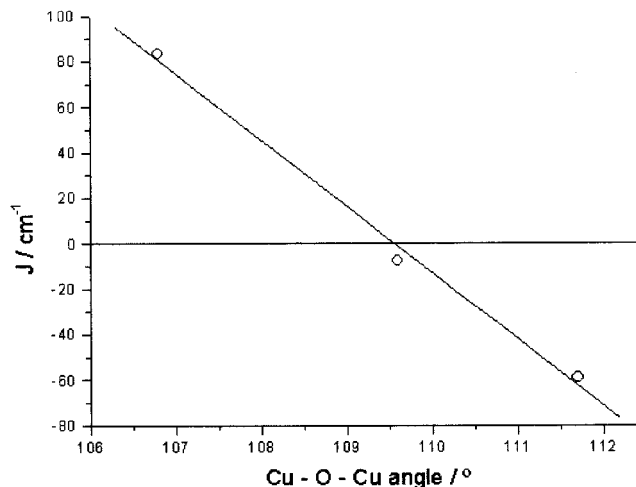
Structural data reported previously in the literature for other tetrameric copper(II) complexes, such as  $[\text{Cu}_4\text{OBr}_6\text{py}_4]$  (py = pyridine),<sup>18</sup> indicate that these complexes should be also treated in  $C_1$  symmetry, since the short and long copper–copper distances, as determined by X-ray diffraction, are also adjacent. The model developed in this paper together with the  $C_{2v}$  symmetry model were used to calculate new  $J$  values for this complex.

Our fit of the experimental data using the  $C_1$  model for  $[\text{Cu}_4\text{OBr}_6\text{py}_4]$  leads to  $J = -7.2 \text{ cm}^{-1}$ ,  $J_{34} = J_S = -4 \text{ cm}^{-1}$ ,  $J_{14} = J_L = -16 \text{ cm}^{-1}$ , and  $g = 2.15$ , while the values of the parameters for the best fit to the  $C_{2v}$  model are  $J = -8.9 \text{ cm}^{-1}$ ,  $J_{23} = J_S = -16 \text{ cm}^{-1}$ ,  $J_{14} = J_L = -4.4 \text{ cm}^{-1}$ , and  $g = 2.18$ . Even though both models predict antiferromagnetic interactions for  $[\text{Cu}_4\text{OBr}_6\text{py}_4]$ , the magnitude of  $J_L$  is inverse in relation to  $J_S$  for the  $C_1$  and  $C_{2v}$  model. Besides, the definition of  $J_S$  in the  $C_{2v}$  model is not in accordance with the crystallographic data.

Since the relative orientation of the magnetic  $d_{z^2}$  copper orbital is toward the apical oxo orbitals, permitting a good overlap between them, it is possible to consider the oxo oxygen atom as the principal pathway for the magnetic exchange in this type of tetrameric copper(II) compound. The dependence of the calculated  $J$  values with the Cu–O–Cu angle for  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  is shown in Figure 4. The obtained linear dependence clearly suggests an inversion in the magnetic behavior as the copper–oxygen–copper angle is varied. A correlation similar

**Table 3.** Energy Values ( $\text{cm}^{-1}$ ) for  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$  and  $[\text{Cu}_4\text{OBr}_6\text{py}_4]$  Obtained from  $J$  Calculated Values using the  $C_{2v}$  and  $C_1$  Models

$[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$		$[\text{Cu}_4\text{OBr}_6\text{py}_4]$	
$C_1$	$C_{2v}$	$C_1$	$C_{2v}$
68.5 ( $E_T$ )	65.0 ( $E_S$ )	12.2 ( $E_Q$ )	14.0 ( $E_Q$ )
60.8 ( $E_S$ )	56.3 ( $E_T$ )	0.4 ( $E_T$ )	0.7 ( $E_T$ )
1.5 ( $E_Q$ )	-2.7 ( $E_Q$ )	-2.2 ( $E_T$ )	-3.8 ( $E_T$ )
-13.8 ( $E_T$ )	-13.0 ( $E_T$ )	-6.8 ( $E_S$ )	-10.9 ( $E_T$ )
-56.2 ( $E_T$ )	-40.7 ( $E_T$ )	-10.4 ( $E_T$ )	-12.7 ( $E_S$ )
-63.9 ( $E_S$ )	-59.7 ( $E_S$ )	-17.6 ( $E_S$ )	-15.3 ( $E_S$ )



**Figure 4.** Dependence of the calculated coupling constants with the Cu–O–Cu angle. The plotted angle value for  $J$  corresponds to the average of the corresponding four angles.

to that observed for dinuclear copper(II) complexes bridged by hydroxo groups has been reported in the literature. For these complexes a change in the sign of  $J$  is found at  $97.6^\circ$ ,<sup>19</sup> while in the case of the tetrameric cluster  $[\text{Cu}_4\text{OCl}_6(\text{IMIDH})_4]$ , a value of  $109^\circ$ – $110^\circ$  is estimated. This large value for the angle of the bridged species can be explained by the existence of a larger degree of electronic density on the oxo group as compared to that of the hydroxo group.

Theoretical calculations have been successfully done for hydroxo bridged  $\text{Cu}_2$  complexes,<sup>20,21</sup> showing a correlation between  $J$  values and the bridging angle. These calculations

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permit us to rationalize the influence of electronic and geometric factors on the magnetic coupling. Recently, this kind of calculations had been extended to the model system  $ML_3O_2-ML_3$ , where  $L = NH_3$ .<sup>22</sup> In this model system the ferromagnetic coupling constant  $J$  shows a decreasing tendency with the growing of the Cu—O—Cu angle, from a large ferromagnetic  $J$  value to a nearly zero value, for angles varying from 80° to 110°, respectively.

The experimental decreasing tendency observed for  $J$  with the increase of the Cu—O—Cu angle for the title compound  $[Cu_4OCl_6(IMIDH)_4]$  (Figure 4) is coincident with the calculated tendency for the oxo model related complex, although in this case no change in the sign of  $J$  is predicted. The difference between the calculated and experimental values may arise from the different coordinating environment of the oxo ion and the influence of the chloride bridges.

### Conclusions

The mathematical model developed in this paper clearly shows that the calculated  $J$  values depend on the symmetry group used.

(21) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano J. *Inorg. Chem.* **1997**, *36*, 3683.

(22) Ruiz, E.; Alvarez, S.; Alemany, P. *Chem. Commun.* **1998**, 2767.

The principal pathway for the magnetic exchange in this type of tetrameric copper(II) compound has been considered to be the oxo atom.

The correlation obtained between the calculated exchange integrals and the observed Cu—O—Cu angles permits us to conclude that the change from antiferromagnetism to ferromagnetism occurs at a larger value of the considered angle than for the hydroxo pathway reported in the literature.

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**Supporting Information Available:** X-ray crystallographic file in CIF format for structure determination of complex  $[Cu_4OCl_6(IMIDH)_4]$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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