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Ferromagnetic Coupling by Spin Polarization in a Trinuclear Copper(II) Metallacyclophane with a Triangular Cage-Like Structure

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A series of trinuclear copper(II) complexes of general formula $A_6[Cu_3L_2]\cdot nH_2O$ [L = benzene-1,3,5-tris(oxamate); A = Li^+ (n = 8), **1a**; Na^+ (n = 11.5), **1b**; and K^+ (n = 8.5), **1c**] have been synthesized, and they have been structurally and magnetically characterized. X-ray diffraction on single crystals of **1c** shows the presence of three square-planar copper(II)−bis(oxamato) moieties which are connected by a double benzene-1,3,5-triyl skeleton to give a unique metallacyclophane-type triangular cage. The copper basal planes are virtually orthogonal to the two benzene rings, which adopt an almost perfect face-to-face alignment. Complexes **1a**−**c** exhibit a quartet (S = 3/2) ground spin state resulting from the moderate ferromagnetic coupling (J values in the range of +7.3 to +16.5 cm^{-1}) between the three Cu^{II} ions across the two benzene-1,3,5-tris(amidate) bridges [$\mathbf{H} = -J(\mathbf{S_1}\cdot\mathbf{S_2} + \mathbf{S_2}\cdot\mathbf{S_3} + \mathbf{S_3}\cdot\mathbf{S_1})$ with $S_1 = S_2 = S_3 = S_{Cu} = 1/2$]. Density functional theory calculations on the $S = 3/2$ Cu^{II}_3 ground spin state of **1c** support the occurrence of a spin polarization mechanism for the propagation of the exchange interaction, as evidenced by the sign alternation of the spin density in the 1,3,5-substituted benzene spacers.

Introduction

The design and synthesis of polytopic organic bridging ligands that are able to self-assemble spontaneously with transition metal ions to form multimetallic species of predetermined structures (nuclearity and topology) are one of the major goals in metallosupramolecular chemistry.[1] Polynuclear metallacyclic complexes with a variety of polygonal or polyhedral cage motifs have been the subject of much attention as model systems for the study of metal-directed self-assembling processes and templating effects.[2] Although their molecule guest inclusion behavior and host−guest chemistry have always attracted great interest,[3] only recently have several groups started to investigate the function of metallacyclic complexes with respect to their magnetic properties.[4,5]

In this context, we have previously reported on a trinuclear copper(II) metallacyclophane of formula $Na_6[Cu_3L_2]\cdot 11.5\ H_2O$ (**1b**), where H_6L is the parent acid derivative of the

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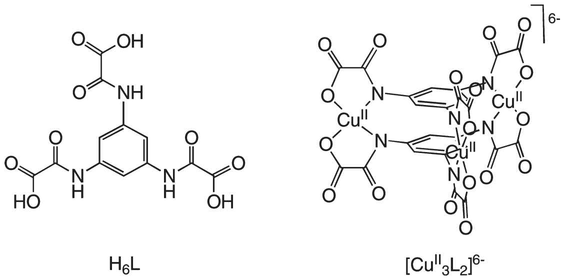
Chart 1



tritopic bridging ligand benzene-1,3,5-tris(oxamate) (Chart 1).[6] A moderate ferromagnetic coupling (J = +11.6 cm^{-1}) between the Cu^{II} ions across the double benzene-1,3,5-tris(amidate) bridge occurs in this triangular tricopper(II) complex. With the lack of a crystal structure, the ferromagnetic nature of the exchange interaction has been ascribed to the spin polarization effects through the π-type orbital pathways of the benzene spacers with a 1,3,5-substitution pattern, by analogy to the parent dinuclear copper(II) metallacyclophane with a benzene-1,3-bis(oxamate) bridging ligand (J = +16.8 cm^{-1}).[4a] This spin polarization approach to ferromagnetism is particularly appealing to get high-spin molecules, but it has received limited attention in polynuclear metal complexes.[7]

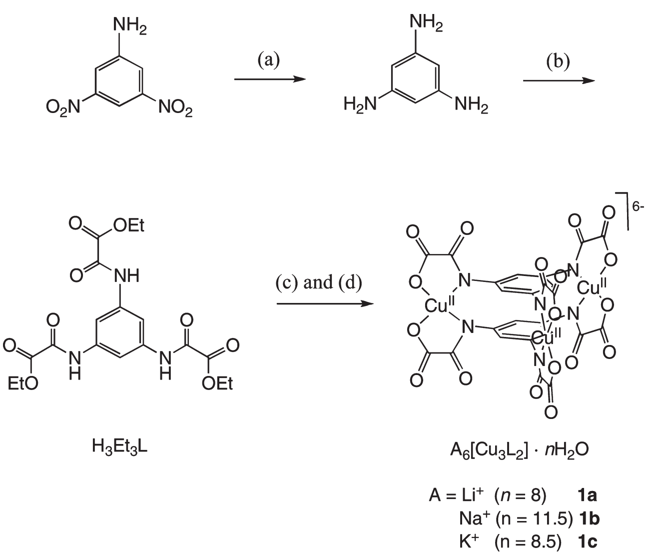
In this work, we report the synthesis, physical characterization, and magnetic properties of the trinuclear copper(II) complexes of general formula $A_6[Cu_3L_2]\cdot nH_2O$ [A = Li$^+$ (n = 8), **1a**; Na$^+$ (n = 11.5), **1b**; and K$^+$ (n = 8.5), **1c**]. The structure of **1c** has been determined by single-crystal X-ray diffraction (XRD) techniques. In addition, density functional theory (DFT) calculations have been carried out on **1c** to establish the general validity of the spin polarization approach to ferromagnetism in such a new class of triangular tricopper(II) metallacyclic complexes.

