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Syntheses and Magneto–Structural Study of Several Polynuclear Copper(II) Complexes Derived from 1,3-Bis(dimethylamino)-2-propanolato

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The syntheses, structural characterization, and magnetic behavior of the three new polynuclear copper(II) complexes with formulas $[Cu_4(\eta^2{:}\mu\text{-}CH_3COO)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)(\mu\text{-bdmap})_2](ClO_4)_2\cdot H_2O$ (**1**), $[Cu_8(NCO)_2(\eta^1{:}\mu\text{-}NCO)_4(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(\mu\text{-}OH_2)_3(\mu\text{-bdmap})_4](ClO_4)_2\cdot 2H_2O$ (**2**), and $[Cu_9(\eta^1{:}\mu\text{-}NCO)_8(\mu_3\text{-}OH)_4(OH_2)_2(\mu\text{-bdmap})_4](ClO_4)_2\cdot 4H_2O$ (**3**), in which bdmapH is 1,3-bis(dimethylamino)-2-propanol, are reported. Tetranuclear complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a = 12.160(1)$ Å, $b = 13.051(1)$ Å, $c = 13.235(1)$ Å, $\alpha = 110.745(1)°$, $\beta = 109.683(1)°$, $\gamma = 97.014(1)$, and $Z = 2$. Octanuclear complex **2** crystallizes in the monoclinic system, space group $C2/c$, with unit cell parameters $a = 26.609(1)$ Å, $b = 14.496(1)$ Å, $c = 16.652(1)$ Å, $\beta = 97.814(1)°$, and $Z = 4$, and nonanuclear complex **3** crystallizes in the monoclinic system, space group $C2/c$, with unit cell parameters $a = 24.104(1)$ Å, $b = 13.542(1)$ Å, $c = 24.355(1)$ Å, $\beta = 109.98(1)°$, and $Z = 4$. The magnetic behavior of the three complexes has been checked showing strong antiferromagnetic coupling in all the cases.

Introduction

In the recent times, an extraordinary evolution has taken place in the chemistry of polymetallic coordination compounds (clusters, cage).[1,2] These compounds have provided substantial stimulus for developments in several fields, as magnetochemistry,[3,4] bioinorganic chemistry,[5−10] materials science, and solid-state physics.[11−13]

Metal compounds with different kinds of bridging ligands both organic and inorganic are known for almost all transition metals throughout the periodic table.[1,14,15] The magnetic properties of most of them have been investigated, and considerable insight has been obtained. On the other hand,

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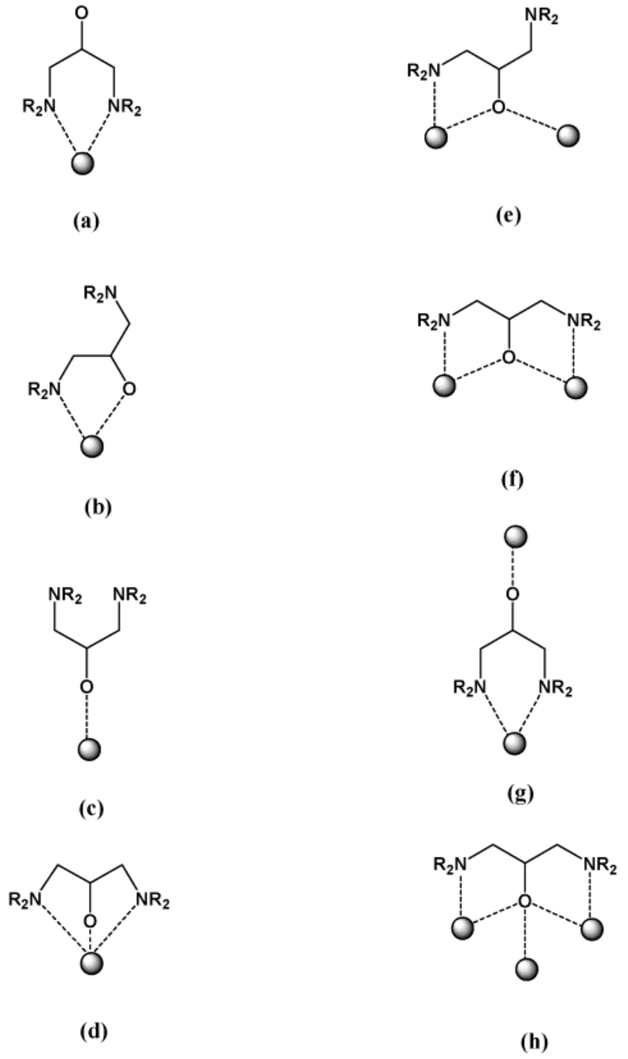
the nature and extension of the magnetic coupling are some of the features to be considered for the preparation of these compounds. Thus, many of them involve carboxylato, oxo, and alkoxo bridges which, in most of the cases, provide interesting exchange coupling. In this sense the use of the aminate/alkoxo−aliphatic ligands or simply the amino−alcohol ligands can be expected to improve the coupling between metallic centers seeing that they have been found to be able to bind two or more metal centers, forming homonuclear or heteronuclear complexes.

For example, 1,3-bis(dimethylamino)-2-propanol ligand (bdmapH) has three binding sites: two neutral amino groups and one hydroxyl group which can be deprotonated readily to bind to two metal ions. Each metal ion still has several free coordination positions that can be used by means of an appropriate ligand to connect to other similar units and increase the nuclearity of the complex. BdmapH also contains four methyl groups which would enhance the solubility of the metal complex in organic solvents. Wang et al.,[16] interested in the search of superconductor precursors systems, have dedicated attention to this ligand: they have structurally characterized a large number of polynuclear Cu(II) compounds, mixing Cu(II)−alkaline-earth or Cu(II)−lanthanide complexes with this ligand. Kivekas et al.[17] have reported a large number of Cu(II) complexes by using the 1,3-bis(amino)-2-propanol ligand (bdapH) in the context of their work consecrated to the coordination chemistry of several amino−alcohols as ligands.

Following our work directed toward the syntheses of molecular magnetic systems, and taking advantage of the versatility of the amino−alcohol ligands which can coordinate in several ways (Chart 1) with the possibility to give high-nuclearity species,[18−20] we have reacted Cu(II) sources with 1,3-bis(dimethylamino)-2-propanol and acetate or cyanate salts. We have been able to isolate tetra-, octa-, and nonanuclear species with formulas $[Cu_4(\eta^2{:}\mu\text{-}CH_3COO)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)(\mu\text{-}bdmap)_2](ClO_4)_2\cdot H_2O$ (**1**), $[Cu_8(NCO)_2(\eta^1{:}\mu\text{-}NCO)_4(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(\mu\text{-}OH_2)_3(\mu\text{-}bdmap)_4](ClO_4)_2\cdot 2H_2O$ (**2**), and $[Cu_9(\eta^1{:}\mu\text{-}NCO)_8(\mu_3\text{-}OH)_4(OH_2)_2(\mu\text{-}bdmap)_4](ClO_4)_2\cdot 4H_2O$ (**3**). From the point of view of the nuclearity of the resulting compounds, other copper(II) complexes with nuclearity four, eight, and nine[21] have been described with magnetic coupling varying between antiferromagnetic and ferromagnetic. In the case of the complexes **1**−**3** the bulk behavior is strongly antiferromagnetic for all the three mainly due to the Cu−O−Cu pathway. In the following work we report the structural characterization and magnetic study of **1**−**3**.

Chart 1



Experimental Section

Starting Materials. Copper(II) perchlorate hexahydrate, 1,3-bis(dimethylamino)-2-propanol, sodium acetate, and sodium cyanate (Aldrich) were used as such.

