

Unprecedented $(\text{Cu}_2\text{Ln})_n$ Complexes ($\text{Ln} = \text{Gd}^{3+}, \text{Tb}^{3+}$): A New “Single Chain Magnet”

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The magnetic study of a trinuclear Cu–Gd–Cu complex confirms that such basic units self-assemble to yield a high spin species. A nice fit of the magnetic data is obtained for an infinite chain of tetranuclear Gd_2Cu_2 motifs linked through the Gd ions located at the opposite vertexes of the tetranuclear motifs according to two Cu–Gd coordination modes, a double bridging through phenoxo and alkoxo oxygen atoms and a single bridging through deprotonated amide functions. The two interaction pathways are ferromagnetic. Alternating current susceptibility measurements confirm that the equivalent copper–terbium entity is a single chain magnet with a barrier height for reversal of the magnetization equal to 28.5 K.

In the past decade, considerable effort has been devoted to the preparation, characterization, and magnetic study of polynuclear metal complexes able to function as nanometer-scale magnets (SMM). This behavior has been observed at low temperature for several types of transition metal clusters^{1–3} which have in common fairly large ground state spin values together with slow relaxing magnetization in relation with significant magnetic anisotropy. Recently, new classes of SMM have been prepared. They involve lanthanide ions (Ln^{3+}) alone⁴ or associated with transition metal ions (M^{n+}).⁵ In this last case, the Ln/M molecular ratio is equal to 1.⁵ The present paper is devoted to the magnetic properties of complexes with Ln/M ratios equal to $1/2$ ($\text{M} = \text{Cu}$; $\text{Ln} =$

Gd, Tb; the intervening ligand LH_3 being 2-hydroxy-*N*-{2-[(2-hydroxyethyl)amino]ethyl}benzamide). The experimental data show that the species with a (Cu_2Tb) core assumes an SMM behavior.

The complexes are prepared from a mononuclear precursor $\text{LCuK}(\text{H}_2\text{O})_{0.5}$.⁶ They are obtained by adding gadolinium or terbium nitrate to a water solution of $\text{LCuK}(\text{H}_2\text{O})_{0.5}$.⁷ Until now, we have not been able to isolate crystals suitable for an X-ray structural determination. Nevertheless, slow evaporation of a water solution containing $\text{LCuK}(\text{H}_2\text{O})_{0.5}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ afforded crystals of the $[(\text{LCu})_2\text{Mg}(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$ complex **1**.⁸ Summarizing the results of the structural determination (Figure 1), it appears that the copper ion is in a square planar environment, surrounded by two nitrogen atoms coming from the secondary amine and the deprotonated amide functions, and two oxygen atoms from the deprotonated phenol and alcohol functions. The oxygen atom of the amide function is not involved in coordination with a metal center. The Mg^{2+} ion is surrounded by six water molecules giving an octahedral coordination geometry. The Mg–O bonds vary from 2.052(1) to 2.093(1) Å, and O–Mg–O angles are close to 90° (88.53(4) to 91.47(4)°).

- (6) $\text{LCuK}(\text{H}_2\text{O})_{0.5}$. A mixture of 2-(2-aminoethylamino)ethanol (1.04 g, 1×10^{-2} mol) and of phenylsalicylate (2.14 g, 1×10^{-2} mol) was heated for 30 min without any solvent. Methanol (40 mL) was added to the syrupy product, followed by copper acetate (2.00 g, 1×10^{-2} mol) and potassium hydroxide (2.00 g, 3.6×10^{-2} mol). The resulting solution was stirred at room temperature for 2 h, yielding a violet precipitate that was filtered off and washed with cold methanol, acetone, and diethyl ether. Yield: 2.3 g (69%). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{CuKN}_2\text{O}_{3.5}$: C, 39.7; H, 4.2; N, 8.4. Found: C, 39.3; H, 4.1; N, 8.2.
- (7) $(\text{LCu})_2\text{Gd}(\text{NO}_3)(\text{H}_2\text{O})$ (**2**). To a water solution (10 mL) of $\text{LCuK}(\text{H}_2\text{O})_{0.5}$ (0.17 g, 5.1×10^{-4} mol) was added gadolinium nitrate $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.23 g, 5.1×10^{-4} mol). The precipitate that appeared immediately was filtered off 1 h later and washed with ethanol and diethyl ether. Yield: 0.17 g (83%). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{Cu}_2\text{GdN}_5\text{O}_{10}$: C, 32.8; H, 3.5; N, 8.7. Found: C, 33.0; H, 3.5; N, 8.3.
- $(\text{LCu})_2\text{Tb}(\text{NO}_3)(\text{H}_2\text{O})$ (**3**). Yield: 0.17 g (82%). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{Cu}_2\text{N}_5\text{O}_{10}\text{Tb}$: C, 32.7; H, 3.5; N, 8.7. Found: C, 32.5; H, 3.4; N, 8.3.
- (8) Crystal structure analysis for $[(\text{LCu})_2\text{Mg}(\text{H}_2\text{O})_6]3\text{H}_2\text{O}$ (**1**): $f_w = 756.00$, monoclinic, space group $C2/c$, $a = 20.3360(18)$ Å, $b = 9.8990(8)$ Å, $c = 15.4056(13)$ Å, $\beta = 91.927(10)^\circ$, $V = 3099.5(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.620$ Mg m^{-3} , $\mu(\text{Mo K}\alpha) = 1.468$ mm⁻¹, $T = 293$ K, reflections collected/independent 13459/3019 ($R_{\text{int}} = 0.0308$), final R indices $R1 = 0.0335$ ($F_o^2 > 2\sigma(F_o^2)$), $wR2 = 0.0413$ (all data).