Results and Discussion

Syntheses of the Ligand and Complexes. The triethyl ester derivative of the benzene-1,3,5-tris(oxamic acid) (H_3Et_3L) was prepared by a slightly modified procedure to that reported previously[6] from the reduction of 3,5-dinitroaniline with an excess of hydrazine hydrate in THF in the presence of 10% Pd/C, followed by the condensation of the resulting 1,3,5-benzenetriamine with ethyl oxalyl chloride ester (1:3 molar ratio) in the presence of triethylamine (Scheme 1a and b).

The anionic trinuclear copper(II) complex $[Cu^{II}_3L_2]^{6-}$ was prepared by the reaction of the proligand H_3Et_3L with Cu^{2+} nitrate (2:3 molar ratio) with either Li$^+$, Na$^+$, or K$^+$ hydroxide as a base in aqueous solution (Scheme 1c and d). It was isolated as the corresponding alkaline salts of general formula $A_6[Cu_3L_2]\cdot nH_2O$ [A = Li$^+$ (n = 8), **1a**; Na$^+$ (n = 11.5), **1b**; and K$^+$ (n = 8.5), **1c**] in a moderate to good yield (40−95%). X-ray-quality green plates of **1c** were obtained by slow vapor diffusion of ethanol into the aqueous solution.

Scheme 1. Synthesis of the Diethyl Ester Derivative of the Ligand H_3Et_3L and the Corresponding Alkaline Salts of the Trinuclear Copper(II) Complex of General Formula $A_6[Cu_3L_2]\cdot nH_2O$ [A = Li$^+$ (n = 8), **1a**; Na$^+$ (n = 11.5), **1b**; and K$^+$ (n = 8.5), **1c**]: (a) NH_2NH_2, 10% Pd/C, THF; (b) $ClCOCO_2Et$, NEt_3, THF; (c) AOH, H_2O; (d) Cu$(NO_3)_2$, H_2O.



The chemical identities of both the ligand and complexes **1a**−**c** were established by elemental analyses, together with ^{1}H NMR and FTIR spectroscopies (see Experimental Section), and the structure of **1c** was further confirmed by single-crystal XRD analysis.

Description of the Structure. The structure of **1c** consists of trinuclear copper(II) anions, $[Cu^{II}_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}L)_2(H_2O)]^{6-}$ (Figure 1), coordinated potassium cations, and both coordinated and crystallization water molecules. Two crystallographically independent trinuclear units are present in the crystal lattice, which are almost identical from structural and conformational points of view (Figure 2). A summary of the crystallographic data is

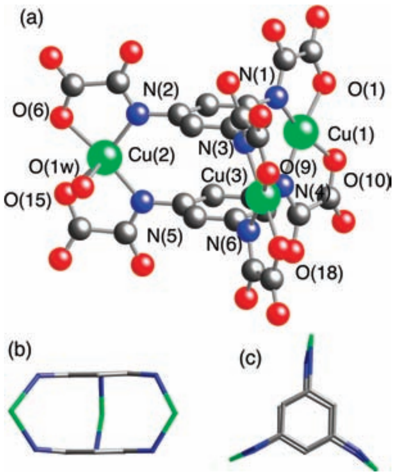


Figure 1. (a) Perspective view of one of the two crystallographically independent anionic trinuclear units of **1c** with the atom labeling of the metal environments (hydrogen atoms are omitted for clarity). (b) Front and (c) top views of the [3.3.3](1,3,5)cyclophane-type metallabicyclic core of **1c**.