Caution! *Although no incidents were recorded in this study, perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.*

Spectral and Magnetic Measurements. Infrared spectra (4000−200 cm^{-1}) were recorded from KBr pellets in a Perkin-Elmer 1330 IR spectrophotometer. Magnetic measurements for **1**−**3** were carried out with a Faraday type magnetometer (MANICS DSM8) equipped with an Oxford CF 1200 S helium continuous-flow cryostat working in the temperature range 300−4 K. The magnetic field was approximately 16 000 G. Diamagnetic corrections were estimated

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Table 1. Crystal Data and Structure Refinement for Complexes **1**−**3**

	1	**2**	**3**
empirical formula	$C_{18}H_{46}Cl_2Cu_4N_4O_{18}$	$C_{34}H_{82}Cl_2Cu_8N_{14}O_{27}$	$C_{36}H_{88}Cl_2Cu_9N_{16}O_{32}$
fw	931.65	1698.37	1899.98
temp (K)	293(2)	293(2)	293(2)
wavelength (Å)	0.710 69	0.710 69	0.710 69
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$
unit cell dimens			
a (Å)	12.160(1)	26.609(1)	24.104(1)
b (Å)	13.051(1)	14.496(1)	13.542(1)
c (Å)	13.235(1)	16.652(1)	24.355(1)
α (deg)	110.745(1)	90.000(1)	90.00(1)
β (deg)	109.683(1)	97.814(1)	109.98(1)
γ (deg)	97.014(1)	90.000(1)	90.00(1)
V (Å^3)	1778.6(2)	6363.4(6)	7471.4(7)
Z	2	4	4
D(calcd) (Mg/m^3)	1.740	1.779	1.689
abs coeff (mm^{-1})	2.584	2.791	2.666
F(000)	952	3488	3868
cryst size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ range for data collcn (deg)	2.86−31.14	1.54−31.16	1.80−28.98
index ranges	$-17 \leq h \leq 16$, $-18 \leq k \leq 17$, $0 \leq l \leq 19$	$-38 \leq h \leq 38$, $0 \leq k \leq 20$, $0 \leq l \leq 22$	$-32 \leq h \leq 30$, $0 \leq k \leq 18$, $0 \leq l \leq 32$
reflcns collcd	14 363	30 707	32 108
indpndnt reflcns	8484 [R(int) = 0.0241]	9033 [R(int) = 0.0401]	9098 [R(int) = 0.0772]
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
data/restraints/params	8484/149/375	9033/0/438	9098/0/439
goodness-of-fit on F^2	1.141	1.039	1.005
final R indices [$I > 2\sigma(I)$]	R1 = 0.0617, wR2 = 0.1969	R1 = 0.0417, wR2 = 0.1222	R1 = 0.0466, wR2 = 0.1334
R indices (all data)	R1 = 0.0839, wR2 = 0.2164	R1 = 0.0633, wR2 = 0.1355	R1 = 0.0996, wR2 = 0.1506
largest diff peak and hole (e Å^{-3})	0.692 and −0.689	0.815 and −0.841	0.530 and −0.572

from the Pascal tables. The EPR spectra have been recorded on an X-band Bruker spectrometer (ESR 300E).

Syntheses. $[Cu_4(\eta^2{:}\mu\text{-}CH_3COO)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)(\mu\text{-bdmap})_2](ClO_4)_2{\cdot}H_2O$ (1). To an aqueous solution of 2 mmol of bdmapH (0.292 g) and 2 mmol of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.74 g) in 30 mL of water was added 2 mmol of sodium acetate (0.272 g) dissolved in 10 mL of water. Slow evaporation of the blue solution gave after 3 days compound **1** as blue crystals suitable for X-ray determination (yield approximately 70%).

$[Cu_8(NCO)_2(\eta^1{:}\mu\text{-}NCO)_4(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(\mu\text{-}OH_2)_3(\mu\text{-bdmap})_4](ClO_4)_2{\cdot}2H_2O$ (2) and $[Cu_9(\eta^1{:}\mu\text{-}NCO)_8(\mu_3\text{-}OH)_4(OH_2)_2(\mu\text{-bdmap})_4](ClO_4)_2{\cdot}4H_2O$ (3). To an aqueous solution of 2 mmol of bdmapH (0.292 g) and 2 mmol of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.74 g) was added 2 mmol of sodium cyanate (0.13 g) dissolved in 10 mL of water. When the addition was completed, the mixture solution (60 mL) was stirred for 30 min. The green precipitate formed was collected in practically quantitative yield (95%) by vacuum filtration. The product was dissolved in 20 mL of acetonitrile and filtered to remove any impurities. Crystals of the complex **2** were grown by adding an equal volume of water to the acetonitrite solution of the solid.

In the same way, if we react 1 mmol of bdmapH, 2 mmol of $Cu(ClO_4)_2{\cdot}6H_2O$, and 2 mmol of sodium cyanate, we obtain from the mixture solution (60 mL) a blue powder (yield approximately 75%). Slow evaporation of the acetonitrile/water solution of the product gave compound **3** as blue crystals suitable for X-ray determination.

IR and Analytical Data. The most characteristic bands are those attributable to acetate registered at 1440 and 1680 cm^{-1} for the complex **1** and cyanate band which appears at 2020 cm^{-1} for compounds **2** and **3**. The perchlorate bands are found at 1100 and 625 cm^{-1} for the three compounds. In the infrared spectra, the absorptions attributed to the μ-bdmap (ν_{C-H} and δ_{CH_2}) are detected easily in the interval from 2800 to 3000 cm^{-1} and close to 1480 cm^{-1}.

The elemental analyses (C, N, H, Cl) for the different syntheses were consistent with the product formulation. Anal.

Found for **1**: C, 23.1; H, 4.8; N, 6.1; Cl, 7.5. Calcd for $C_{18}H_{46}Cl_2Cu_4N_4O_{18}$: C, 23.21; H, 4.98; N, 6.01; Cl, 7.61. Found for **2**: C, 24.0; H, 4.2; N, 11.6; Cl, 4.0. Calcd for $C_{34}H_{82}Cl_2Cu_8N_{14}O_{27}$: C, 24.04; H, 4.86; N, 11.54; Cl, 4.17. Found for **3**: C, 23.0; H, 4.5; N, 11.9; Cl, 3.6. Calcd for $C_{36}H_{88}Cl_2Cu_9N_{16}O_{32}$: C, 22.76; H, 4.67; N, 11.80; Cl, 3.73.

X-ray Crystallography. Good quality crystals of compounds **1**−**3** were selected and mounted on a MAR345 diffractometer with an image plate detector. The crystallographic data, conditions retained for the intensity data collection, and some features of the structure refinements are listed in Table 1. The accurate unit-cell parameters were determined from automatic centering of 10 093 reflections ($3 < \theta < 21°$) for **1**, 18 423 ($3 < \theta < 31°$) for **2**, and 13 650 ($3 < \theta < 31°$) for **3** and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo Kα radiation. Totals of 14 363 (**1**), 30 707 (**2**), and 32 108 (**3**) reflections were measured in the $2.86° \leq \theta \leq 31.14°$, $1.54° \leq \theta \leq 31.16°$, and $1.80° \leq \theta \leq 28.98°$ range for **1**−**3,** respectively. Totals of 8484 (**1**), 9033 (**2**), and 9098 (**3**) reflections were nonequivalent by symmetry, with R_{int} (on I) = 0.024 (**1**), 0.040 (**2**), and 0.077 (**3**). The observed reflections applying the condition $I > 2\sigma(I)$ were 6190 for **1,** 6870 for **2**, and 6133 for **3**. Lorentz polarization and absorption corrections were made for **1**−**3**. The structures were solved by Patterson synthesis using the SHELXS computer program[22a] and refined by the full-matrix least-squares method, using the SHELX97 computer program[22b] with 8484 reflections for **1**, 9033 for **2**, and 9098 for **3**. (Very negative intensities were not assumed.) The functions minimized were $\Sigma w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.1480P)^2]^{-1}$ for **1**, $w = [\sigma^2(I) + (0.0945P)^2]^{-1}$

