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Ferromagnetic Coupling between Copper(II) Centers through the Diamagnetic Zinc(II) Ion: Crystal Structure and Magnetic Properties of $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)]\cdot 0.5H_2dmg\cdot H_2O$ (H_2dmg = Dimethylglyoxime)

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A new heterotrinuclear complex of formula $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)]\cdot 0.5H_2dmg\cdot H_2O$ ($C_{18}H_{34}Cu_2N_9O_{11}Zn$, **1**) ($H_2dmg$ = dimethylglyoxime) has been synthesized and its crystal structure determined by single-crystal X-ray diffraction. It crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 11.414(1)$ Å, $b = 11.992(3)$ Å, $c = 12.567(10)$ Å, $\alpha = 91.27(6)°$, $\beta = 111.46(2)°$, $\gamma = 112.24(2)°$, and $Z = 2$. The structure consists of a chain of neutral $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)]$ trinuclear units and noncoordinated H_2dmg and water molecules. The configuration around the zinc atom is distorted trigonal bipyramidal with four oximate oxygens from two $[Cu(Hdmg)(dmg)]^-$ fragments (each one acting as a bidentate ligand through its deprotonated oximate oxygens in *cis* positions) occupying one axial and the three equatorial positions and an additional oximate oxygen from a symmetry-related $[Cu(Hdmg)(dmg)]^-$ fragment filling the remaining axial position. The environment around Cu(1) and Cu(2) is distorted square pyramidal with four oximate nitrogen atoms building the equatorial plane. An oxygen atom [O(9)] from a water molecule and an oximate oxygen from a symmetry-related $[Cu(Hdmg)(dmg)]^-$ fragment occupy the apical position of the square pyramids around Cu(1) and Cu(2), respectively. The trinuclear units are repeated through inversion centers standing at the middle of the $Zn(1)\cdots Zn(1)^{i}$ and $Cu(2)\cdots Cu(2)^{ii}$ vectors leading to a chain which runs parallel to the diagonal of the *ac*-plane. The $Cu(1)\cdots Cu(2)$, $Zn(1)\cdots Zn(1)^{i}$, and $Cu(2)\cdots Cu(2)^{ii}$ separations are 5.506(2), 3.390(2), and 3.930(2) Å, respectively. **1** exhibits a characteristic ferromagnetic behavior with a continuous increase of the $\chi_M T$ product as the temperature is lowered from 300 to 2.0 K. The field dependence of the magnetization at 2.0 K is consistent with a low-lying quintet state. The only efficient exchange pathways responsible for the overall ferromagnetic coupling in **1** are the diamagnetic zinc(II) ion and the out-of-plane double-oximato bridge, the magnitude of the magnetic coupling between the copper(II) ions through these bridging units being 3.9 and 5.1 cm^{-1}, respectively.

Introduction

Ferromagnetic exchange interaction between distinct metal centers has been widely observed in molecular magnetism provided that the magnetic orbitals of each metal ion are orthogonal.[2] This approach proved to be successful for Cu^{II}-VO^{IV} dimers,[3] $Cr^{III}Ni^{II}_3$ tetramers,[4] $Cu^{II}Mn^{III}$ chains,[5] and even two-[6] or three-dimensional $Cr^{III}Ni^{II}$ networks.[7] The same strategy was proposed to achieve a ferromagnetic exchange interaction also between two identical magnetic centers when using an appropriate bridging ligand.[2] In fact, preferred parallel spin alignment occurs in this case if the individual building blocks containing unpaired electrons are assembled in such a way that the magnetic orbitals are kept orthogonal to each other. This idea materialized a few years ago with π-type organic radicals which are bound to a diamagnetic metal ion [*i.e.*, titanium(IV), germanium(IV), tin(IV), or gallium(III)][8,9] properly selected to fulfill this last requirement. Moreover, the superexchange interactions are mediated by the metal ion through their empty or fully occupied orbitals, leading thus to a moderately strong ferromagnetic coupling between the organic radicals. For instance, this interaction is as large as 56 cm^{-1} for the Ti(IV) derivative.[8] Along this line, it would be desirable to extend this organic approach to ferromagnetism to purely inorganic molecules (*i.e.*, transition metal complexes).

With this idea in mind, we synthesized the trinuclear complex of formula $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)]\cdot 0.5H_2dmg\cdot H_2O$ (**1**) (H_2dmg = dimethylglyoxime) by the reaction of the Zn(II) cation with the $[Cu(Hdmg)_2]$ precursor. In fact, $[Cu(Hdmg)_2]$ is known to coordinate to metal ions in a chelating or a bis(chelating) fashion after the loss of either one or two oxime

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protons. Moreover, the NO oxime group has a remarkable efficiency to mediate magnetic interactions when it acts as a bridging ligand.[10,11] Finally, the fact that the zinc(II) ion commonly assumes tetrahedral or trigonal bipyramidal geometries in its complexes makes our choice particularly well suited in order to give rise to a non-negligible ferromagnetic interaction between the copper(II) ions mediated by the zinc(II) ion due to the strict orthogonality between the copper magnetic orbitals with this peculiar topology. We report in this paper on the crystal structure and the magnetic properties of complex **1**, which constitutes a representative example of this new approach in designing inorganic ferromagnetic materials.