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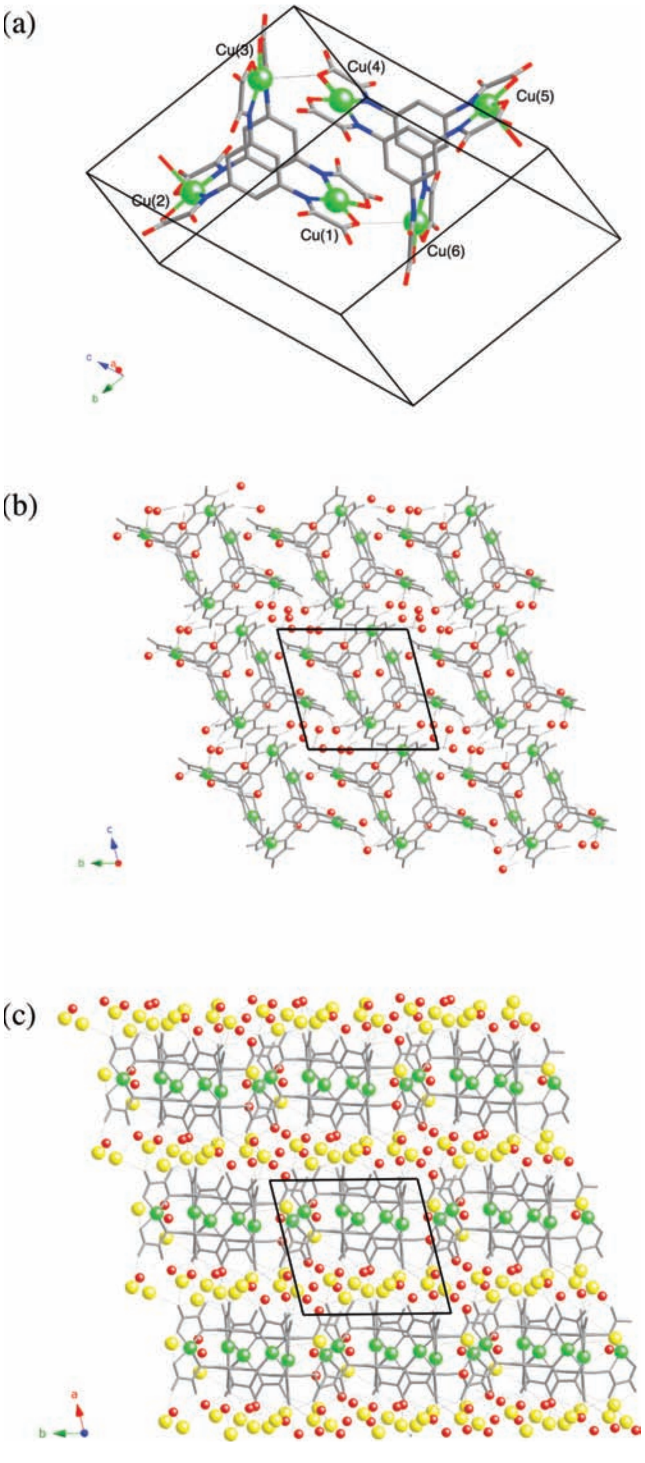

Figure 2. (a) Perspective view of the dimer of two crystallographically independent anionic trinuclear entities of **1c** with the atom-numbering scheme for the metal atoms (weak coordinative interactions are represented by solid lines). (b and c) Crystal paking views of **1c** along the *a* and *c* axes, respectively (hydrogen bonds with the water molecules and coordinative bonds with the potasium(I) cations are represented by dotted and solid lines, respectively).

Table 1. Summary of Crystallographic Data for **1c**

formula	$C_{24}H_{23}Cu_3K_6N_6O_{26.5}$
M (g mol^{-1})	1244.70
cryst syst	triclinic
space group	$P1$
a (Å)	13.4725(19)
b (Å)	13.710(2)
c (Å)	13.733(2)
α (deg)	67.915(12)
β (deg)	62.217(10)
γ (deg)	68.617(11)
V (Å^3)	2029.1(6)
Z	2
ρ_{calcd}, (g cm^{-3})	2.037
F(000)	1244
μ (mm^{-1})	2.278
T (K)	200(2)
R^a [$I > 2\sigma(I)$]	0.0487
wR^b [$I > 2\sigma(I)$]	0.1136
S^c	1.023

$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $^c S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1c**[a]

