

Antiferromagnetic Behavior Based on Quasi-Orthogonal MOs: Synthesis and Characterization of a Cu₃ Oxidase Model

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We report the synthesis and structural and magnetic characterization of an original Cu₃ oxidase model. The Schiff base ligand used in the synthesis derives from condensation of acetylacetone with glycine amino acid. The K[Cu₃(L)₃(μ₃-OH)]·(H₂O)₂ complex crystallizes at room temperature in the tetragonal P₄₃2₁2 space group with *a* = 20.540(3) Å and *c* = 15.866(6) Å and consists of triangular Cu₃ units. The magnetic behavior interpretation suggests the presence of spin frustration, which has been investigated by means of ab initio DDCI calculations. It is shown that the system should be viewed as a “ménage à trois” spin-coupled pattern mediated by a central hydroxo group, lifting the doublet degeneracy by ~8 cm⁻¹.

Introduction

Polynuclear metal complexes have been the focus of tremendous attention for many years due to the richness of their implications in catalysis, magnetism, and biology. Within the scope of such applications, experimental and theoretical investigations of simple paramagnetic clusters have turned out to be a promising route to the understanding of biological analogues.¹ Among the richness of metalloenzymes, copper-based systems have attracted much attention since many, such as hemocyanine and laccase, have been reported as determining agents in the activation of the O₂ molecule.² While the former consists of Cu₂ units,³ the O₂

reduction involving multicopper oxidases proceeds through the so-called “native intermediate” which can be described as an antiferromagnetically coupled trinuclear copper(II) cluster.⁴ This particular type of architecture has been reported in the literature as prototypes to model the structural, magnetic, and functional properties of multicopper oxidases.

Most of the reported trinuclear copper(II) complexes have either a linear arrangement of the metal centers⁵ or a Cu₃(μ₃-X) unit (X = Cl, OR). Architectures containing a μ₃-OH link are associated with either pyrazolide,⁶ triazolide,⁷ oximate,⁸ or ketonate⁹ peripheral ligands. The ketonate derivatives are based on tridentate N,N,O Schiff-base ligands derived from the 1:1 condensation of acetylacetone and

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various diamines. While O,N,O Schiff bases are known to generate molecular architectures with various nuclearity, to the best of our knowledge, no example of trinuclear Cu₃ involving such donor ligand has been reported so far.

Apart from the biological significance, this particular type of architecture can be viewed as geometrically spin frustrated and prototypes for evaluation of the relevance of magnetic exchange models.¹⁰ The concept of spin frustration was originally introduced in 1977 in relation with the phenomenon of spin-glass behavior.¹¹ Since this pioneering work, this concept has been widely applied in solid-state physics^{10b,12} and appeared more recently in the molecular magnetism community.^{10a,13} For instance, such metallic anti-ferromagnetic systems have been proposed as promising targets for molecular-based quantum information processing.¹⁴ In perfect D_{3h}/C_{3v}-symmetric trimers, with antiferromagnetically coupled integer spins, the ground state is diamagnetic and nondegenerate. In contrast, the S = 1/2 ground state resulting from half-integer spin arrangement is doubly degenerate.¹³ However, this picture does not hold as soon as the triangular arrangement deviates from the three-fold symmetry which is observed in most of the synthetic models.

Density functional theory (DFT) and explicitly correlated ab initio calculations have been tentatively used to propose a detailed description of their electronic structures and rationalize the physical origin of their magnetic and spectroscopic features. A combined quantum mechanical and molecular mechanical (QM/MM) study has been recently