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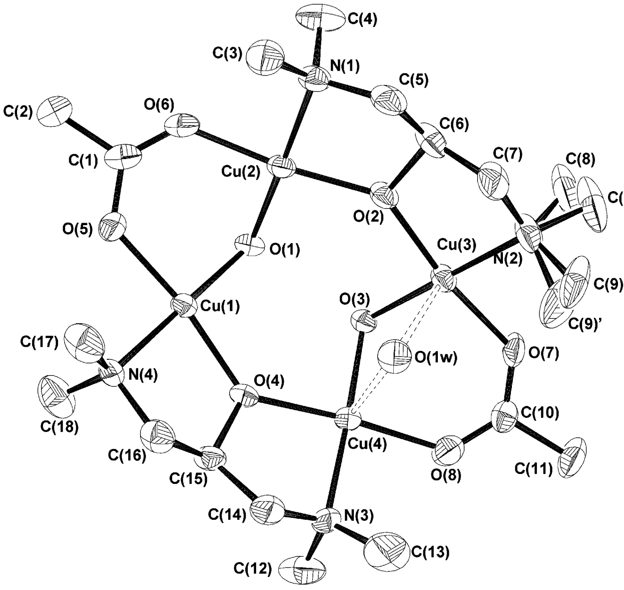

Figure 1. ORTEP drawing of the cation unit of **1** showing the atom-labeling scheme. Ellipsoids are at the 50% probability level. Water and the perchlorate molecules are omitted for clarity.

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

Cu(1)−O(1)	1.879(2)	Cu(3)−O(2)	1.957(2)
Cu(1)−O(4)	1.998(3)	Cu(3)−O(3)	1.938(2)
Cu(1)−O(5)	1.947(3)	Cu(3)−O(7)	1.972(3)
Cu(1)−N(4)	2.005(3)	Cu(3)−N(2)	2.022(4)
Cu(2)−O(1)	1.884(2)	Cu(4)−O(3)	1.921(2)
Cu(2)−O(2)	1.949(3)	Cu(4)−O(4)	2.018(3)
Cu(2)−O(6)	1.964(4)	Cu(4)−O(8)	1.985(3)
Cu(2)−N(1)	1.984(4)	Cu(4)−N(3)	2.015(3)
Cu(3)−O(1w)	2.403(4)	Cu(4)−O(1w)	2.504(2)
Cu(1)···Cu(2)	3.096(1)	Cu(3)···Cu(4)	3.120(1)
Cu(2)···Cu(3)	3.658(1)	Cu(4)···Cu(1)	3.739(1)
O(1)−Cu(1)−O(4)	92.8(1)	O(2)−Cu(3)−N(2)	88.0(2)
O(1)−Cu(1)−O(5)	92.2(1)	O(3)−Cu(3)−O(7)	91.6(1)
O(1)−Cu(1)−N(4)	176.0(1)	O(3)−Cu(3)−N(2)	178.4(2)
O(4)−Cu(1)−O(5)	170.3(1)	O(7)−Cu(3)−N(2)	87.2(2)
O(4)−Cu(1)−N(4)	86.1(1)	O(3)−Cu(4)−O(4)	92.3(1)
O(5)−Cu(1)−N(4)	88.4(1)	O(3)−Cu(4)−O(8)	92.5(1)
O(1)−Cu(2)−O(2)	94.0(1)	O(3)−Cu(4)−N(3)	177.5(1)
O(1)−Cu(2)−O(6)	90.4(1)	O(4)−Cu(4)−O(8)	175.2(1)
O(1)−Cu(2)−N(1)	175.1(1)	O(4)−Cu(4)−N(3)	85.3(1)
O(2)−Cu(2)−O(6)	172.9(1)	O(8)−Cu(4)−N(3)	89.9(1)
O(2)−Cu(2)−N(1)	86.6(1)	Cu(1)−O(1)−Cu(2)	110.7(1)
O(6)−Cu(2)−N(1)	88.5(2)	Cu(2)−O(2)−Cu(3)	138.9(1)
O(2)−Cu(3)−O(3)	93.0(1)	Cu(3)−O(3)−Cu(4)	107.9(1)
O(2)−Cu(3)−O(7)	170.8(1)	Cu(1)−O(4)−Cu(4)	137.1(1)
Cu(3)−O(1w)−Cu(4)	78.9(1)		

for **2**, and $w = [\sigma^2(I) + (0.0890P)^2]^{-1}$ for **3** and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were taken from ref 23. All H atoms for **1**, 49 H atoms for **2**, and 33 H atoms for **3** were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked. The carbon atoms labeled C(8) and C(9) in compound **1** and the atoms C(8)−C(10) and C(12)−C(14) in compound **2** corresponding to the μ-bdmap ligand were found in disordered positions. Occupancy factors of 0.5 and 0.5 were assigned to each position according to the high of the peaks of the Fourier syntheses, and all were refined with an overall isotropic temperature factor. The final R (on F) factor was 0.061, 0.041, and 0.046 for **1**−**3**, respectively; wR (on $|F_o|^2$) was 0.197 for **1**, 0.122 for **2**, and 0.133 for **3**. The number of refined parameters was 375, 438, and 439 for **1**−**3**, respectively. The maximum and the minimum shift/esd was 0.00 for **1**−**3**. The maximum and the minimum peaks in final difference synthesis were 0.692 and −0.689, respectively, for **1**, 0.815 and −0.841, respectively, for **2**, and 0.530 and −0.572, respectively, for **3**. The molecular plots were obtained using the Ortep32 program.[24]

Results and Discussion

[$Cu_4(\eta^2$:μ-$CH_3COO)_2(\mu$-$OH)_2(\mu$-$OH_2)(\mu$-bdmap$)_2](ClO_4)_2\cdot H_2O$ (1). Description of the Structures. The structure of the cation in **1** is illustrated in Figure 1. The relevant bond distances and angles are listed in Table 2. This unit consists of a rectangular arrangement involving four copper(II) atoms bridged alternatively by the μ-bdmap ligand through oxygen and two nitrogen atoms, by one acetate ligand and one μ-OH group. In the compound the nearest-neighbor Cu···Cu distances are 3.658(1)−3.739(1) and 3.096(1)−3.120(1) Å corresponding to the two sets of μ-bdmap and acetate/μ-hydroxide oxygen bridges, respectively. The coordination around the Cu(1) and Cu(2) centers is a square-planar environment. The deviations of the atoms from the least-squares planes [O(1)−O(4)−O(5)−N(4)−Cu(1)] and [O(1)−O(2)−O(6)−N(1)−Cu(2)] are as follows: O(1) = 0.027(3), O(4) = −0.069(3), O(5) = −0.070(4), N(4) = 0.030(4), Cu(1) = 0.0815(1) Å, respectively; O(1) = −0.012(3), O(2) = −0.036(5), O(6) = −0.035(6), N(1) = −0.009(5), Cu(2) = 0.0916(8) Å, respectively. In the title compound, one water oxygen atom O(1w) is placed above the Cu(3) and Cu(4) atoms to provide weak axial contacts (Cu(3)−O(1w) 2.403(4), Cu(4)−O(1w) 2.504(2) Å). As a consequence of this fact the coordination polyhedra around the copper atoms Cu(3) and Cu(4) are best described as distorted square pyramid. The deviations of the atoms from the least-squares planes [O(2)−O(3)−O(7)−N(2)−Cu(3)] and [O(3)−O(4)−O(8)−N(3)−Cu(4)] are as follows: O(2) = −0.088(4), O(3) = 0.043(3), O(7) = −0.087(6), N(2) = 0.046(8) Å, Cu(3) = 0.0856(8) Å, respectively; O(3) = 0.000(3), O(4) = −0.003(3), O(8) = −0.003(4), N(3) = 0.001(4), Cu(4) = 0.0056(6) Å, respectively. The Cu−O distances are in the range 1.879(2)−1.998(3) Å, whereas the Cu−N bond lengths are varying between 1.984(4) and 2.022(4) Å. All these distances should be considered as normal. In the compound there are three different sets of Cu−O−Cu angles in the ranges 107.9(1)−110.7(1), 137.1(1)−138.9(1), and 78.9(1)° corresponding to μ_2-hydroxide, μ_2-alkoxide, and μ_2-OH_2 oxygen bridges, respectively. The bond distances and angles related with the acetate ligand are in good agreement with the data reported in the literature.