Cu(1)−N(1)	1.986(5)	Cu(4)−N(7)	1.967(5)
Cu(1)−N(4)	1.964(5)	Cu(4)−N(10)	1.983(4)
Cu(1)−O(1)	1.949(4)	Cu(4)−O(19)	1.991(4)
Cu(1)−O(10)	1.991(4)	Cu(4)−O(28)	1.974(4)
Cu(2)−N(2)	1.983(5)	Cu(5)−N(8)	2.009(5)
Cu(2)−N(5)	1.994(4)	Cu(5)−N(12)	1.987(4)
Cu(2)−O(6)	1.994(4)	Cu(5)−O(24)	1.988(4)
Cu(2)−O(15)	2.000(4)	Cu(5)−O(33)	1.981(4)
Cu(2)−O(1W)	2.407(4)	Cu(5)−O(2W)	2.421(5)
Cu(3)−N(3)	1.997(5)	Cu(6)−N(9)	1.968(5)
Cu(3)−N(6)	1.973(5)	Cu(6)−N(11)	1.966(5)
Cu(3)−O(9)	1.953(4)	Cu(6)−O(27)	1.987(4)
Cu(3)−O(18)	1.990(4)	Cu(6)−O(36)	1.978(4)
O(1)−Cu(1)−N(4)	170.49(18)	N(7)−Cu(4)−O(28)	169.35(17)
O(1)−Cu(1)−N(1)	84.17(18)	N(7)−Cu(4)−O(19)	82.93(17)
N(4)−Cu(1)−N(1)	105.33(19)	N(7)−Cu(4)−N(10)	104.54(18)
O(1)−Cu(1)−O(10)	87.13(17)	O(28)−Cu(4)−O(19)	88.40(16)
N(4)−Cu(1)−O(10)	83.41(18)	O(28)−Cu(4)−N(10)	83.97(17)
N(1)−Cu(1)−O(10)	168.75(18)	N(10)−Cu(4)−O(19)	172.32(17)
N(2)−Cu(2)−O(6)	82.65(17)	O(24)−Cu(5)−N(8)	83.02(18)
N(2)−Cu(2)−N(5)	105.01(19)	N(12)−Cu(5)−N(8)	105.65(19)
O(6)−Cu(2)−N(5)	171.96(19)	O(24)−Cu(5)−N(12)	169.78(19)
N(2)−Cu(2)−O(15)	169.4(2)	O(33)−Cu(5)−N(8)	170.01(19)
O(6)−Cu(2)−O(15)	88.97(16)	O(33)−Cu(5)−O(24)	88.06(17)
N(5)−Cu(2)−O(15)	83.14(18)	O(33)−Cu(5)−N(12)	82.84(17)
N(2)−Cu(2)−O(1W)	100.31(18)	N(8)−Cu(5)−O(2W)	99.23(18)
O(6)−Cu(2)−O(1W)	88.20(16)	O(24)−Cu(5)−O(2W)	88.78(18)
N(5)−Cu(2)−O(1W)	92.73(18)	N(12)−Cu(5)−O(2W)	95.02(18)
O(15)−Cu(2)−O(1W)	85.81(17)	O(33)−Cu(5)−O(2W)	85.01(17)
O(9)−Cu(3)−N(6)	163.79(19)	N(11)−Cu(6)−O(27)	167.66(19)
O(9)−Cu(3)−O(18)	87.37(18)	O(36)−Cu(6)−O(27)	86.68(18)
N(6)−Cu(3)−O(18)	83.09(19)	N(11)−Cu(6)−O(36)	83.47(19)
O(9)−Cu(3)−N(3)	83.27(19)	N(9)−Cu(6)−O(27)	83.18(19)
N(6)−Cu(3)−N(3)	105.4(2)	N(9)−Cu(6)−N(11)	105.7(2)
O(18)−Cu(3)−N(3)	170.33(18)	N(9)−Cu(6)−O(36)	168.10(19)

[a] The estimated standard deviations are given in parentheses.

listed in Table 1. Selected bond lengths and angles are summarized in Table 2.

Each of the two crystallographically independent trinuclear units of **1c** consists of one five-coordinate square-pyramidal and two four-coordinate square-planar copper(II)−bis(oxamate) moieties, with an axially coordinated water molecule in the former case, which are connected by a double benzene-1,3,5-triyl skeleton (Figure 1a). This leads to one of the rare examples of structurally characterized triangular metal cages of the [3.3.3](1,3,5)cyclophane type reported in the literature.[8] Within the $Cu_3(1,3,5\text{-}N_3C_6H_3)_2$ bicyclic metallacyclophane core of each crystallographically independent trinuclear unit of **1c**, there is an almost perfect face-to-face alignment of the two benzene rings from each

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pseudo-C_{3v}-symmetric, nonplanar tris(bidentate) ligand along the 3-fold molecular axis [dihedral angles (φ) of 1.2 (2) and 2.1(2)°]. Interestingly, the mean basal planes of the copper atoms are almost perpendicular to those of the benzene rings [dihedral angles (ψ) in the range of 82.9(2)−89.3(2)°] (Figure 1b and c). Hence, the average value of the C−C distance between the two facing benzene rings is 3.261(8) Å, while the values of the Cu−N−C−C torsion angles (ϕ) are in the range of 71.8(7)−90.2(7)°. Overall, this gives a triangular cage of pseudo-D_{3h} molecular symmetry which encloses a small-size internal cavity of trigonal prismatic shape and approximate dimensions of 4.93 × 3.15 Å (defined by the N−N distances between the amidate-nitrogen atoms occupying the corners of the trigonal prism). The values of the intratrimer copper−copper distances through the two benzene-1,3,5-tris(amidate) bridges vary in the range of 6.898(1)−7.064(1) Å.