undertaken to analyze the O₂ reductive cleavage in the catalytic cycle of multicopper oxidase.¹⁵ Whereas DFT combined with the broken symmetry approach¹⁶ has been successfully applied to calculation of magnetic exchange interactions of binuclear systems,¹⁷ few examples are devoted to trinuclear transition-metal complexes.^{5c,e,18} Magnetostructural correlations have been performed in linear trinuclear^{5c,18b} copper(II) complexes bridged by either by μ -hydroxo or mixed μ -hydroxo μ -acetato ligands. Surprisingly, none of the triangular Cu₃ systems which have been treated by DFT^{18c-e} possess a bridging μ_3 -ligand. The scarcity of theoretical studies based on monodeterminantal approaches might be explained by the known deficiencies of such methods^{19,20} in the treatment of spin states with a multireference character. To overcome these limitations, correlated multireference correlations are appealing approaches. The only example proposed by Chalupsky and co-workers proceeds through a thorough analysis of spectroscopic parameters based on complete active space second-order perturbation theory (CASPT2)²¹ and multireference difference dedicated configuration interaction (CI)²² calculations for a series of (μ_3 -hydroxo)- and (μ_3 -oxo)-bridged trinuclear Cu(II) models.¹⁹

In this paper, we report the synthesis as well as structural and magnetic characterization of a new copper(II) trinuclear complex exhibiting a triangular shape with a μ_3 -OH central group. Ab initio theoretical calculations were performed to establish the spectroscopy of the energy levels of the system and discuss the presence or not of spin frustration. Special attention has been devoted to the energy splitting between the expected doublet states.

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Table 1. Crystal Data and Structural Refinement Parameters for **1**

mol formula	C ₂₁ H ₃₂ Cu ₃ K ₁ N ₃ O ₁₂
fw (g·mol ⁻¹)	748.23
cryst syst	tetragonal
space group	<i>P</i> 4 ₃ 2 ₁ 2 (No. 96)
<i>a</i> (Å)	20.540 (3)
<i>c</i> (Å)	15.866 (6)
<i>V</i> (Å ³)	6694 (3)
<i>Z</i>	8
Mo Kα wavelength (Å)	0.71073
cryst color	green
cryst shape	cubic
cryst size (mm ³)	0.30 × 0.33 × 0.45
no. of reflns	5890
<i>R</i> _{int}	0.022
<i>T</i> (K)	293
<i>D</i> (g·cm ⁻³)	1.485
<i>μ</i> (mm ⁻¹)	2.068
<i>R</i> / <i>R</i> _w [<i>I</i> / <i>σ</i> (<i>I</i>) > 3] ^a	0.0367/0.0416
<i>S</i>	1.02
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e ⁻ ·Å ⁻³)	0.62/-0.25
used reflns	4018
refined params/restraints	362/0
Flack parameter	0.42 (2)

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

Experimental Section

Synthesis. *Synthesis of the Ligand LHK.* A cold aqueous solution (10 mL) of KOH (1.10 g, 25 mmol) was slowly added to a cold aqueous solution (10 mL) of glycine (1.88 g, 25 mmol) under stirring. After 30 min of additional stirring, acetylacetone (2.0 g, 20 mmol) in methanol (10 mL) was added dropwise. The solution was stirred overnight, concentrated, washed with petroleum ether, dissolved in methanol, and filtered. Removal of the solvent left crude product (yield 71%).

*Synthesis of K[Cu₃(L)₃(μ₃-OH)]·(H₂O)₂ (**1**).* LHK was dissolved in 10 mL of methanol (195 mg, 1 mmol), and CuCl₂·2H₂O (170 mg, 1 mmol) was added dropwise under stirring. Addition of triethylamine (0.3 mL) leads to a deep-blue solution. Slow evaporation of the solvent leads in a few days to crystals of K[Cu₃(L)₃(μ₃-OH)]·(H₂O)₂ (**1**).

Crystallographic Data Collection and Refinement. Diffraction data were collected at room temperature using a Nonius KappaCCD and the related analysis software:²³ Lorentz-polarization correction, peak integration, and background determination were carried out with the DENZO program; frame scaling and unit-cell parameters refinement were made with the SCALEPACK program. The lattice constants were refined by least-squares refinement using 4018 reflections (0.99° < θ < 24.8°). No absorption correction was applied to the data sets. The structure was solved by direct methods using the SIR97 program²⁴ combined with Fourier difference syntheses and refined against *F* using reflections with [*I*/*σ*(*I*) > 3] via the CRYSTALS program.²⁵ All atomic displacements for non-hydrogen atoms have been refined with anisotropic terms. Hydrogen atoms have been located either theoretically or by Fourier difference and refined keeping some constraints on their positions and the isotropic atomic displacements. X-ray crystallographic data and refinement details and results are summarized in Table 1. Selected