Experimental Section

Materials. H_2dmg and $Zn(CH_3COO)_2\cdot 2H_2O$ were purchased from commercial sources and used as received. The complex $[Cu(Hdmg)_2]$ was prepared as reported previously.[10b] Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Universidad Autónoma de Madrid, Spain. Metal contents were determined by absorption spectrometry.

Synthesis. Zinc(II) acetate dihydrate (110 mg, 0.5 mmol) dissolved in a minimum amount of methanol was added to a hot ethanolic solution (50 cm^3) of $[Cu(Hdmg)_2]$ (294 mg, 1.0 mmol). The mixture was charged with triethylamine (2 cm^3) and refluxed with stirring for 1 h. Then, the solution was filtered and allowed to evaporate slowly at room temperature. Black rhombic prisms of **1** suitable for X-ray analysis were obtained after 2 weeks. They were collected by filter suction and air-dried. Anal. Calcd for $C_{18}H_{34}N_9O_{11}Cu_2Zn$ (**1**): C, 29.02; H, 4.60; N, 16.92; Cu, 17.05; Zn, 8.79. Found: C, 29.59, H, 4.55; N, 16.58; Cu, 16.91; Zn, 8.61. Selected IR data:[10] $\nu(CN) = 1577s$ (sp), $\nu(NO) = 1201s$ (sp), $\nu(OH\cdots O) = 2450$ w (br), and $\gamma(OH\cdots O) = 849$ w (sp).

Physical Techniques. The IR spectrum (KBr pellets) was recorded on a Perkin-Elmer 1750 FTIR spectrometer. Magnetic susceptibility measurements (2.0−300 K) under an applied magnetic field of 0.2 T and variable-field (0−6 T) magnetization data at 2.0 K were carried out with a Metronique Ingenierie SQUID magnetometer. Diamagnetic corrections to the susceptibility of complex **1** were calculated from Pascal's constants.[12] Magnetic susceptibility data were also corrected for temperature-independent paramagnetism [60×10^{-6} cm^3 per copper(II) ion].

X-ray Data Collection and Structure Refinement. A crystal of dimensions $0.60 \times 0.45 \times 0.20$ mm was mounted on a Philips PW 1100 four-cycle diffractometer and used for data collection. Diffraction data were collected at 18 °C by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) with the $\omega-2\theta$ scan technique. The unit-cell parameters were determined from least-squares refinement of 25 strong reflections in the $15° \leq \theta \leq 16°$ range. The crystallographic data are summarized in Table 1. Two standard reflections measured every 2 h showed no change during data collection. Intensity data were corrected for Lorentz-polarization. An empiric absorption correction was also carried out by using the DIFABS program.[13] The introduction of a secondary extinction coefficient was unnecessary.

The structure was solved by direct methods followed by successive Fourier syntheses and least-squares refinements on *F*. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms could not be found on difference maps, and only those of the methyl groups were geometrically located. Their positions were not refined, and they were given an overall isotropic thermal parameter. Least-squares refinements with approximation in five blocks were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$ ($|F_o|$ and $|F_c|$ are the observed and calculated structure factors). Atomic scattering factors with an anomalous dispersion correction were taken from CRYSTALS.[14] Of the 4537 measured reflections, 3022 were unique with $I > 3\sigma(I)$. These data were used in the final refinement of the structural parameters to converge to final residuals R and R_w of 0.074 and 0.082, respectively. The values of the residual maxima and minima in the final Fourier-difference maps were 1.1 and −1.0 e Å^{-3}, respectively. The occurrence of a significant number of weak intensity reflections for which the *R* value is high accounts for the magnitude of the crystallographic residuals. Molecular drawings were performed with the CAMERON program.[15] Final atomic fractional coordinates for non-hydrogen atoms and main interatomic bond lengths and angles are listed in Tables 2 and 3, respectively. A complete list of crystal data and structure refinement, anisotropic temperature factors, hydrogen atom coordinates, nonessential bond distances and angles, least-squares planes, and intermolecular hydrogen bonds (Tables S1−S6) are available as Supporting Information.

Table 1. Crystallographic Data for $Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)\cdot 0.5H_2dmg\cdot H_2O$ (**1**)

formula	$C_{18}H_{34}N_9O_{11}Cu_2Zn$
a, Å	11.414(1)
b, Å	11.992(3)
c, Å	12.567(10)
α, deg	91.27(6)
β, deg	111.46(2)
γ, deg	112.24(2)
V, Å^3	1456(3)
Z	2
fw	745.0
space group	$P\bar{1}$ (No. 2)
T, °C	18
ρ_{calcd}, g cm^{-3}	1.70
λ, Å	0.710 73
μ, cm^{-1}	23.6
R^a	0.074
$R_w{}^b$	0.082

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

Results and Discussion

Description of the Structure. The structure of complex **1** consists of polymeric neutral $[Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)]$ units, uncoordinated H_2dmg ligands, and crystallization water molecules. A perspective view of the asymmetric heterotrinuclear unit with the atom-numbering scheme is shown in Figure 1. Two partially deprotonated $[Cu(Hdmg)(dmg)]^-$ complexes coordinate to the zinc(II) cation through the oximate oxygens to afford the trinuclear skeleton doubly bridged by oximate groups in a *cis* arrangement. In the crystal, each trinuclear entity is polymerized through two crystallographic inversion centers located in the middle of the four-membered $Zn(1)O(1)O(1)^iZn(1)^i$ [Figure 2a, hexanuclear unit containing the Cu(1), Cu(2), Zn(1), Zn(1)^i, Cu(2)^i, and Cu(1)^i metal atoms] and six-membered $Cu(2)N(6)O(6)N(6)^{ii}O(6)^{ii}Cu(2)^{ii}$ [Figure 2b, hexanuclear unit containing the Cu(1), Zn(1), Cu(2), Cu(2)^{ii}, Zn(1)^{ii}, and Cu(1)^{ii} metal atoms] rings leading to a chain which runs parallel to the diagonal of the *ac*-plane (Figure S1, Supporting Information).