In the crystal lattice of **1c**, there are weak apical coordinative interactions between a copper atom and the carboxylate-oxygen atom of an oxamato group from two neighboring crystallographically independent trinuclear units to give a dimeric entity [Cu−O = 2.824(16) and 2.776(16) Å; Cu−O−Cu = 122.3(2) and 122.7(2)°] (Figure 2a). In addition, these "dimer-of-trimers" entities establish weak hydrogen bonds with the coordinated and crystallization water molecules and coordination bonds with the potassium(I) cations through the *cis* carboxylate and carbonyl-oxygen atoms from the oxamato groups (Figure 2b and c). Such an outward coordination has been rarely exploited for metallacyclic cages, inward binding being more commonly observed.[2,3] This leads to an intricate three-dimensional network where the tricopper (II) anions and the coordinated potassium(I) cations are segregated, forming layers in the *bc* plane which alternate regularly along the *a* axis. The intertrimer copper−copper distances through the axial carboxylate-oxygen bridge are 4.200(12) and 4.236(12) Å, while the shortest intertrimer copper−copper separations through the hydrogen-bonded water molecules and the coordinated potassium(I) cations are 5.847(10) and 4.200(10) Å, respectively.

Magnetic Properties. The magnetic properties of **1a**−**c** in the form of the $\chi_M T$ versus T plots (χ_M being the molar magnetic susceptibility per trinuclear unit and T the temperature) are typical of ferromagnetically coupled triangular Cu_3^{II} entities (Figure 3). At room temperature, $\chi_M T$ varies in the range of 1.24−1.35 cm^3 mol^{-1} K for **1a**−**c**, values which are close to that expected for three magnetically noninteracting Cu^{II} ions [$\chi_M T = 3(N\beta^2 g_{Cu}{}^2/3k)S_{Cu}(S_{Cu} + 1) = 3N\beta^2 g_{Cu}{}^2/4k = 1.30$ cm^3 mol^{-1} K with $S_{Cu} = 1/2$ and $g_{Cu} = 2.15$]. Upon cooling, $\chi_M T$ increases smoothly for all three complexes to reach a sort of plateau around 5.0 K for **1c**. The value of $\chi_M T$ of 2.25 cm^3 mol^{-1} K for **1c** is close to that expected for a quartet ($S = 3/2$) ground spin state resulting from the ferromagnetic intramolecular interaction between the three local spin doublets of each Cu^{II} ion [$\chi_M T = (N\beta^2 g^2/3k)S(S + 1) = 5N\beta^2 g^2/4k = 2.17$ cm^3 mol^{-1} K with $g = g_{Cu} = 2.15$]. Below 5.0 K, $\chi_M T$ increases sharply for **1b** and **1c** to reach $\chi_M T$ values of 2.36 and 2.43 cm^3 mol^{-1} K at 2.0 K, respectively, while $\chi_M T$ decreases abruptly for **1a** to reach a $\chi_M T$ value of 1.66 cm^3 mol^{-1} K at 2.0 K (inset of Figure 3). This behavior suggests the presence of either weak ferro- or antiferromagnetic intermolecular interactions between the $S = 3/2$ Cu$^{II}{}_3$ entities for **1a**−**c**.

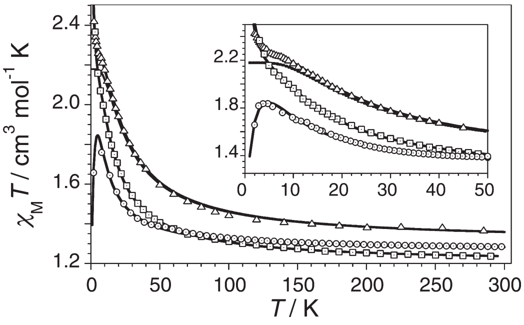

Figure 3. Temperature dependence of $\chi_M T$ for **1a** (○), **1b** (□), and **1c** (△). The inset shows the temperature dependence of $\chi_M T$ in the low-temperature region. The solid and dotted lines are the best-fit curves (see text).