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

Cu1–O1	2.350(4)	Cu3–O3	2.520(4)	Cu1–O1–Cu2	94.9(2)
Cu1–O4	2.062(3)	Cu3–O4	1.976(3)	Cu2–O2–Cu3	92.0(1)
Cu1–O3	1.903(4)	Cu3–O2	1.906(4)	Cu1–O3–Cu3	92.2(2)
Cu2–O2	2.398(4)	Cu1–Cu3	3.217(1)	Cu1–O4–Cu2	104.8(1)
Cu2–O4	1.968(3)	Cu1–Cu2	3.194(1)	Cu1–O4–Cu3	105.6(2)
Cu2–O1	1.972(4)	Cu2–Cu3	3.115(1)	Cu2–O4–Cu3	104.4(1)

interatomic distances, bond lengths, and bond angles are listed in Table 2.

Magnetic Measurements. The magnetic measurements were performed on a polycrystalline sample of **1** using of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from –5 to 5 T. The magnetic data were corrected for the sample holder and diamagnetic contribution.

Computational Details. It is known that ab initio quantum chemical calculations are a powerful tool to extract both information upon excitation energies and representations of the ground- and excited-state wavefunctions. The strategy we used consists of the evaluation of the differential contributions which are likely to account for the energy splitting in the low part of the spectrum. A reasonable zeroth-order description is accessible by means of complete active space self-consistent field (CASSCF) calculations which incorporate qualitatively the leading electronic configurations with a so-called CAS(*n*,*m*) including *n* electrons in *m* molecular orbitals (MOs). At this level of calculation, the static correlation effects are taken into account variationally. On top of the CASSCF wavefunction, dynamical polarization and correlation effects arising from excitations out of the active space were then included following the dedicated difference configuration interaction (DDCI)^{2b} method implemented in the CASDI code.²⁶ The configuration interactions expansion excludes all double excitations from inactive (i.e., doubly occupied) to virtual (i.e., vacant) molecular orbitals. In fact, it is shown that for vertical transitions which involve excitations depicted by the active space choice (i.e., at zeroth-order) such contributions cancel out at the second order of perturbation theory.²⁷ Degrees of freedom defined as a hole or a particle created in doubly occupied or empty MOs in all reference configurations account for the CI expansion. Thus, one defines successively DDCI-1, -2, and -3 levels of calculation with respect to the number of degrees of freedom solicited in the configuration generation.

Our calculations were performed using the MOLCAS package.²⁸ Basis sets and pseudo-potentials²⁹ on the Cu atoms (9s6p6d)/[3s3p4d] as well as ANO basis sets on the nearest-neighbor atoms (10s6p3d)/[3s2p1d] for N and (10s6p3d)/[3s2p1d] for O were used (i.e., double-ζ plus polarization for the valence), whereas the rest of the molecule was described with smaller basis sets (double-ζ), i.e., (10s6p3d)/[3s2p] for C and O and (7s3p)/[2s] for H.³⁰ Many cluster calculations using this particular DDCI framework for vertical transition analyses have been reported in the literature. However, for specific issues such as spin transition effects, the need for polarization functions has been recently reported.³¹

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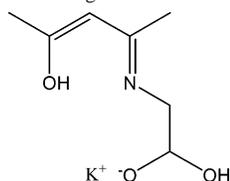
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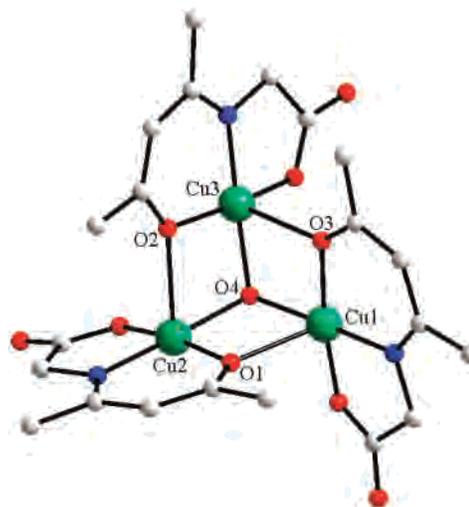
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Scheme 1. Schematic Drawing of the LHK Ligand