The coordination geometry around the two crystallographically independent Cu(1) and Cu(2) copper atoms is distorted square pyramidal, CuN_4O: the four oxime nitrogen atoms from

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Table 2. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for Non-Hydrogen Atoms of Compound **1**

atom	*x/a*	*y/b*	*z/c*	10^4U_{eq}, Å^2
Zn(1)	0.0972(1)	0.4703(1)	0.62494(9)	282(6)
Cu(1)	−0.1744(1)	0.2072(1)	0.6011(1)	312(6)
Cu(2)	0.3323(1)	0.5295(1)	0.9293(1)	312(6)
O(1)	−0.0971(6)	0.4554(6)	0.5334(5)	284(4)
O(2)	−0.4205(8)	0.0811(7)	0.6471(7)	472(4)
O(3)	0.0889(7)	0.3119(6)	0.5648(6)	321(6)
O(4)	−0.2537(9)	−0.0124(7)	0.7057(8)	480(5)
O(5)	0.2691(7)	0.6160(6)	0.7006(5)	352(5)
O(6)	0.6098(7)	0.6243(7)	1.1189(6)	382(4)
O(7)	0.0399(7)	0.4222(7)	0.7596(6)	407(5)
O(8)	0.4134(9)	0.5136(8)	1.1821(6)	508(4)
O(9)	−0.2975(8)	0.0754(7)	0.4181(7)	526(5)
O(10)	0.111(1)	0.7511(9)	0.6659(8)	744(7)
O(11)	0.219(1)	0.811(1)	0.8948(8)	742(6)
N(1)	−0.1938(7)	0.3594(7)	0.5527(6)	267(4)
N(2)	−0.3496(7)	0.1812(7)	0.6142(7)	292(4)
N(3)	0.0051(7)	0.2219(7)	0.6016(7)	282(5)
N(4)	−0.1582(8)	0.0659(7)	0.6731(7)	360(4)
N(5)	0.3617(8)	0.6282(8)	0.8092(7)	348(4)
N(6)	0.5315(9)	0.6385(7)	1.0131(7)	380(5)
N(7)	0.1266(8)	0.4409(8)	0.8676(7)	338(5)
N(8)	0.3105(9)	0.4857(8)	1.0745(7)	398(5)
N(9)	0.334(1)	0.914(1)	0.8964(9)	599(7)
C(1)	−0.3054(9)	0.3651(9)	0.5465(8)	319(5)
C(2)	−0.3997(9)	0.2608(8)	0.5769(8)	288(5)
C(3)	0.042(1)	0.1363(9)	0.6392(8)	330(5)
C(4)	−0.054(1)	0.0433(9)	0.6782(9)	394(6)
C(5)	0.485(1)	0.7139(9)	0.8421(8)	344(5)
C(6)	0.584(1)	0.7202(9)	0.9592(9)	318(5)
C(7)	0.077(1)	0.397(1)	0.9443(9)	323(6)
C(8)	0.181(1)	0.424(1)	1.062(1)	456(7)
C(9)	0.440(1)	0.946(1)	0.996(1)	510(7)
C(11)	−0.338(1)	0.474(1)	0.514(1)	426(6)
C(21)	−0.538(1)	0.246(1)	0.569(1)	387(7)
C(31)	0.174(1)	0.133(1)	0.646(1)	437(6)
C(41)	−0.036(2)	−0.067(1)	0.720(1)	563(9)
C(51)	0.528(1)	0.799(1)	0.766(1)	532(7)
C(61)	0.730(1)	0.811(1)	1.011(1)	479(7)
C(71)	−0.072(1)	0.323(1)	0.914(1)	580(8)
C(81)	0.147(2)	0.384(1)	1.164(1)	650(9)
C(91)	0.439(1)	0.879(1)	1.095(1)	622(8)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table 3. Selected Bond Lengths (Å) and Angles (deg)[a,b] for Compound **1**