With the lack of a crystal structure, the magnetic susceptibility data of **1a** and **1b** were analyzed through a spin Hamiltonian for a trinuclear model with an equilateral triangle topology that takes into account the presence of weak intermolecular interactions within the mean field approximation (eq 1 with $S_i = S_{Cu} = 1/2$ for $i = 1{-}3$):

$$H = -J(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) + zj < S_z > S_z + g\beta(S_1 + S_2 + S_3)B \quad (1)$$

where J and zj are the intra- and intermolecular magnetic coupling parameters, respectively, and g is the Zeeman factor of the Cu^{II} ions ($g = g_i$ for $i = 1{-}3$). A good fit to the experimental data was obtained through the appropriate expression (eq 2) with $J = +7.3$ cm^{-1}, $g = 2.12$, and $\theta = -0.51$ K for **1a** and $J = +11.6$ cm^{-1}, $g = 2.07$, and $\theta = +0.41$ K for **1b** (solid lines in Figure 3), where θ is the Weiss factor defined as $\theta = zjS(S + 1)/3k$ [that is, $zj = -0.28$ (**1a**) and $+0.23$ cm^{-1} (**1b**) with $S = 3/2$] (Table 3). So, a moderate ferromagnetic coupling between the Cu^{II} ions through the double benzene-1,3,5-tris(amidate) bridge is operative in **1a** and **1b**, while a very weak but non-negligible intermolecular either antiferro- (**1a**) or ferromagnetic interaction (**1b**) occurs through the coordinated alkaline ions.

$$\chi_M = [N\beta^2 g^2/4k_B(T - \theta)][5 + \exp(-3J/2kT)]/[1 + \exp(-3J/2kT)] \quad (2)$$

Alternatively, the analysis of the magnetic susceptibility data of **1c** was carried out by full-matrix diagonalization of the appropriate spin Hamiltonian for a "dimer-of-trimers" model, in agreement with its crystal structure (eq 3 with $S_i = S_{Cu} = 1/2$ for $i = 1{-}6$):

$$H = -J(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) - J(S_4 \cdot S_5 + S_4 \cdot S_6 + S_5 \cdot S_6) - J'(S_1 \cdot S_6 + S_3 \cdot S_4) + g\beta(S_1 + S_2 + S_3 + S_4 + S_5 + S_6)B \quad (3)$$

where J ($J = J_{12} = J_{13} = J_{23} = J_{45} = J_{46} = J_{56}$) and J' ($J' = J_{16} = J_{34}$) are the intra- and intertrimer magnetic coupling parameters, respectively, and g is the Zeeman factor of the Cu^{II} ions ($g = g_i$ for $i = 1{-}6$). The least-squares fit gave $J = +16.5$ cm^{-1}, $J' = +0.70$ cm^{-1}, and $g = 2.16$ (Table 3). The theoretical curve matches very

Table 3. Selected Magnetic Data for **1a−c**

complex	J (cm^{-1})^a	zj (cm^{-1})^a	J' (cm^{-1})^b	g^c	$R^f \times 10^{-5}$
1a	+7.3	−0.28		2.12	5.0
1b	+11.6	+0.23			6.0
1c	+16.5		+0.70	2.16	4.8

[a] J and zj are the intra- and intermolecular magnetic coupling parameters, respectively (eq 1, see text). [b] J and J' are the intra- and intertrimer magnetic coupling parameters, respectively (eq 3, see text). [c] g is the Zeeman factor (eqs 1 and 3, see text). [d] R is the agreement factor defined as $R = \sum[(\chi_M T)_{\text{exp}} - (\chi_M T)_{\text{calcd}}]^2/\sum[(\chi_M T)_{\text{exp}}]^2$.

well the experimental data of **1c** over the whole temperature range (solid line in Figure 3). This latter curve may be compared with that resulting when the intertrimer interactions are neglected ($J' = 0$), which exhibit a plateau at low temperatures where the $S = 3/2$ ground spin state would be the only thermally populated state (dotted line in the inset of Figure 3). Hence, a moderate intratrimer ferromagnetic coupling between the Cu$^{\text{II}}$ ions through the double benzene-1,3,5-tris(amidate) bridge is operative in **1c**, as in **1a** and **1b**. In addition, a very weak but non-negligible intertrimer ferromagnetic coupling occurs through the axial carboxylate-oxygen bridge, as previously observed for related oxalato-bridged dicopper(II) complexes with an "out-of-plane" disposition (see Figure 2a).[9]

The large variation found in the J values along this series of trinuclear copper(II) complexes (J values in the range of +7.3 to +16.5 cm^{-1}) depending on the nature of the alkali metal countercation is most likely associated with the differences in the overall torsion of the molecule. A greater twisting of the molecular structure causes the loss of orthogonality between the copper basal planes and the benzene rings, leading thus to a reduced interaction between the Cu $d_{x^2-y^2}$ orbitals through the π system of the aromatic rings. In fact, the influence of geometric effects on the magnitude of the ferromagnetic coupling via the spin polarization mechanism has been previously reported for a related series of trinuclear copper(II)−triplesalen complexes with a triangular topology (J values in the range of +2.0 to +3.1 cm^{-1}).[10]

Theoretical Calculations. DFT energy calculations on the trinuclear model molecule of **1c** with a D_{3h} ideal molecular symmetry (see Computational Details) show a quartet ($S = 3/2$) ground spin state lying well below the two degenerated doublet ($S = 1/2$) excited spin states, in agreement with the observed intratrimer ferromagnetic coupling. The calculated J value of +23.7 cm^{-1} is somewhat greater than the experimental one for **1c** ($J = +16.5$ cm^{-1}), likely due to the partial loss of orthogonality between the copper and benzene planes when considering the experimental values of the Cu−N−C−C torsion angles [$\phi = 71.8(7){-}90.2(7)°$].