Results and Discussion

Synthesis. Schiff base ligands are typically formed by condensation of primary amines and aldehydes or ketones. A tremendous amount of work has been devoted to the chemistry of metal complexes with such ligands containing several donor atoms, particularly those deriving from β -diketone such as acetylacetonone.³² The resulting multidentate ligands are widely used in the research field of molecular magnetism. In that sense, we recently reported several examples of molecular clusters exhibiting interesting magnetic properties involving N,N,O or O,N,O ligands.³³ The starting idea of the present study was to use amino acid as the primary amine in the condensation as a carboxylic group may generate various coordination modes with metal ions. However, the glycine amino acid is not soluble in the usual organic solvents such as methanol is generally used for such reaction. Obviously, amino acids are soluble in water, but the imine function of the Schiff base ligand formed is quite sensitive to water. Moreover, when using a minimum amount of water in methanol, the reaction does not occur because of precipitation of the amine in the solvent mixture. This was reversed using a base (KOH) to generate the anionic form of the amine and make it react with acetylacetonone. The ligand can then be obtained in good yield (71%) in its salt form (Scheme 1). The trinuclear complex was then obtained by reacting the ligand with copper chloride in methanol in the presence of triethylamine to deprotonate the ligand. Blue single crystals appear after several days of slow evaporation of the solvent.

X-ray Single-Crystal Structure. The complex crystallizes in the tetragonal $P4_32_12$ space group (No. 96) with the $K[Cu_3(L)_3(\mu_3-OH)] \cdot (H_2O)_2$ refined formula. The crystal structure is built from association of anionic $[Cu_3(L)_3(\mu_3-OH)]^-$ trinuclear units (**1**, Figure 1) with K^+ cations that ensure structural neutrality. The metallic cluster is constituted by three CuL subunits in which each Cu(II) ion is coordinated to a deprotonated tridentate O,N,O L^{2-} ligand. The subunits are held together by two distinct bridging systems: (i) the μ_3 -hydroxy group (O4) which is coordinated to each of the three copper centers as often encountered^{6–9} and (ii) the three bridging carbonyl oxygen atoms, each of them belonging to a different ligand. The resulting trinuclear species does not


Figure 1. Molecular structure of **1** (hydrogen atoms have been omitted for clarity).

contain any C_3 threefold symmetry axis, and it can be viewed as a cubane-like architecture with one corner missing.

All the copper(II) ions are surrounded by five donor atoms (four oxygen and one nitrogen atoms). The Addison parameters τ^{34} of 0.13, 0.13, and 0.15 for Cu1, Cu2, and Cu3, respectively, indicate a slightly distorted square pyramid. Each copper(II) ion lies in the center of the square plane with long Cu–O apical bond lengths (Figure 1 and Table 2), one significantly differing from the other two. Indeed, at 293 K, the Cu3–O3 distance is equal to 2.520(4) Å, in contrast with 2.350(4) and 2.398(4) Å for Cu1–O1 and Cu2–O2, respectively. Therefore, the Cu– μ_2 -O(L)–Cu cores are characterized by the alternation of a long and a short Cu–O bond length with Cu–O–Cu angles close to 92° for Cu2–O2–Cu3 and Cu3–O3–Cu1, and 95° for Cu1–O1–Cu2 (Table 2). The bond lengths between the metal ions and the central μ_3 -O(H) Cu2–O4 and Cu3–O4 are almost identical (1.968(3) and 1.976(3) Å, respectively), whereas Cu1–O4 is slightly longer (2.062(3) Å) (Table 2). The μ_3 -O4 atom is located 0.805(2) Å above the plane defined by the three copper(II) ions. This induces a Cu–O–Cu bond angle of nearly 104°. Regarding the Cu–Cu distances, it clearly appears that the Cu₃ triangle is not equilateral as one distance is shorter (3.1153(8) Å) than the other two (3.1937(9) and 3.2169(9) Å).