Cu(1) Environment		Cu(2) Environment	
Cu(1)−N(1)	2.001(7)	Cu(2)−N(5)	1.985(8)
Cu(1)−N(2)	1.973(7)	Cu(2)−N(6)	1.982(8)
Cu(1)−N(3)	1.987(7)	Cu(2)−N(7)	1.997(8)
Cu(1)−N(4)	1.977(8)	Cu(2)−N(8)	1.986(8)
Cu(1)−O(9)	2.357(8)	Cu(2)−O(6)^{ii}	2.318(7)
N(1)−Cu(1)−N(2)	80.0(3)	N(5)−Cu(2)−N(6)	80.1(3)
N(1)−Cu(1)−N(3)	105.7(3)	N(5)−Cu(2)−N(7)	103.2(3)
N(1)−Cu(1)−N(4)	170.2(3)	N(5)−Cu(2)−N(8)	160.2(4)
N(2)−Cu(1)−N(3)	173.6(3)	N(6)−Cu(2)−N(7)	168.1(3)
N(2)−Cu(1)−N(4)	94.3(3)	N(6)−Cu(2)−N(8)	93.2(4)
N(3)−Cu(1)−N(4)	79.6(3)	N(7)−Cu(2)−N(8)	79.9(3)
O(9)−Cu(1)−N(1)	99.3(3)	O(6)^{ii}−Cu(2)−N(5)	98.9(3)
O(9)−Cu(1)−N(2)	90.6(3)	O(6)^{ii}−Cu(2)−N(6)	89.7(3)
O(9)−Cu(1)−N(3)	91.4(3)	O(6)^{ii}−Cu(2)−N(7)	100.9(3)
O(9)−Cu(1)−N(4)	88.6(3)	O(6)^{ii}−Cu(2)−N(8)	99.7(3)
		Cu(2)^{ii}−O(6)−N(6)	102.7(5)
Zinc Environment			
Zn(1)−O(1)	2.024(6)	Zn(1)−O(3)	1.984(6)
Zn(1)−O(5)	1.943(6)	Zn(1)−O(7)	2.047(7)
Zn(1)−O(1)^{i}	2.199(6)		
O(1)−Zn(1)−O(3)	102.8(3)	O(7)−Zn(1)−O(5)	102.5(3)
O(1)−Zn(1)−O(5)	129.7(3)	O(7)−Zn(1)−O(1)^{i}	158.8(3)
O(3)−Zn(2)−O(5)	123.1(3)	O(1)^{i}−Zn(2)−O(1)	73.3(2)
O(7)−Zn(3)−O(1)	87.7(3)	O(1)^{i}−Zn(3)−O(3)	93.9(3)
O(7)−Zn(3)−O(3)	99.6(3)	O(1)^{i}−Zn(3)−O(5)	83.4(2)
Zn(1)−O(1)−Zn^{i}	106.7(2)		

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b]Symmetry code: (i) −*x*, 1 − *y*, 1 − *z*; (ii) 1 − *x*, 1 − *y*, 2 − *z*.

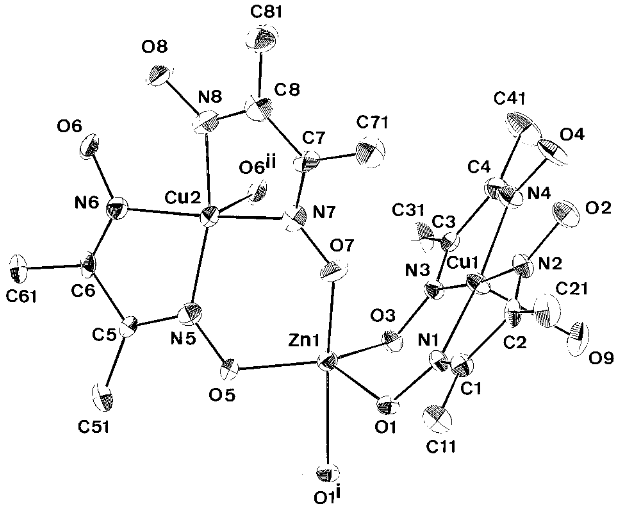

Figure 1. Perspective view of the asymmetric heterotrinuclear [$Cu_2Zn(Hdmg)_2(dmg)_2(H_2O)$] unit of compound **1** with the atomic labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

$Hdmg^-$ and dmg^{2-} chelating ligands build the corresponding basal planes at both metal atoms. The equatorial Cu−N bond lengths lie in the range 1.973(7)−2.001(7) Å, and they are common for in-plane Cu−N(oxime) distances.[10,11,16−18] The apex of the square pyramid is occupied by a weakly-bound water molecule at Cu(1) [2.357(8) Å for Cu(1)−O(9)] and an oximate oxygen atom at Cu(2) [2.318(7) Å for Cu(2)−O(6)^{ii}]. The out-of-plane oximate Cu(2)−O(6)^{ii} bond distance is slightly larger that that observed in the parent $[Cu(Hdmg)_2]_2$ dinuclear complex (2.301 Å).[16] The four equatorial nitrogen atoms around the copper atoms are nearly coplanar, with both metal atoms slightly displaced from their mean least-squares basal planes [0.073 and 0.206 Å for Cu(1) and Cu(2), respectively] toward the apical position. The dihedral angle between these mean basal planes is 57.2°. Larger deviations from the ideal value of 90° observed in the angles subtended at the copper atoms are due to the occurrence of five-membered [80.0(3), 79.6(3), 80.1(3), and 79.9(3)° for N(1)−Cu(1)−N(2), N(3)−Cu(1)−N(4), N(5)−Cu(2)−N(6), and N(7)−Cu(2)−N(8), respectively] and six-membered chelate rings [105.7(3) and 103.2(3)° for N(1)−Cu(1)−N(3) and N(5)−Cu(2)−N(7), respectively].