The atomic spin densities obtained by NBO analysis on the ground quartet ($S = 3/2$) spin configuration of **1c** conform to a spin polarization mechanism for the propagation of the exchange interaction between the $d_{x^2-y^2}$-type unpaired electrons of the three square-planar Cu$^{\text{II}}$ ions through the π-type orbital pathway of the benzene-1,3,5-tris(amidate) bridges (Figure 4a). This is clearly evidenced by the sign alternation of the spin density on the carbon atoms of the benzene-1,3,5-triyl spacers, which leads to spin densities of the same sign on the nitrogen atoms that are coordinated to the three copper atoms (Figure 4b). A net ferromagnetic exchange interaction thus results for **1c**, as experimentally observed.

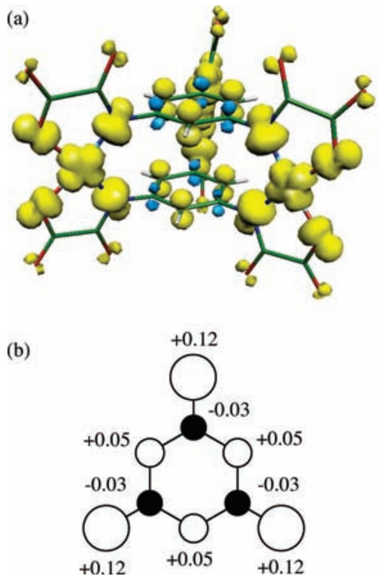

Figure 4. (a) Perspective view of the calculated spin density distribution for the ground quartet spin configuration of **1c**. Yellow and blue contours represent positive and negative spin densities, respectively. The isodensity surface corresponds to a value of 0.0025e bohr^{-3}. (b) Schematic representation of the spin density distribution of **1c** on the bridge region with the calculated average atomic spin densities. Empty and full contours represent positive and negative spin densities, respectively.

Conclusion

In summary, a unique series of ferromagnetically coupled trinuclear copper(II) complexes with the benzene-1,3,5-tris(oxamate) ligand has been obtained which possesses a unique triangular metallacyclic cage structure, as confirmed by single-crystal XRD methods. The $S = 3/2$ Cu$_3^{\text{II}}$ ground state results from the spin polarization effects through the two 1,3,5-substituted benzene spacers connecting the three square-planar Cu$^{\text{II}}$ ions, as evidenced by DFT calculations. We are currently searching for related ferromagnetically coupled metallacyclic cages of higher nuclearity with octahedral M$^{\text{II}}$ ions (M = Ni and Co), which would possess larger spin and magnetic anisotropy values, as potential candidates for molecular nanomagnets.

Experimental Section

Materials. All chemicals were of reagent-grade quality, and they were purchased from commercial sources and used as received.

H_3Et_3L. An excess of hydrazine hydrate (3.20 g, 100 mmol) was added to a mixture of 3,5-dinitroaniline (1.83 g, 10 mmol) and 10% Pd/C (0.50 g) in THF (100 mL) under Ar. The reaction mixture was refluxed for 4 h at 90 °C under continuous stirring, and then it was filtered under an Ar current. A solution of ethyl

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oxalyl chloride ester (3.35 mL, 30 mmol) in diethylether (20 mL) was added dropwise to the filtered slightly yellow solution of the freshly made 1,3,5-benzenetriamine previously charged with triethylamine (4.21 mL, 30 mmol) under Ar. The reaction mixture was refluxed for 2 h at 90 °C under continuous stirring and then handled in the air. The resulting white precipitate of $HNEt_3Cl$ was removed by filtration and washed with warm tetrahydrofuran (50 mL). After evaporation of the filtered solution on a rotatory evaporator, a beige solid was obtained which was washed with water, ethanol, and diethyl ether and dried under vacuum conditions (3.53 g, 83% yield). Anal. calcd for $C_{18}H_{21}N_3O_9$ (423): C, 51.07; H, 5.00; N 9.92. Found: C, 50.54; H, 5.04; N, 9.62. ^1H NMR ([D$_6$]DMSO): 1.32 (t, 9H; $3CH_3$), 4.31 (q, 6H; $3CH_2O$), 7.90 (s, 3H; C_6H_3), 10.88 ppm (s, 3H; 3NH). ^{13}C NMR ([D$_6$]DMSO): 161.50 (3C; 3COO), 156.90 (3C; 3CONH), 138.62 (3C; C_6H_3), 110.57 (3C; C_6H_3), 63.18 (3C; $3CH_2O$), 14.67 ppm (3C; $3CH_3$). IR (KBr): 3267 (NH), 1742 and 1693 cm^{-1} (C=O).