Within the network the trinuclear units are connected to each other through ionic bonds involving the potassium cations and the free oxygen atoms of the acid function and through hydrogen bonds with water molecules, leading to a dense 3D packing.

Magnetic Properties. The experimental thermal behavior of the magnetic susceptibility shows a continuous decrease from 1.16 (300 K) to 0.42 cm³ K mol⁻¹ (2 K) (Figure 2), indicating antiferromagnetic (AF) interactions. In a first approximation, this behavior was fitted using the $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3)$ spin Hamiltonian for a perfectly C_3

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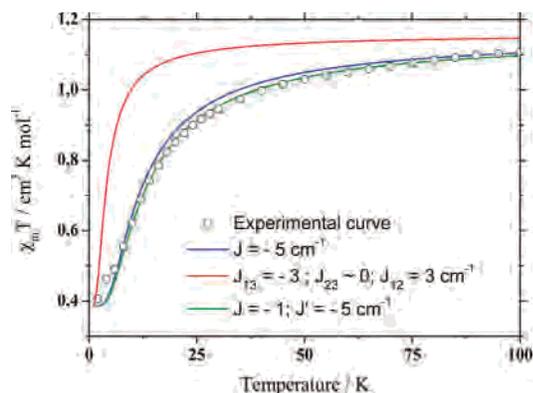


Figure 2. Experimental and simulated χ_{MT} vs T curves (see text).

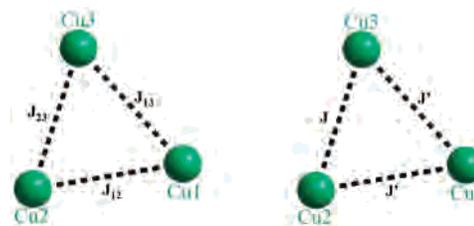
spin 1/2 arrangement. The single $J = -5 \text{ cm}^{-1}$ ($g = 2.03$) constant allows a good reproduction of the experimental behavior (Figure 2). However, since the Cu–Cu distances range from 3.115(1) to 3.217(1) Å, the triangle deviates from perfect C_3 symmetry. To account for this deviation introduction of two or three constants leads to several sets of parameters whose relevance and underlying physics has to be clarified. In addition, due to the kinship of **1** with the “native intermediate”, we felt that a detailed inspection of the electronic structure of such an open-shell system would be desirable.

Ab Initio Calculations. Explicitly correlated multireference calculations were carried out to clarify the magnetic patterns in this biological model. These calculations aim to investigate (i) the influence of the ML_5 structural variations which are likely to modulate the $\{Q, D_1, D_2\}$ spectrum where $|Q\rangle = 1/\sqrt{3}(|12\bar{3}\rangle + |\bar{1}23\rangle + |\bar{1}\bar{2}3\rangle)$, $|D_1\rangle = 1/\sqrt{2}(|\bar{1}23\rangle - |12\bar{3}\rangle)$, and $|D_2\rangle = 1/\sqrt{6}(|\bar{1}23\rangle + |12\bar{3}\rangle - 2|\bar{1}\bar{2}3\rangle)$ stand for the quartet and two doublet states and 1, 2, and 3 stand for the singly occupied magnetic orbitals localized on the respective copper ions and (ii) the role of the copper-solvated hydroxy group linked to the three Cu(II) ions.