The zinc atom has a distorted trigonal bipyramidal coordination sphere ZnO_5 with oximato oxygens in both equatorial [O(1), O(3), and O(5)] and axial [O(7) and O(1)^{i}] positions. The Zn−O(oxime) bond distances are markedly different from each other, one of the axial distances [2.199(6) Å for Zn(1)−O(1)^{i}] being somewhat longer than the other four [2.047(7), 2.024(6), 1.984(6), and 1.943(6) Å for Zn(1)−O(7), Zn(1)−O(1), Zn(1)−O(3), and Zn(1)−O(5), respectively]. The zinc atom is slightly displaced from the equatorial plane by 0.178 Å in the direction of the O(7) axial oxygen atom. The large deviations from the ideal values corresponding to a trigonal bipyramidal geometry observed in the angles subtended at the zinc atom

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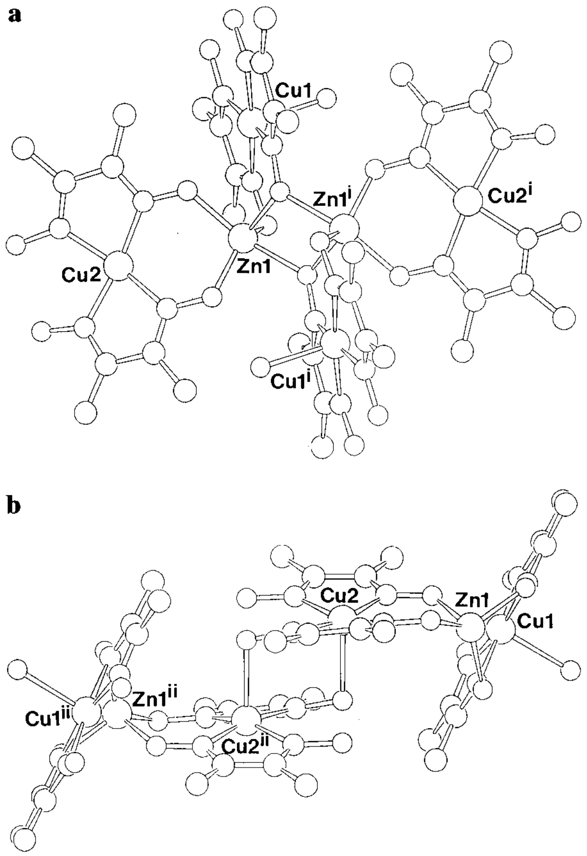


Figure 2. (a) View of two symmetry-related units by the inversion center standing at the middle of the Zn(1)···Zn(1)^{i} distance (i = $-x$, 1 $-$ y, 1 $-$ z). (b) View of two symmetry-related units by the inversion center standing at the middle of the Cu(2)···Cu(2)^{ii} distance (ii = 1 $-$ x, 1 $-$ y, 2 $-$ z). Atoms are plotted with arbitrary atomic radii. Hydrogen atoms have been omitted for clarity.

are due to the occurrence of six-membered [102.8(3) and 102.5° for O(1)−Zn(1)−O(3) and O(5)−Zn(1)−O(7) bond angles, respectively] and four-membered [73.3(2)° for O(1)−Zn(1)−O(1)^{i}] chelate rings. The six-membered Zn(1)O(1)N(1)Cu(1)-N(3)O(3) ring exhibits a chair conformation where the zinc and copper atoms are 0.013 and 1.06 Å above and below the mean plane, respectively. By contrast, the Zn(1)O(5)N(5)Cu(2)-N(7)O(7) ring has a boat conformation, the zinc and copper atoms being located at 0.589 and 0.290 Å out of the mean plane. The dihedral angle between the O(5)Zn(1)O(7) and O(1)-Zn(1)O(3) planes is 82.3°.

Charge-balance considerations dictate that there are three oxime protons per trinuclear unit (including the half free dimethylglyoxime ligand). However, no oxime hydrogen atom was found in the X-ray diffraction study. In light of the structural reports concerning dimethylglyoxime-containing copper(II) complexes,[10b−d,16−18] it may be anticipated that the O(1), O(3), O(5), and O(7) oxime oxygens are ionized and consequently the three oxime hydrogens would be attached to the remaining O(2), O(4), O(6), O(8), or O(11) oxime oxygen atoms. The short O(2)···O(4) and O(6)···O(8) separations [2.460(2) and 2.553(2) Å, respectively] are consistent with the occurrence of a hydrogen bond within each pair of oxygen atoms. These oxygen−oxygen distances are very close to that observed for O−H···O oxime distances in other structurally-characterized dimethylglyoximato complexes.[10b−d,16] Consequently, it can be concluded that one $Hdmg^-$ and one dmg^{2-} are bound to the two Cu(1) and Cu(2) atoms and thus a neutral H_2dmg ligand is present. The $Hdmg^-$ and dmg^{2-} ligands coordinate simultaneously in a bidentate fashion through their oxime nitrogen atoms to each copper, and in a monodentate fashion through one oxime oxygen atom to the zinc atom, thus leading to the formation of alternating five- and six-membered chelating rings around both copper atoms. Each five-membered ring is almost planar [largest deviations are 0.047 and 0.037 Å at N(2) and N(4) around Cu(1), and 0.022 and 0.010 Å at N(5) and C(7) around Cu(2), respectively]. The nitrogen−oxygen single bond distances lie in the range 1.31−1.36 Å, being somewhat shorter than that of the neutral free H_2dmg ligand [1.42(1) Å]. This shortening reflects a greater percentage of double-bond character for the coordinated dimethylglyoxime ligands in agreement with the occurrence of their oxime deprotonation. Meanwhile, the average value of the carbon−nitrogen bond distance (1.30 Å) is as expected for a double carbon−nitrogen bond.