$Li_6[Cu_3L_2]\cdot 8H_2O$ (1a). An aqueous solution (10 mL) of $LiOH\cdot H_2O$ (0.25 g, 6.0 mmol) was added to a stirred suspension of H_3Et_3L (0.42 g, 1.0 mmol) in 10 mL of water, and then an aqueous solution (15 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (0.56 g, 1.5 mmol) was added dropwise under stirring to the reaction mixture. The resulting deep green solution was then filtered to remove the small amount of solid particles. The filtered solution was concentrated in a rotatory evaporator until a green solid of **1a** appeared, which was collected by filtration and air-dried (0.24 g, 46%). Anal. calcd for $C_{24}H_{22}Cu_3Li_6N_6O_{26}$ (1042.7): C, 27.65; H, 2.13; N, 8.06. Found: C, 27.35; H, 2.11; N, 7.92. IR (KBr): 3435 (O−H), 1646 and 1603 cm^{-1} (C=O).

$Na_6[Cu_3L_2]\cdot 11.5H_2O$ (1b). An aqueous solution (10 mL) of NaOH (0.24 g, 6.0 mmol) was added to a stirred suspension of H_3Et_3L (0.42 g, 1.0 mmol) in 10 mL of water, and then an aqueous solution (15 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (0.56 g, 1.5 mmol) was added dropwise under stirring to the reaction mixture. The resulting deep green solution was then filtered to remove the small amount of solid particles. The filtered solution was concentrated in a rotatory evaporator until a green solid of **1b** appeared, which was collected by filtration and air-dried (0.57 g, 95%). Anal. calcd for $C_{24}H_{29}Cu_3Na_6N_6O_{29.5}$ (1202.7): C, 23.98; H, 2.43; N, 6.99. Found: C, 23.94; H, 2.42; N, 6.99. IR (KBr): 3435 (O−H), 1654 and 1598 cm^{-1} (C=O).

$K_6[Cu_3L_2]\cdot 8.5H_2O$ (1c). An aqueous solution (10 mL) of KOH (0.35 g, 6.0 mmol) was added to a stirred suspension of H_3Et_3L (0.42 g, 1.0 mmol) in 10 mL of water, and then an aqueous solution (15 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (0.56 g, 1.5 mmol) was added dropwise under stirring to the reaction mixture. The resulting deep green solution was then filtered to remove the small amount of solid particles. Slow vapor diffusion of ethanol into the aqueous solution gave X-ray-quality green plates of **1c**, which were filtered on paper and air-dried (0.25 g, 40%). Anal. calcd for $C_{24}H_{23}Cu_3K_6N_6O_{26.5}$ (1244.7): C, 23.14; H, 1.85; N, 6.75. Found: C, 23.35; H, 1.91; N, 6.92. IR (KBr): 3436 (O−H), 1647 and 1602 cm^{-1} (C=O).

Physical Techniques. Elemental analyses (C, H, N) were performed at the Service Central d'Analyze du CNRS in Vernaison (France). IR spectra were recorded on Bio-Rad FTS165 spectrophotometers as KBr pellets. Variable-temperature (2.0−300 K) magnetic susceptibility measurements were carried out on powdered samples of **1a**−**c** under an applied field of 1 T ($T \geq 25$ K) and 250 G ($T < 25$ K) with a Quantum Design SQUID magnetometer. The magnetic data were corrected for the diamagnetism of the constituent atoms and the sample holder.

Crystal Structure Data Collection and Refinement. X-ray diffraction data of **1c** were collected with graphite-monochromated Mo Kα radiation using a Bruker Nonius Kappa CCD diffractometer. Data collection and data reduction were done with the COLLECT[11] and EVALCCD[12] programs. The structure was solved by direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXS-97 and SHELXL-97 programs.[13] All calculations for the structure solution and refinement were done by standard procedures (WINGX).[14] The final geometrical calculations and the graphical manipulations were carried out with the PARST97[15] and CrystalMaker[16] programs, respectively. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic ligands were set on calculated positions and refined with a riding model, while those of the water molecules were neither found nor calculated.

Computational Details. The molecular geometry of the trinuclear model molecule was not optimized, but the average bond lengths and interbond angles were taken from the real crystal structure of **1c** with imposed D_{3h} symmetry. Electronic structure calculations were carried out with the hybrid density functional B3LYP method[17] combined with the broken-symmetry approach,[18] as implemented in the GAUSSIAN 03 program,[19] by using the triple-ζ (TZV) quality basis sets proposed by Ahlrichs and co-workers.[20] The spin density data were obtained from natural bond orbital analysis.[21]

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Supporting Information Available: Crystallographic data in CIF format for the structure reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structure reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-716695. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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