[$Cu_8(NCO)_2(\eta^1$:μ-$NCO)_4(\mu$-$OH)_2(\mu_3$-$OH)_2(\mu$-$OH_2)_3(\mu$-bdmap$)_4](ClO_4)_2\cdot 2H_2O$ (2). The structure of the asymmetric unit of the cation in **2** is illustrated in Figure 2a. Selected bond distances and angles are listed in Table 3. The structure of **2** can be described as two folded rectangular units of Cu(II) related by a crystallographic axis C_2 to give an arrangement of eight Cu(II) atoms (Figure 2b). In the asymmetric part, the copper atoms are bridged alternatively

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(23) *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99−100 and 149.

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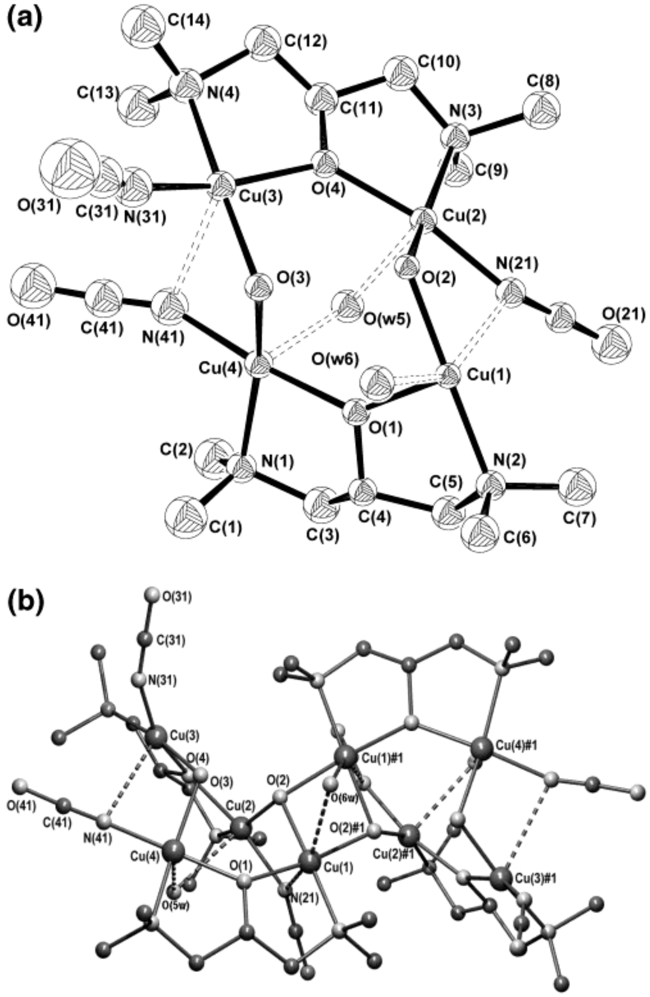

Figure 2. (a) ORTEP drawing of the asymmetric unit of **2** showing the atom-labeling scheme. Ellipsoids are at the 50% probability level. Water and perchlorate molecules are omitted for clarity. (b) Molecular structure of **2**.

by two μ-bdmap ligands through oxygen and two nitrogen atoms and by one cyanate ligand and one μ-OH group. The nearest-neighbor Cu···Cu distances vary between 3.595(1) and 3.599(1), 2.832(1) and 3.704(1), and 3.128(1) and 3.676(1) Å corresponding to the three sets of μ_2-alkoxide, μ_2-hydroxide, and μ_3-hydroxide oxygen bridges. The environments of Cu(2), Cu(3), and Cu(4) atoms can be described as distorted square pyramids with two geometrically different square-pyramidal copper(II) centers, with N_2O_3 donor set for Cu(2) and Cu(4) and N_3O_2 donor set for Cu(3). The Cu(1) geometry can be described as a distorted octahedral environment with O_4N_2 donor set. The Cu−O distances range from 1.934(2) to 2.576(2) Å, whereas the Cu−N bond lengths are varying between 2.021(2) and 2.049(2) Å and between 1.931(4) and 2.617(2) Å corresponding respectively to $Cu-N_{bdmap}$ and $Cu-N_{cyanate}$ bond lengths. The Cu−O−Cu units corresponding to the μ_2-alkoxide bridges are close to 135.3(1) and 134.7(1)°. In the case of Cu−O−Cu angles corresponding to the μ_3-hydroxide set, it can be distinguished three different angles which are close to 91.2(1), 104.3(1), and 135.9(1)°. In the Cu−O−Cu angles corresponding to the μ_2-hydroxide set can be distinguished three different angles which are close to 66.7(1), 94.9(1), and 110.0(1)°. The bond angles related with the cyanate ligand vary between 149.6(2) and 155.3(4) and 84.1(1) and 85.5(1)° corresponding to Cu−N−C and Cu−N−Cu angles, respectively.

Table 3. Relevant Bond Lengths (Å) and Angles (deg) for **2**[a]

Cu(1)−O(1)	1.946(2)	Cu(3)−O(3)	1.934(2)
Cu(1)−O(2)	1.979(2)	Cu(3)−O(4)	1.961(2)
Cu(1)−O(2)$^{\#1}$	1.984(2)	Cu(3)−N(4)	2.025(3)
Cu(1)−O(6)	2.576(2)	Cu(3)−N(31)	1.931(4)
Cu(1)−N(2)	2.021(2)	Cu(3)−N(41)	2.752(2)
Cu(1)−N21	2.617(2)	Cu(4)−O(1)	1.946(2)
Cu(2)−O(4)	1.934(2)	Cu(4)−O(3)	1.988(2)
Cu(2)−O(2)	1.983(2)	Cu(4)−O(5)	2.458(2)
Cu(2)−O(5)	2.570(2)	Cu(4)−N(1)	2.040(3)
Cu(2)−N(3)	2.049(2)	Cu(4)−N(41)	1.944(3)
Cu(2)−N(21)	1.949(2)	C(21)−O(21)	1.188(4)
N(21)−C(21)	1.180(4)	C(31)−O(31)	1.211(7)
N(31)−C(31)	1.125(6)	C(41)−O(41)	1.230(5)
N(41)−C(41)	1.140(5)	Cu(1)···Cu(2)	3.128(1)
Cu(1)···Cu(1)$^{\#1}$	2.832(1)	Cu(3)···Cu(4)	3.213(1)
Cu(2)···Cu(3)	3.595(1)	Cu(2)···Cu(1)$^{\#1}$	3.676(1)
Cu(4)···Cu(1)	3.599(1)	Cu(2)···Cu(4)	3.704(1)