One of the most noticeable structural features of **1** concerns the central Zn_2O_2 and $Cu_2(NO)_2$ bridging networks which link the symmetry-related trinuclear units. Perspective drawings of the corresponding hexanuclear cores resulting from the polymerization of the asymmetric trinuclear unit of compound **1** are shown in Figure 2a,b. The Zn(1) and Zn(1)^{i} atoms in Figure 2a are doubly-bridged by oximate groups in the unexpected M−O−M monoatomic form. The rhombohedral four-membered Zn(1)O(1)Zn(1)^{i}O(1)^{i} ring is strictly planar as a result of centrosymmetry, the Zn(1)O(1)Zn(1)^{i} bridging angle being 106.7(2)°. In Figure 2b, the Cu(2) and Cu(2)^{ii} atoms are doubly-bridged by *trans*-oximate groups in the usual out-of-plane M−NO−M diatomic pathway as previously reported for the complex $[Cu(Hdmg)_2]_2$.[16] The six-membered Cu(2)O(6)N(6)-Cu(2)^{ii}O(6)^{ii}N(6)^{ii} ring adopts a chair conformation, with copper atoms being 1.257 Å above and below the mean plane. The Cu(2)^{ii}−O(6)−N(6) bridging angle is equal to 102.7(5)°, a value very close to that found in $[Cu(Hdmg)_2]_2$ (102.5°).[16]

The free dimethylglyoxime ligand adopts a *trans* conformation with respect to the central C(9)−C(9)^{iii} bond (iii = 1 $-$ x, 2 $-$ y, 2 $-$ z), with both oxime groups being present as their *syn* isomers (*syn* and *anti* define the configuration for the two possible arrangements of the oxime groups around the double C═N bond with respect to the methyl substituent). The observed C(9)−N(9) and N(9)−O(11) bond distances [1.30(2) and 1.42(1) Å, respectively] agree with those expected for double and single bonds, respectively. The values of the O(3)···O(10)^{i}, O(5)···O(10), O(9)···O(10)^{i}, and O(10)···O(11) distances [2.817(12), 2.783(12), 2.892(14), and 2.637(14) Å] suggest the occurrence of hydrogen bonding involving the lattice and coordinated water molecules and the free and coordinated dimethylglyoxime ligands. The Cu(1)···Zn(1), Cu(2)···Zn(1), Cu(1)···Cu(2), Zn(1)···Zn(1)^{i}, and Cu(2)···Cu(2)^{ii} distances are 3.395(2), 3.641(1), 5.506(2), 3.390(2), and 3.930(2) Å, respectively. Larger metal−metal separations are found for Cu(1)···Cu(2)^{i} [7.355(2) Å], Cu(1)···Cu(1)^{i} [7.759(2) Å], and Cu(2)···Cu(2)^{i} [10.495(2) Å].

Magnetic Properties. The magnetic behavior of **1** is shown in Figure 3 as the $\chi_M T$ *versus* T plot, χ_M being the magnetic susceptibility per $[Cu_4Zn_2]$ hexanuclear unit and T the temperature. At room temperature, $\chi_M T$ is equal to 1.73 cm^3 K mol^{-1}, a value that is slightly higher than expected for four non-interacting copper(II) ions. As the temperature is decreased, $\chi_M T$ increases smoothly, reaching a maximum value of 2.90 cm^3 K mol^{-1} at 2.0 K. This behavior is typical of an overallferromagnetic exchange interaction between the copper(II) ions in **1**. In fact, the $\chi_M T$ value at 2.0 K is greater than that expected for two magnetically isolated Cu_2Zn triplets, indicating that a ferromagnetic coupling also occurs between the trinuclear units.

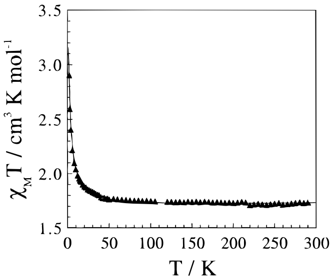
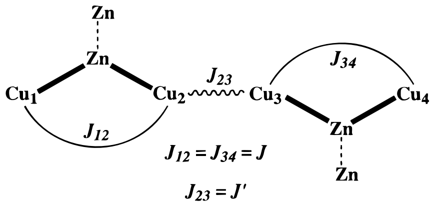


Figure 3. Thermal variation of the magnetic susceptibility per [Cu_4Zn_2] hexanuclear unit of complex **1** in the form of a $\chi_M T$ versus T plot: (▲) experimental data; theoretical curve (see text).