It is known that single-determinantal methods might not be adapted to predict the multiplets of spin-coupled systems.³⁵ Complete active space self-consistent field calculations (CASSCF) including n electrons in m molecular orbitals (MOs) were performed (CAS(n,m)) on a simplified complex (methyl groups replaced by H atoms) to incorporate the leading configurations in the states of interest. Since the ratio between the ionic and neutral forms can be dramatically increased,³⁶ one has to incorporate dynamical correlation effects to fully account for the energy gaps. This particular framework has been shown to provide accurate results for magnetic multicopper compounds.³⁷

Considering the architecture of **1**, a first approach lies in a dimer description of the Cu_3 cluster involving three magnetic exchange coupling constants (Scheme 2) account-

Scheme 2. Three-Parameter (left) and Two-Parameter (right) Models



ing for the singlet–triplet energy difference in the Cu_2 units.³⁸ Thus, CAS(2,2) and subsequent DDCI-3 calculations were performed and led to $J_{13} = -3$, $J_{23} \approx 0$, and $J_{12} = 3 \text{ cm}^{-1}$. Any enlargement of this active space leaves the extra MOs either empty or doubly occupied. On the basis of the Heisenberg spin Hamiltonian $\hat{H} = -2\sum_{i,j} J_{ij}\hat{S}_i\hat{S}_j$, this set of parameters leads to $\Delta E_1 = -\Delta E_2 = 5 \text{ cm}^{-1}$, with $\Delta E_1 = E(D_1) - E(Q)$ and $\Delta E_2 = E(D_2) - E(Q)$. Even though the AF character is conserved, this set of parameters fails to accurately reproduce the experimental data (Figure 2). As expected, this drawback can be ascribed to the prime role played by the central oxygen atom O4. As a consequence, this Cu_3 architecture may not be split into three pieces.

Therefore, CAS(3,3)SCF calculations were carried out on the whole Cu_3 unit extracted from the 293 K crystal structure. On the basis of the quartet MOs, the energy splitting in the $\{Q, D_1, D_2\}$ spectrum was estimated using the DDCI approach. For analytical purposes and reduction of the CI space, these MOs were relocalized on each Cu atom (Figure 3) and consist mainly of the copper(II) $d_{x^2-y^2}$ components perpendicular to the long Cu–O distance. As expected, the D_1, D_2 , and Q Ms = 1/2 wavefunctions are largely dominated by the Heisenberg eigenstates.³⁹ Our results are summarized in Table 3. Strikingly, the deviation from orthogonality between the magnetic orbitals (Figure 3) is rather small ($\sim 10^\circ$), and ferromagnetic interactions might be anticipated. As seen in Table 3, the ferromagnetic behavior survives up to a DDCI-2 level of calculation. In order to reduce the multireference expansion in the demanding DDCI-3 calculations, only the most relevant determinants were selected according to spatial proximity considerations through a threshold on the exchange integral values.⁴⁰ ΔE_2 and ΔE_1 were calculated for different threshold values, and extrapolation to the full DDCI-3 space was ultimately performed.^{37,41} Thus, the energy difference between the two doublets $\Delta E_2 - \Delta E_1 \approx 8 \text{ cm}^{-1}$ obtained at this level of calculation suggests that spin frustration should be ruled out, Scheme 3.

Nevertheless, our results show that the polarization effects are likely to stabilize a doublet ground state (i.e., Q and D_1 are almost degenerate in Table 3 and Scheme 3) in agreement with the experimental AF behavior. Using the extrapolated DDCI-3 ΔE_1 and ΔE_2 values, one can evaluate the magnetic

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(39) Calculated quartet $|Q\rangle = 0.57(|12\bar{3}\rangle + |\bar{1}23\rangle + |\bar{1}\bar{2}3\rangle)$ and doublets $|D_1\rangle = -0.09|12\bar{3}\rangle + 0.64|\bar{1}23\rangle - 0.73|\bar{1}\bar{2}3\rangle$ and $|D_2\rangle = 0.79|12\bar{3}\rangle - 0.47|\bar{1}23\rangle - 0.32|\bar{1}\bar{2}3\rangle$.