O(1)−Cu(1)−O(2)	93.4(1)	N(31)−Cu(3)−O(3)	92.6(1)
O(1)−Cu(1)−O(2)$^{\#1}$	171.6(1)	N(31)−Cu(3)−O(4)	161.2(1)
O(2)−Cu(1)−O(2)$^{\#1}$	82.1(1)	O(3)−Cu(3)−O(4)	89.9(1)
O(1)−Cu(1)−N(2)	86.1(1)	N(31)−Cu(3)−N(4)	94.1(2)
O(2)−Cu(1)−N(2)	177.8(1)	O(3)−Cu(3)−N(4)	171.5(1)
O(2)$^{\#1}$−Cu(1)−N(2)	98.6(1)	O(4)−Cu(3)−N(4)	85.4(1)
O(4)−Cu(2)−N(21)	168.7(1)	N(41)−Cu(4)−O(1)	173.4(1)
O(4)−Cu(2)−O(2)	91.4(1)	N(41)−Cu(4)−O(3)	87.5(1)
N(21)−Cu(2)−O(2)	89.7(1)	O(1)−Cu(4)−O(3)	91.7(1)
O(4)−Cu(2)−N(3)	85.9(1)	N(41)−Cu(4)−N(1)	97.7(1)
N(21)−Cu(2)−N(3)	97.2(1)	O(1)−Cu(4)−N(1)	85.4(1)
O(2)−Cu(2)−N(3)	157.8(1)	O(3)−Cu(4)−N(1)	158.6(1)
Cu(1)−O(1)−Cu(4)	135.3(1)	Cu(3)−O(3)−Cu(4)	110.0(1)
Cu(1)−O(2)−Cu(2)	104.3(1)	Cu(3)−N(41)−Cu(4)	84.5(1)
Cu(1)−O(2)−Cu(1)$^{\#1}$	91.2(1)	C(21)−N(21)−Cu(2)	149.6(2)
Cu(1)−O(6w)−Cu(1)$^{\#1}$	66.7(1)	N(21)−C(21)−O(21)	177.7(4)
Cu(2)−O(2)−Cu(1)$^{\#1}$	135.9(1)	C(31)−N(31)−Cu(3)	155.3(4)
Cu(2)−O(5w)−Cu(4)	94.9(1)	N(31)−C(31)−O(31)	178.0(7)
Cu(2)−O(4)−Cu(3)	134.7(1)	C(41)−N(41)−Cu(4)	152.7(4)
Cu(2)−N(21)−Cu(1)	85.1(1)	N(41)−C(41)−O(41)	177.1(5)

[a] Symmetry transformation used to generate equivalent atoms: (#1) $-x$, y, $-z + 1/2$.

$[Cu_9(\eta^1{:}\mu\text{-}NCO)_8(\mu_3\text{-}OH)_4(OH_2)_2(\mu\text{-}bdmap)_4](ClO_4)_2\cdot 4H_2O$ (3). The structure of the cation in **3** is illustrated in Figure 3a,b. Selected bond distances and angles are listed in Table 4. As it is shown in Figure 3b the arrangement of the Cu atoms may be described as a distorted cube, with the ninth copper atom in the center. The eight Cu(II) atoms are bridged alternatively by the μ-bdmap ligand through oxygen and two nitrogen atoms and by two cyanate ligand and one μ_3-OH group. The μ_3-OH group connects at the same time with the central Cu(1) atom. In the compound the nearest-neighbor Cu···Cu distances vary between 3.577(1) and 3.588(1), 2.944(1) and 2.971(1), and 3.151(1) and 3.660(1) Å corresponding to the three sets of μ_2-alkoxide, cyanate/μ_3-hydroxide, and μ_3-hydroxide oxygen bridges. The copper atoms are found in a distorted square pyramid environment except the central Cu(1) atom which is found in a distorted (4 + 2) octahedral environment. The coordination of Cu(1) is completed by two H_2O molecules which are located at 2.543(5) and 2.512(7) Å. The other Cu(1)−O distances range from 1.943(2) to 1.949(3) Å. The Cu−O distances corresponding to the μ_2-alkoxide set range from 1.905(3) to 1.931(3) Å, whereas the Cu−O distances corresponding to the μ_3-hydroxide set are varying from 1.980(3) to 2.020(3)

Table 4. Relevant Bond Lengths (Å) and Angles (deg) for **3**[a]

Cu(1)−O(3)	1.943(2)	Cu(2)−O(1)	1.905(3)
Cu(1)−O(3)$^{\#1}$	1.943(2)	Cu(2)−O(3)	1.996(3)
Cu(1)−O(5)$^{\#1}$	1.949(3)	Cu(2)−O(1w)	2.822(2)
Cu(1)−O(5)	1.949(3)	Cu(2)−N(21)	1.931(4)
Cu(1)−O(1w)	2.543(5)	Cu(2)−N(41)	2.794(5)
Cu(1)−O(2w)	2.512(7)	Cu(2)−N(1)	2.023(4)
Cu(3)−O(1)	1.929(3)	Cu(4)−O(2)	1.931(3)
Cu(3)−O(5)	2.019(3)	Cu(4)−O(3)	2.020(3)
Cu(3)−N(31)	1.902(5)	Cu(4)−N(41)	1.922(4)
Cu(3)−N(51)$^{\#1}$	2.645(4)	Cu(4)−N(21)	2.717(4)
Cu(3)−N(2)	2.028(4)	Cu(4)−N(3)	2.048(5)
Cu(5)−O(2)	1.916(3)	Cu(5)−N(4)	2.024(5)
Cu(5)−O(5)$^{\#1}$	1.980(3)	Cu(5)−N(51)	1.972(4)
Cu(5)−O(2w)	2.945(2)	Cu(5)−N(31)#1	2.713(5)
N(21)−C(21)	1.121(7)	C(21)−O(21)	1.211(8)
N(31)−C(31)	1.136(8)	C(31)−O(31)	1.212(9)
N(41)−C(41)	1.153(6)	C(41)−O(41)	1.183(6)
N(51)−C(51)	1.139(6)	C(51)−O(51)	1.185(6)
Cu(1)···Cu(2)	3.151(1)	Cu(1)···Cu(3)	3.654(1)
Cu(1)···Cu(5)	3.172(1)	Cu(1)···Cu(4)	3.660(1)
Cu(2)···Cu(4)	2.971(1)	Cu(2)···Cu(3)	3.577(1)
Cu(4)···Cu(5)	3.588(1)	Cu(3)···Cu(5)$^{\#1}$	2.944(1)
O(3)−Cu(1)−O(3)$^{\#1}$	168.6(2)	O(3)−Cu(1)−O(5)$^{\#1}$	90.9(1)
O(3)$^{\#1}$−Cu(1)−O(5)$^{\#1}$	90.6(1)	O(3)−Cu(1)−O(5)	90.6(1)
O(3)$^{\#1}$−Cu(1)−O(5)	90.9(1)	O(5)$^{\#1}$−Cu(1)−O(5)	164.8(2)
O(1)−Cu(2)−O(3)	90.0(1)	N(21)−Cu(2)−O(3)	87.5(1)
O(1)−Cu(2)−N(1)	86.3(1)	N(21)−Cu(2)−N(1)	97.9(2)
O(3)−Cu(2)−N(1)	165.4(1)	O(1)−Cu(2)−Cu(4)	119.0(1)
N(21)−Cu(2)−Cu(4)	63.2(1)	O(3)−Cu(2)−Cu(4)	42.6(1)
N(1)−Cu(2)−Cu(4)	128.9(1)	O(1)−Cu(2)−N(21)	172.2(1)
N(31)−Cu(3)−O(5)	86.1(1)	O(1)−Cu(3)−O(5)	94.6(1)
N(31)−Cu(3)−N(2)	94.6(2)	O(1)−Cu(3)−N(2)	85.1(1)
O(5)−Cu(3)−N(2)	175.0(1)	N(31)−Cu(3)−Cu(5)$^{\#1}$	63.9(1)
O(1)−Cu(3)−Cu(5)$^{\#1}$	120.3(1)	O(5)−Cu(3)−Cu(5)$^{\#1}$	42.1(1)
N(2)−Cu(3)−Cu(5)$^{\#1}$	134.3(1)	N(31)−Cu(3)−O(1)	173.7(2)
N(41)−Cu(4)−O(2)	176.9(2)	N(41)−Cu(4)−O(3)	85.4(2)
O(2)−Cu(4)−O(3)	94.8(1)	N(41)−Cu(4)−N(3)	94.2(2)
O(2)−Cu(4)−N(3)	86.0(1)	O(3)−Cu(4)−N(3)	173.5(2)
N(41)−Cu(4)−Cu(2)	65.6(2)	O(2)−Cu(4)−Cu(2)	116.5(1)
O(3)−Cu(4)−Cu(2)	42.0(1)	N(3)−Cu(4)−Cu(2)	132.2(1)
O(2)−Cu(5)−N(51)	169.6(2)	O(2)−Cu(5)−O(5)$^{\#1}$	91.8(1)
N(51)−Cu(5)−O(5)$^{\#1}$	86.3(1)	O(2)−Cu(5)−N(4)	86.3(1)
N(51)−Cu(5)−N(4)	98.2(2)	O(5)$^{\#1}$−Cu(5)−N(4)	164.0(2)
O(2)−Cu(5)−Cu(3)$^{\#1}$	122.9(1)	N(51)−Cu(5)−Cu(3)$^{\#1}$	61.4(1)
O(5)$^{\#1}$−Cu(5)−Cu(3)$^{\#1}$	43.1(1)	N(4)−Cu(5)−Cu(3)$^{\#1}$	126.7(2)
Cu(1)−O(3)−Cu(2)	106.3(1)	Cu(1)−O(3)−Cu(4)	134.9(1)
Cu(1)−O(5)−Cu(5)$^{\#1}$	107.6(1)	Cu(1)−O(5)−Cu(3)	134.1(1)
Cu(2)−O(1)−Cu(3)	137.7(1)	Cu(2)−O(3)−Cu(4)	95.4(1)
Cu(3)−O(5)−Cu(5)$^{\#1}$	94.8(1)	Cu(5)−O(2)−Cu(4)	137.7(2)
N(21)−C(21)−O(21)	176.9(1)	C(21)−N(21)−Cu(2)	159.9(5)
N(31)−C(31)−O(31)	177.6(1)	C(31)−N(31)−Cu(3)	162.1(6)
N(41)−C(41)−O(41)	177.8(7)	C(41)−N(41)−Cu(4)	164.2(5)
N(51)−C(51)−O(51)	178.3(7)	C(51)−N(51)−Cu(5)	144.8(4)