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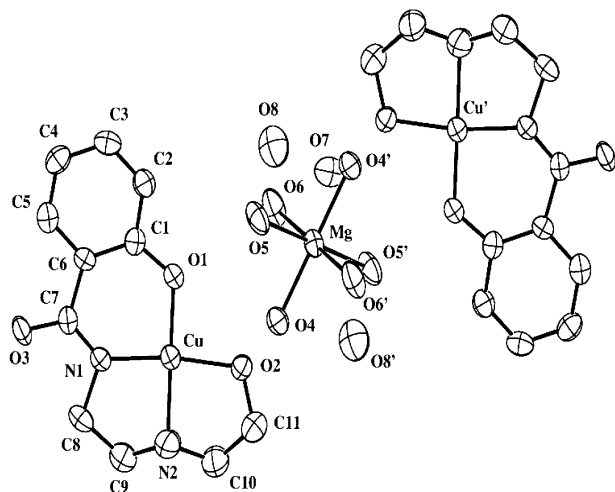


Figure 1. ZORTEP plot of **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted.

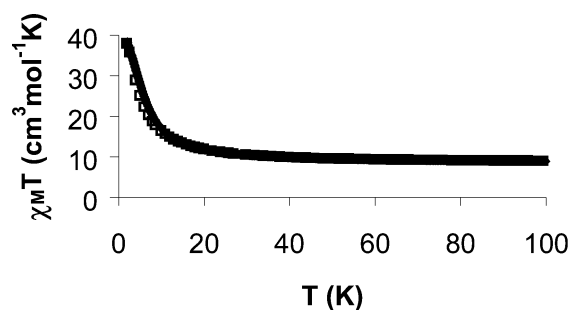


Figure 2. Temperature dependence of $\chi_M T$ for **2** at 0.1 T.

These distances and angles are similar to those found in other $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ containing compounds.^{3,9} Three water molecules of crystallization are also present. All of these water molecules are mainly involved in hydrogen bonds with the three oxygen atoms of the anionic LCu entity.

The complexes obtained by reacting Ln^{3+} ions ($\text{Ln} = \text{Gd}, \text{Tb}$) with $\text{LCuK}(\text{H}_2\text{O})_{0.5}$ may be formulated $[(\text{LCu})_2\text{Ln}(\text{NO}_3)]$ on the basis of chemical analysis. Their formulation is quite reminiscent of the previous structurally determined complex in which $\text{Ln}(\text{NO}_3)$ replaces $[\text{Mg}(\text{H}_2\text{O})_6]$.

The thermal variation of the $\chi_M T$ product for the (Cu_2, Gd) **2** complex, corrected for the diamagnetism of the ligands,¹⁰ is shown in Figure 2, with the χ_M value corresponding to the trinuclear species $[(\text{LCu})_2\text{GdNO}_3(\text{H}_2\text{O})]$. At 300 K, $\chi_M T$ is equal to $8.32 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ that is slightly smaller than expected ($8.62 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) for three insulated ions ($2\text{Cu}^{2+} + 1\text{Gd}^{3+}$). Upon lowering the temperature, $\chi_M T$ increases slowly to reach a value of c.a. $10.60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 25 K and then more heavily up to $37.90 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K which is much larger than expected for the three ferromagnetically coupled ions ($S_T = 9/2$). This value confirms the presence of ferromagnetic Cu–Gd interactions in the trinuclear unit and also between these trinuclear units. It may be recalled that within each $[(\text{LCu})_2\text{Gd}]$ entity

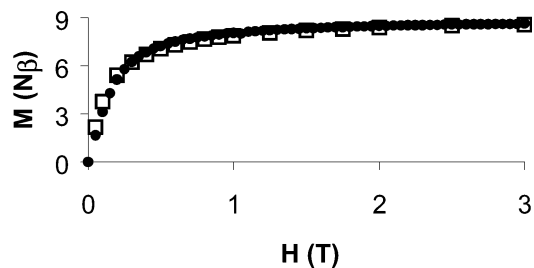


Figure 3. Field-dependent magnetization of **2** at 2 K (\square). The circles correspond to the Brillouin function for the parameters extracted from the static susceptibility data.