Scheme 1



In light of the structure of **1**, two possible exchange pathways between the trinuclear Cu_2Zn units are possible: one involves the Zn(1)O(1)O(1)^{i}Zn(1)^i skeleton (Figure 2a), and the other one, the Cu(2)N(6)O(6)N(6)^{ii}O(6)^{ii}Cu(2)^{ii} (Figure 2b) network. The magnetic behavior of **1** should correspond to an alternating chain if both pathways were operative. In a first approach, we have neglected the magnetic interactions between the copper(II) ions through the first pathway, that is the Zn_2O_2 framework (the copper−copper distances being larger than 7.3 Å). In this approach, the magnetic interactions can be illustrated by means of Scheme 1. The appropriate spin Hamiltonian to treat this problem is $\hat{\mathbf{H}} = -J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_3\cdot\hat{S}_4) - J'\,\hat{S}_2\cdot\hat{S}_3$, where J and J' are the exchange coupling constants occurring within the Cu(1)Zn(1)Cu(2) and Cu(2)Cu(2)^{ii} units, respectively. Least-squares fitting to the magnetic susceptibility expression (eq 1)

$$\chi_M T = (N\beta^2 g^2/k)[10 + \exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)]/[5\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)] \quad (1)$$

with

$$E_1 = -J/2 - J'/4$$

$$E_2 = J/2 - J'/4$$

$$E_3 = J'/4 + (J^2 + J'^2)^{1/2}/2$$

$$E_4 = J'/4 - (J^2 + J'^2)^{1/2}/2$$

$$E_5 = J/2 + J'/4 + (4J^2 - 2JJ' + J'^2)^{1/2}/2$$

$$E_6 = J/2 + J'/4 - (4J^2 - 2JJ' + J'^2)^{1/2}/2$$

derived through this Hamiltonian by means of the Van Vleck formula and assuming identical Lande factors for the four copper atoms,[19] leads to $J = 3.9$ cm^{-1}, $J' = 5.1$ cm^{-1}, $g = 2.12$, and $R = 8.0 \times 10^{-5}$ (R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$). The theoretical curve matches very well the experimental data in agreement with the low value of R. The results of the fit reveal the occurrence of ferromagnetic coupling in both exchange pathways within the Cu_4Zn_2 hexameric unit, that is through the diamagnetic zinc(II) ion and through the out-of-plane oximato bridge, the former being slightly less efficient than the latter. Variable-field magnetization data of **1** at 2.0 K (Figure 4) provide a further confirmation of the occurrence of ferromagnetic interactions within the Cu_4Zn_2 hexanuclear unit under consideration. The experimental data are very close to the theoretical curve corresponding to a quintet spin state and far above those arising from two non-interacting triplets and four isolated doublets ($g = 2.12$ and no zero-field splitting). So, our scheme of magnetic interactions within the Cu_4Zn_2 hexameric unit accounts quite well for the observed magnetic behavior of **1**.

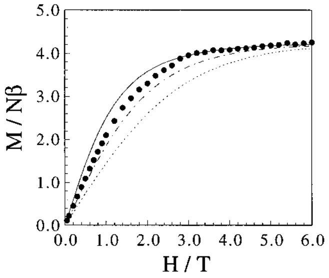


Figure 4. Field dependence of the magnetization per [Cu_4Zn_2] hexanuclear unit for complex **1** in the form of M versus H at $T = 2.0$ K: (●) experimental data; (—), (−•−), and (•••) are the Brillouin functions for a quintet, two non-interacting triplets, and four isolated doublets with $g = 2.12$, respectively.

The occurrence of two distinct ferromagnetic interactions (J and J') in **1** is the key point of the present paper. As far as we are aware, this is the first time that a ferromagnetic coupling ($J = 3.9$ cm^{-1}) between two copper(II) ions is mediated by the diamagnetic zinc(II) ion. This amazing result could be interpreted as follows: the point group symmetry of the Cu(1)Zn(1)Cu(2) trinuclear entity is roughly C_s (the mirror plane containing the three metal atoms), and consequently, the two $d_{x^2-y^2}$ type magnetic orbitals (Scheme 2) which are centered on each copper(II) ion transform as the a′ and a″ irreducible representations. The strict orthogonality of the two magnetic orbitals of the Cu(1)Zn(1)Cu(2) unit [the dihedral angle between the O(1)Zn(1)O(3) and O(5)Zn(1)O(7) planes is 82.3°] accounts for the ferromagnetic coupling observed in this trinuclear entity. Anyway, the mechanism by which the two electrons of the copper(II) ions feel each other may probably involve the filled d-orbitals of the zinc(II) ion, which have the appropriate energy and symmetry to mismatch with the copper(II) magnetic orbitals. This implicates that the spin density of each unpaired electron is delocalized not only over the oxime NO bridge but also partially onto the metal zinc ion, providing thus the main orthogonal superexchange pathway. Previous examples of ferromagnetic coupling between spin doublets through diamagnetic first-row transition metal ions are the compounds of formula [Cu(immepy)$_2$]PF_6[20] (immepy = bidentate iminonitroxide) and [Cu_2(acpa)$_2$(CrO_4)]·$4CH_3OH$·$4H_2O$[21] [Hacpa = *N*-(1-acetyl-2-propylidene)-*N*-(2-pyridylmethyl)amine]. The strict orthogonality between the magnetic orbitals of the immepy radicals through copper(I) and the accidental orthogonality of the σ-type frontier orbitals through the tetrahedral tetraoxo-