[a] Symmetry transformation used to generate equivalent atoms: (#1) −*x*, *y*, −*z* + 1/2.

Å. The Cu−N$_{bdmap}$ bond lengths are varying between 2.023(4) and 2.048(5) Å. The Cu−N$_{cyanate}$ bond lengths are found between 1.902(5) and 1.931(4) and 2.645(4) and 2.794 Å (short and long distances). The Cu−O−Cu angles corresponding to the μ_2-alkoxide set are close to 137.7(2)° while, in the case of the Cu−O−Cu angles corresponding to the μ_3-hydroxide set, it can be distinguished three different angles which are close to 134.1(1), 94.8(1), and 107.6(1)°. The bond angles related with the cyanate ligand vary between 144.8(4) and 164.2(5) and 75.58(4) and 77.71(4)° corresponding to Cu−N−C and Cu−N−Cu angles, respectively.

Magnetic Study. Magnetic measurements were carried out on polycrystalline powder samples ranging from 4.0 to 300 K at 16 kG applied field. The compounds **1**−**3** show similar behavior. In Figure 4 we represent the magnetic behavior of **1**−**3** in the forms of $\chi_M T$ vs T plots.

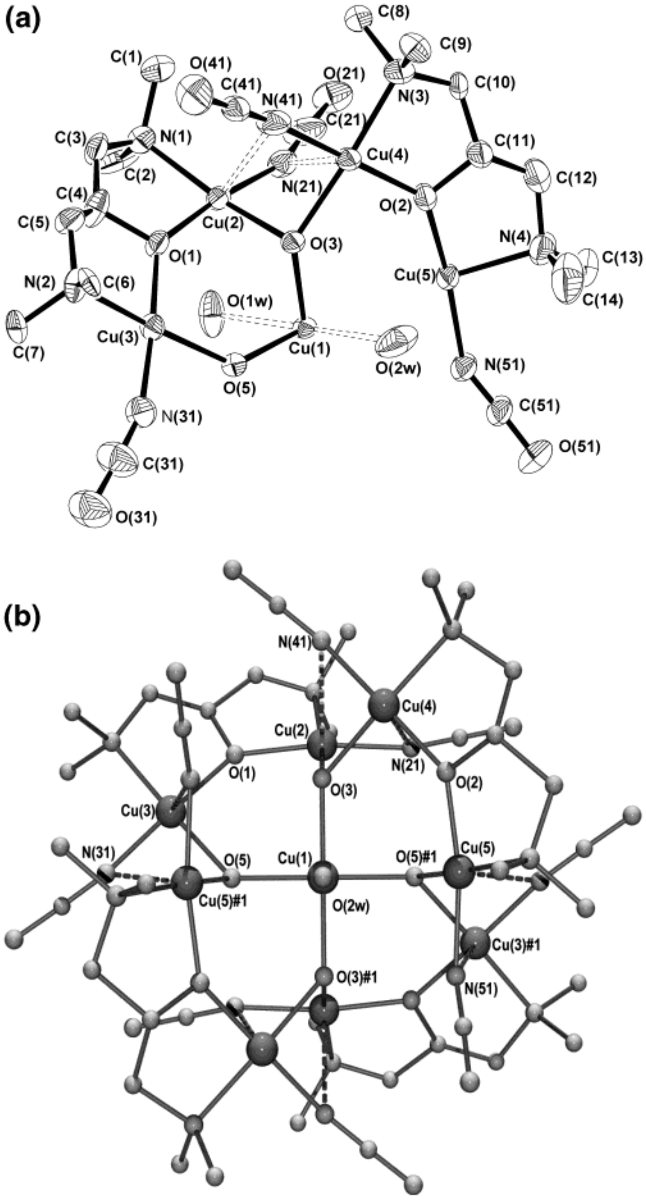

Figure 3. (a) ORTEP drawing of the asymmetric unit of **3** showing the atom-labeling scheme. Ellipsoids are at the 50% probability level. Water and perchlorate molecules are omitted for clarity. (b) Molecular structure of **3**.

It is well-known that the magnetic behavior of divalent copper complexes bridged by a pair of hydroxide[25−28] or alkoxide[29,30] oxygen atoms is highly dependent on the Cu−O−Cu bridge angle. Also it can be influenced, but in smaller measure, by the Cu−O$_{bridge}$ distance, the Cu···Cu separation, the geometry around the copper(II) center, and the geometry

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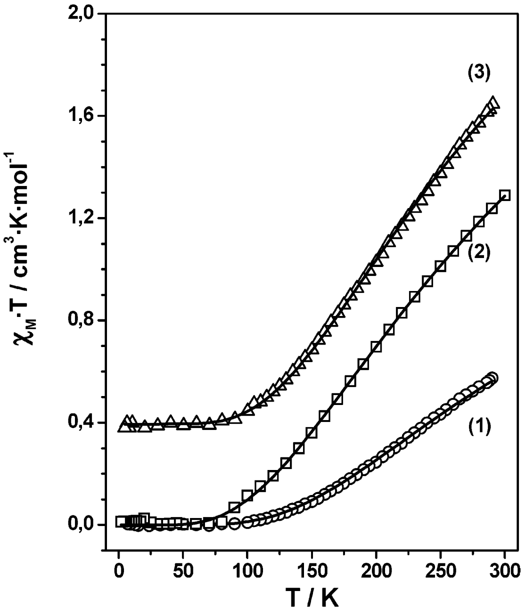

Figure 4. Plot of observed $\chi_M T$ vs T for **1**−**3**. The solid lines represent the best theoretical fits (see text).

around the bridging oxygen atom. Hatfield and Hodgson[25] have found a linear correlation between the experimentally determined exchange coupling constant and the Cu−O−Cu angle (θ). An antiferromagnetic character is found for complexes with θ larger than 97.6°, while ferromagnetic appears for smaller values of θ. An apparent similar linear relationship for alkoxide cases shows that at angles around 95.6° the exchange integral approaches zero, the point of the "accidental orthogonality".