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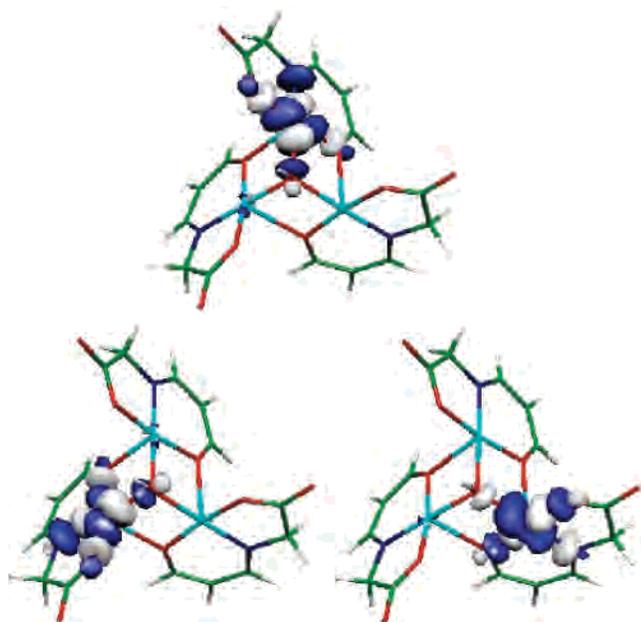
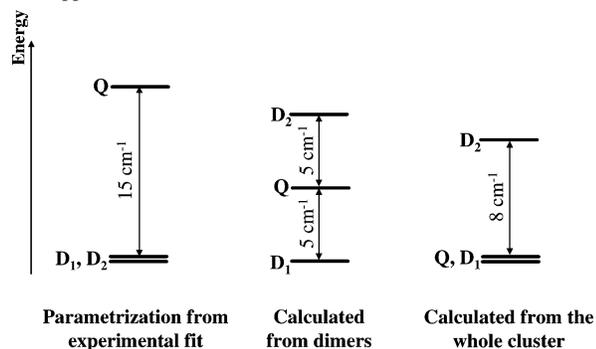


Figure 3. Relocalized magnetic orbitals of **1**.

Scheme 3. Q , D_1 , and D_2 Energy Spectrum with Respect to the Model Approaches Described in the Text



exchange constants difference $J - J' = 4 \text{ cm}^{-1}$ (Scheme 2). Under this constraint, the experimental data were finally fitted with temperature-independent $J = -1$ and $J' = -5 \text{ cm}^{-1}$ values (Figure 2). In C_3 symmetry it is known that the ground state is degenerate ($E(D_1) = E(D_2)$) with the quartet lying $-3J$ higher in energy (Scheme 3). This is to be contrasted with our calculated low-energy spectrum of **1**. The non-equivalence between the three ML_5 subunits clearly accounts for the observed degeneracy lifting. Nevertheless, this instability of the C_3 geometry leads to important spin density variations¹³ which might be accessible through polarized neutron diffraction. Interestingly, a valence-only picture would fail to properly account for this rather original situation.

Table 3. Calculated Doublet–Quartet Energy Gaps (cm^{-1}) on the Whole Cu_3 Cluster

	DDCI-1	DDCI-2	extrapolated DDCI-3
ΔE_1	7.0	5.0	~ 0
ΔE_2	14	11	8.0

Concluding Remarks

Our accurate multireference calculations have provided insightful information into the magnetic pattern of a newly synthesized trinuclear oxidase model. It is known that the electronic factors related to the position of the central μ_3 -OH group are crucial. The shorter the distance of the OH group above the plane formed by the three copper ions and the larger Cu–O(H)–Cu' angle, the stronger the antiferromagnetic character. All extracted/calculated exchange coupling constants agree with this general trend.^{9b,e} Importantly, the splitting of the Cu_3 complex into three dimers does not allow one to fit the magnetic susceptibility curve. As a result of the relatively large system under interest and the absence of any symmetry element, our strategy was to extrapolate the best available results on the whole cluster. Using the 293 K structure, we found that the doublets splitting in this three spin 1/2 system is $\sim 8 \text{ cm}^{-1}$ with a quartet–doublet quasi-degeneracy (Table 3) a reflection of the nonfrustrated character. These results extracted from rigorous multireference calculations make **1** a very promising synthetic model of multicopper oxidases. Not only the spin-coupled system must be described as a global “ménage à trois” spin 1/2, but high enough a level of calculation is also necessary to account for the observed antiferromagnetic behavior. Due to the tiny energy differences and possible structural deformations at low temperature, further theoretical and experimental investigations on this “native intermediate” analogue are currently in progress.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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