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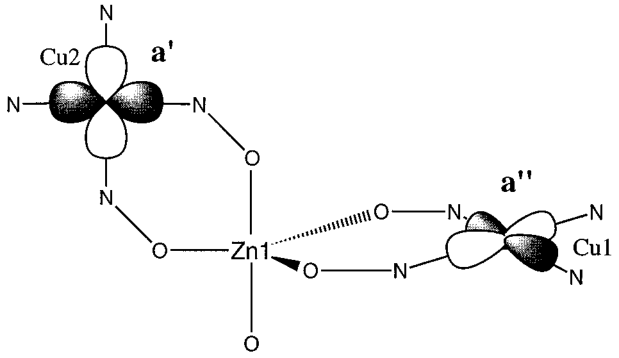
Scheme 2



chromate(VI) account for the observed ferromagnetic coupling. Finally, it is interesting to compare **1** with the complex of formula $[Cu_2Ni(dmg)_2(Me_3[9]N_3)_2(H_2O)_2](ClO_4)_2$[18] ($Me_3[9]N_3$ = 1,4,7-trimethyl-1,4,7-triazacyclonanane). Both compounds have a similar trinuclear skeleton, the square planar $[Ni(dmg)_2]^{2-}$ fragment acting as a bridge between the two copper(II) ions in the latter compound and playing thus the role of the zinc(II) ion in **1**. However, the two $d_{x^2-y^2}$ type magnetic orbitals centered on each copper(II) ion in the nickel compound are coplanar, leading thus to a nonzero overlap through the diamagnetic nickel(II) ion. In fact, the value of the antiferromagnetic coupling in $[Cu_2Ni(dmg)_2(Me_3[9]N_3)_2(H_2O)_2](ClO_4)_2$ is -5.2 cm^{-1}, the singlet being the low-lying state. This significant antiferromagnetic coupling is another evidence of the importance of the spin delocalization of the magnetic orbitals from the copper(II) ions in the common region of the diamagnetic metal ion. Symmetry considerations (coplanar magnetic orbitals) allow also an understanding of the antiferromagnetic coupling between copper(II) ions through the diamagnetic zinc(II) ($J = -1.6$ cm^{-1}) in the $\{[Cu(apox)]_2Zn(H_2O)_2\}X_2$ ($X = ClO_4^-$, BPh_4^-) complex[22] using more extended bridging ligands such as oxamidate.

Finally, as far as the nature and magnitude of the magnetic exchange interaction J' (5.1 cm^{-1}) between the Cu(2) and Cu(2)^{ii} copper atoms in **1** is concerned, it deserves to be noted that in a recent magnetostructural work we have reported a quasi-linear correlation between the value of the exchange coupling and that of the angle at the out-of-plane oxime to copper bond (α) in a series of out-of-plane oximato-bridged copper(II) dinuclear complexes.[10d] We have found that the magnitude of this exchange interaction also depends on the oxime to copper axial bond distance (R_{ax}) but its influence is significantly less than that of α. According to this correlation, the magnetic coupling in this kind of complex is ferromagnetic for values of α less than 106.9°. In light of the value of α for the Cu(2)N(6)O(6)-N(6)^{ii}O(6)^{ii}Cu(2)^{ii} fragment in **1** (102.7°) a ferromagnetic coupling is expected as observed. Given that the value of α of this unit is very close to that found in $[Cu(Hdmg)_2]_2$ (102.5°),[16] the values of the ferromagnetic coupling should be very close. That the values of the ferromagnetic coupling in **1** (5.1 cm^{-1}) and $[Cu(Hdmg)_2]_2$ (9.1 cm^{-1}) differ somewhat is due to the fact that the value of R_{ax} for the latter (2.301 Å) is somewhat shorter than that for the former (2.318 Å).

Conclusions. As far as we are aware, compound **1** is the first reported example of a coordination compound where a diamagnetic metal ion mediates a ferromagnetic interaction between paramagnetic metal centers as a result of the strict orthogonality of their magnetic orbitals. Unfortunately, the small value of the ferromagnetic coupling which can be achieved in that case (*ca.* 4 cm^{-1}) severely limits the use of this strategy for the design of molecular-based ferromagnets as an alternative to those which were mentioned in the Introduction. In this regard, it deserves to be noted that ferromagnetic interaction between iron(III) metal ions through a diamagnetic low-spin iron(II) ion was found to be operative in the well-known Prussian blue. This three-dimensional compound of formula $Fe_4[Fe(CN)_6]_3\cdot 15H_2O$ exhibits a long-range ferromagnetic ordering at 5.6 K.[23,24] However, for this compound, symmetry considerations alone would predict an antiferromagnetic ground state, according to the local O_h symmetry of the Fe(II) ion, and thus a different mechanism was invoked to explain the observed ferromagnetic interaction.[20]

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Supporting Information Available: Tables of crystal data and structure refinement (Table S1), atomic coordinates and thermal parameters (Table S2), anisotropic thermal parameters for non-hydrogen atoms (Table S3), nonessential bond distances and angles (Table S4), least-squares planes (Table S5), and intermolecular hydrogen bonds (Table S6) and figure showing the crystal packing (Figure S1) (11 pages). Ordering information is given on any current masthead page.

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