The magnetic response of compounds **1**−**3** probably will be dominated by the expected strong antiferromagnetic coupling through the alkoxo bridge which shows the largest Cu−O−Cu bond angles (between 134.1 and 138.9°). Therefore, each compound has different structural and magnetic features that should be analyzed separately.

Compound **1** shows a $\chi_M T$ value of 0.57 cm^3 K mol^{-1} for the tetranuclear unit, smaller than that expected for four uncoupled $S = 1/2$ ions with $g = 2.0$ (1.5 cm^3 K mol^{-1}). On cooling, $\chi_M T$ decreases quickly reaching a practically diamagnetic behavior below 80 K, indicating a very strong AF coupling (Figure 4). Taking into account the compound topology, we count four exchange pathways in **1** (Figure 5a), grouped into two averaged different exchange parameters, J_1 and J_2, corresponding to the alkoxide and acetate/hydroxide bridges, respectively. As a consequence of the coupling scheme the Hamiltonian to use is $H = -J_1(S_1S_4 + S_2S_3) - J_2(S_1S_2 + S_3S_4)$. The fit on the indicated scheme was performed by means of the computer program CLUMAG.[31]

The best fit parameters found were $J_1 = -446.9$ cm^{-1}, $J_2 = 48.8$ cm^{-1}, and $g = 2.14$. The J_1 value of -446.9 cm^{-1} is the mean value corresponding to the alkoxo bridges with Cu−O−Cu angles of 137.1(1) and 138.9(1)° corresponding to Cu(1)−O(4)−Cu(4) and Cu(2)−O(2)−Cu(3), respectively. The positive J_2 value can be surprising: it is well-known that the *syn-syn* carboxylato bridge and the hydroxo bridge with Cu−O−Cu angles larger than 97.5° cause separately antiferromagnetic coupling. In compound **1** the angles are 110.7(1) and 107.9(1)° for Cu(1)−O(1)−Cu(2) and Cu(3)−O(3)−Cu(4), respectively. Consequently, the expected J_2 value should be negative. However, if two different bridging ligands act simultaneously between two metallic centers, they can cause the well-known orbital complementarity or orbital countercomplementarity phenomena.[32] In several compounds with similar simultaneous presence of bridging *syn-syn* acetate and hydroxo ligands and similar Cu−O−Cu angles, it has been observed that the antiferromagnetic contributions of each bridge almost canceled each other out (countercomplementarity) and the ferromagnetic term dominates.[33]

Taking into account the relatively low J_2 value, we can consider that in compound **1** the magnetic coupling is mainly dominated by the strongest interaction, J_1, which reduces the system to two dinuclear units magnetically isolated. To prove this possibility, the experimental magnetic data were fitted again using the Bleaney−Bowers expression, based on the following Hamiltonian: $H = -J(S_1S_2)$.

$$\chi_M = (2Ng^2\mu_B{}^2/KT)[3 + \exp(-J/KT)]^{-1} \qquad (1)$$

The parameters N, μ_B, and K in the equation have their usual meanings. Least-squares fitting of the experimental data leads to the best fit parameters $J = -448.2$ cm^{-1} and $g = 2.16$. J is very similar to J_1 and confirms the above adopted assumption.

Compound **2** shows a $\chi_M T$ value of 1.29 cm^3 K mol^{-1} for the octanuclear unit, smaller than that expected for eight uncoupled $S = 1/2$ ions with $g = 2.0$ (3.0 cm^3 K mol^{-1}). On cooling, $\chi_M T$ decreases quickly reaching diamagnetic behavior below 70 K, indicating a very strong AF coupling (Figure 4). Taking into account the compound topology, there are 11 exchange pathways in **2** (Figure 5b), which can be grouped into five averaged different exchange parameters J_1, J_2, J_3, J_4, and J_5 corresponding to the alkoxo bridge of the μ-bdmap ligand, η^1:μ-cyanate/μ_3-hydroxide (e.g. Cu(1)···Cu(2)), η^1:μ-cyanate/μ-hydroxide (e.g. Cu(3)···Cu(4)), single μ_3-hydroxide (e.g. Cu(1)···Cu(2)$^{\#1}$), and double μ_3-hydroxide (e.g. Cu(1)···Cu(1)$^{\#1}$) sets, respectively. As a consequence of the coupling scheme, the Hamiltonian to use is $H = -J_1(S_1S_4 + S_2S_3 + S_6S_7 + S_5S_8) - J_2(S_1S_2 + S_5S_6) - J_3(S_3S_4 + S_7S_8) - J_4(S_1S_6 + S_2S_5) - J_5S_1S_5$. The fit on the indicated scheme was performed by means of the computer program CLUMAG.[31]

On the other side, handling all these interactions at the same time is difficult due to the overparametrization and the correlation between the parameters. Some approaches are needed, relating the different J values with the structural parameters and bibliographic data. As first approach we

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(31) The series of calculations were made using the computer program CLUMAG which uses the irreducible tensor operator formalism (ITO): Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

(32) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(33) (a) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borrás, J.; Castiñeiras, A. *Inorg. Chem.* **2000**, *39*, 3608. (b) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borrás, J.; Castiñeiras, A. *Eur. J. Inorg. Chem.* **2002**, 2094.

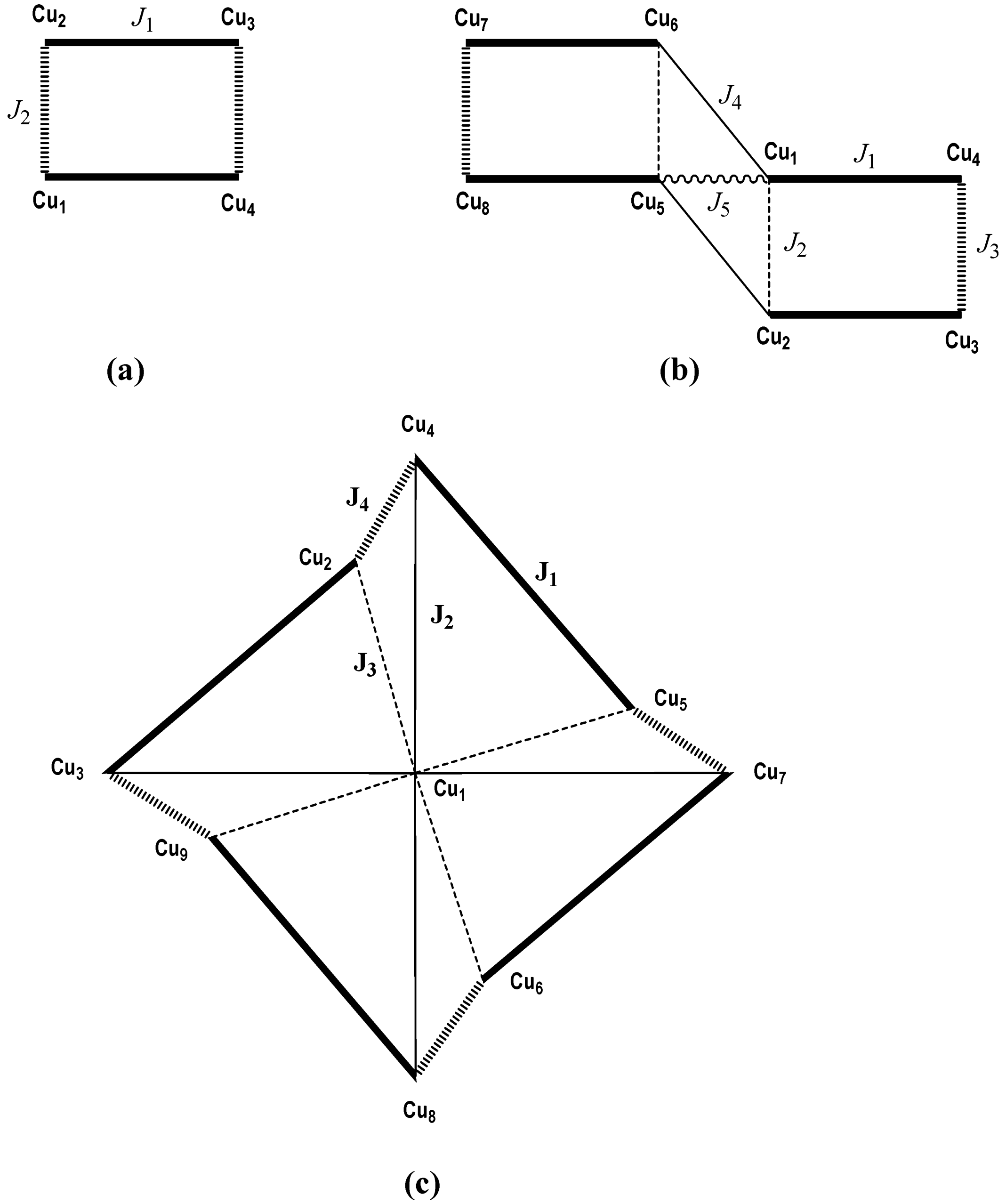

Figure 5. Schematic diagrams representing the exchange interactions within (a) complex **1**, (b) complex **2**, and (c) complex **3**.

considered in all the theoretical calculations that $g = 2.08$, as a fixed value. The above value was determined from the EPR spectrum of the crystalline powdered sample. Then we considered that $J_1 < J_2 = J_3 = J_4$ and $J_5 > 0$ in light of the Cu−O−Cu means angles in the structure: the $|J_1|$ value should be expected very high, due to the high angle values of Cu(1)−O(1)−Cu(4) and Cu(2)−O(4)−Cu(3) (135.3(1) and 134.7(1)°, respectively). J_5 corresponds to the superexchange way through double μ_3-hydroxide bridge with a Cu(1)−O(2)−Cu(1)$^{\#1}$ angle of 91.24(7)°, and it should be expected as positive. The best fit parameters were $J_1 = -373.5$, $J_2 = J_3 = J_4 = -139.5$, and $J_5 = 298.6$ cm^{-1}. In the second approach we kept this J_1 value constant and fitted J_2, J_3, J_4, and J_5 with $J_2 = J_3 \neq J_4$ and J_5. The best values obtained were $J_2 = J_3 = -139.9$, $J_4 = -144.5$, and $J_5 = +279.1$ cm^{-1}. The same procedure was repeated next, but with $J_2 \neq J_3 \neq J_4$ and $J_5 = +279.1$ cm^{-1}, affording values of −107.5, −140.8, and −153.3 cm^{-1} for J_2, J_3, and J_4, respectively. The J_2 value of −107.5 cm^{-1} is the value corresponding to the superexchange way through η^1:μ-cyanate/μ_3-hydroxide bridges. The J_3 value of −140.8 cm^{-1} corresponds to the superexchange through η^1:μ-cyanate/μ-hydroxide bridges. The J_4 value of −153.3 cm^{-1} corresponds to the superexchange way through μ_3-hydroxo bridge with a Cu(1)−O(2)−Cu(2)$^{\#1}$ angle of 135.86(9)°.

The experimental magnetic data have been fitted again using the Bleaney−Bowers expression, eq 1. Least-squares fitting of the experimental data leads to the following parameters: $J = -338.4$ cm^{-1}; $g = 1.86$. The simplified assumption is that the spin coupling is dominated by the strongest alternating interaction J_1, which reduces the system to four dinuclear units magnetically isolated; despite the apparent good fit of the plot, it becomes unrealistic due to the low *g* values found.

Compound **3** shows a $\chi_M T$ value of 1.646 cm^3 K mol^{-1} for nonanuclear unit, smaller than that expected for nine uncoupled $S = 1/2$ ions with $g = 2.0$ (3.375 cm^3 K mol^{-1}). On cooling, $\chi_M T$ decreases quickly reaching the value corresponding to an isolated Cu(II) atom at 4 K (0.38 cm^3 K mol^{-1}) (Figure 4). Taking into account the topology of the compound, we can count 16 exchange pathways in **3** which can be grouped into four coupling parameters, J_1, J_2, J_3, and J_4, corresponding to alkoxide (e.g. Cu(2)$\cdots$Cu(3)), μ_3-hydroxide(a) (e.g. Cu(1)$\cdots$Cu(4)), μ_3-hydroxide(b) (e.g. Cu(1)$\cdots$Cu(2)), and cyanate/hydroxide (e.g. Cu(2)$\cdots$Cu(4)) superexchange ways, respectively (Figure 5c). As a consequence, a fit on the indicated scheme was performed by means of the computer program CLUMAG[31] using the Hamiltonian $H = -J_1(S_2S_3 + S_4S_5 + S_6S_7 + S_8S_9) - J_2(S_1S_3 + S_1S_4 + S_1S_7 + S_1S_8) - J_3(S_1S_2 + S_1S_5 + S_1S_6 + S_1S_9) - J_4(S_2S_4 + S_3S_9 + S_5S_7 + S_6S_8)$.

As before, we carried out some approximation to get coherent values of the superexchange $|J|$ on the basis of the structural parameters of **3**. First, we fixed the *g* value on 2.04 extracted from the EPR spectrum of the complex **3**. Then we fitted J_1, J_2, J_3, and J_4 with $J_1 = J_2 < J_3 = J_4$ on the basis of the Cu−O−Cu mean angles in the structure: the values of $|J_1|$ and $|J_2|$ should be expected high and approached each other in value due to the high angle values of Cu−O$_{bdmap}$−Cu (137.7(2) and 134.1(1)°) while J_3 and J_4, which correspond to the superexchange way through μ_3-hydroxide(b) bridges with angles Cu−O−Cu (=106.3(1), 107.6(1)°) and through cyanate/hydroxide bridges with angles Cu−O−Cu (=95.4(1), 97.8(1)°), respectively, should be low and may be positive. The best fit parameters were $J_1 = J_2 = -358.6$ and $J_3 = J_4 = +190.1$ cm^{-1}. Then we kept these $J_1 = J_2$ values constant and fitted on J_3 and J_4 with $J_3 \neq J_4 > 0$. The best values obtained were $J_3 = -104.5$ and $J_4 = +197.2$ cm^{-1}.

The experimental magnetic data have been also fitted by using the Bleaney−Bowers expression, eq 1, multiplied by four, plus the contribution of one paramagnetic Cu(II). Least-squares fitting of the experimental data leads to the parameters $J = -386.3$ cm^{-1} and $g = 2.03$ for complex **3.** In this case, *J* and *g* values are reasonable and we can assume that the spin coupling is dominated by the strongest alternating interaction J_1, which reduces the system to four dinuclear units plus one paramagnetic Cu(II) magnetically isolated.

Strong antiferromagnetic coupling in the above compounds is mainly due to the Cu−O$_{bdmap}$−Cu pathway. The values of the superexchange parameter $J_1 = -446.9$, -373.5, and -358.6 cm^{-1} for **1**−**3**, respectively, are in good agreement with similar Cu−OR−Cu compounds reported in the literature.[25−30]

Conclusions

Here we have presented the syntheses, crystal structures, and magnetic study of three compounds with different nuclearities (four, eight, and nine) obtained by reacting simultaneously 1,3-bis(dimethylamino)-2-propanol and acetate or cyanate with Cu(II) sources. The successful syntheses of these compounds confirms the ability of the μ-bdmap ligand in giving species with different compositions and structures, depending on the stoichiometry of the starting materials and the reaction conditions. All the complexes show very strong antiferromagnetic behavior which has been related to the structural parameters, mainly the large Cu−O$_{bdmap}$−Cu angle.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray data also available as CCDC reference nos. 220657 for **1**, 220658 for **2**, and 220659 for **3**.

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