which can be considered as the basis unit, and according to the structural determination of the $(\text{Cu}_2\text{–Mg})$ complex, the gadolinium ion must be doubly bridged to each copper ion through the phenoxo and alkoxo oxygen atoms, leaving free the oxygen atom of the external amido group which may coordinate to a second Gd^{3+} ion. This type of structure has been recently found in tetranuclear $(\text{Cu–Gd})_2$ entities.^{11,12} In the absence of any precise structural data, we may restrict ourselves to a rough estimate of the interaction parameters. Owing to the two coordination modes available, (CuO_2Gd) and (CuNCOGd) , we fitted the experimental data to a two-term spin Hamiltonian^{13–15}

$$\hat{H} = - \sum_{i=1}^{\infty} J(S_{\text{Gd}}^i S_{\text{Cu}_1}^i + S_{\text{Gd}}^i S_{\text{Cu}_2}^i) + J'(S_{\text{Gd}}^i S_{\text{Cu}_1}^{i-1} + S_{\text{Gd}}^i S_{\text{Cu}_2}^{i+1})$$

in which a particular gadolinium ion interacts with the two copper ions of the trinuclear basic unit (J term) and with the copper ions of the previous and next basic units (J' term). Such an assembly leads to a chain of tetranuclear Gd_2Cu_2 motifs which are linked through the gadolinium ions located at the opposite vertexes. Using exact diagonalization of a closed-chain of 4 trinuclear units, a very good agreement ($R = 1 \times 10^{-5}$) between the experimental and calculated values is obtained by taking $J = 2.5 \text{ cm}^{-1}$ and $J' = 1.75 \text{ cm}^{-1}$, with $g = 1.985$. As expected, the two parameters are ferromagnetic. The larger one is attributed to the double bridge (CuO_2Gd) and the smaller to the (CuNCOGd) link in accordance with previous data.^{11,12} Let us emphasize the approximate significance of these values although they also allow a satisfying description of the field variation of the magnetization M (Figure 3). It may be noted that on increasing the applied field M increases up to $8.70 N\beta$ which differs little from the saturation value expected for a ferromagnetically coupled (Cu_2, Gd) entity, i.e., $M_{\text{sat}} = Ng\beta S_T$

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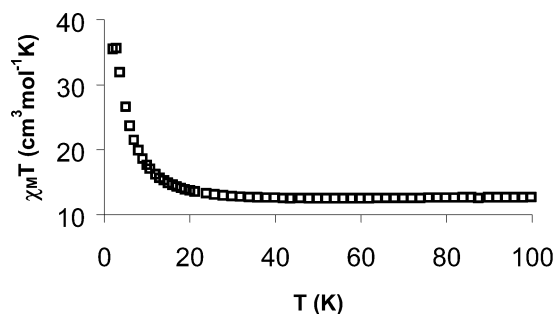


Figure 4. Temperature dependence of $\chi_M T$ for **3** at 0.1 T.

$= 9N\beta$ with $g = 2$ and $S_T = 9/2$, due to the wide energy level pattern of the 4 tetramers chain.

The $\chi_M T$ versus T curve for (Cu₂, Tb) complex **3** is reported in Figure 4. In the low-temperature regime, decreasing the temperature causes $\chi_M T$ to increase steeply from 12.53 cm³ mol⁻¹ K (value related to a (Cu₂, Tb) species) at 50 K to 35.50 cm³ mol⁻¹ K at 2 K. The last value is large compared to the value expected for three insulated ions. On the basis of the free ion value (11.75 cm³ mol⁻¹ K) for Tb³⁺ (⁷F₆) and a contribution of 0.37 cm³ mol⁻¹ K for each copper ion, the calculated value is ca. 12.50 cm³ mol⁻¹ K, not far from the experimental value observed at 300 K, 12.70 cm³ mol⁻¹ K. Finally, the profile of the $\chi_M T$ versus T curve in the 300–2 K interval seems to show a minimum around 50 K. We have to keep in mind that the Tb³⁺ ion possesses a large orbital momentum with strong spin–orbit coupling which is responsible for the decrease of the $\chi_M T$ product as T decreases. But if we remember that the Cu–Tb interaction has been shown to be ferromagnetic here (Figure 4) and in few examples,^{16,17} the coexistence of antagonist effects in the (Cu₂, Tb) species can easily explain the presence of a minimum in the $\chi_M T$ versus T curve.

The results of alternating field susceptibility measurements are more significant. The data are represented in Figure 5 as the plots of the in-phase (χ'_M) and out-of-phase (χ''_M) susceptibilities versus T for different frequencies of the external field. The profiles of these plots are unambiguous and characteristic of a single molecule magnet for they figure the onset of a slow relaxation regime of the magnetization on the measurement timescale. They are not observed for **2**. The position of the out-of-phase signals is directly related to the temperature at which the relaxation rate is equal to the ac frequency. Fitting the experimental data to the Arrhenius equation, $1/T = k_B/\Delta[\ln(2\pi\nu) + \log z_0]$, gives the barrier height for reversal of the magnetization. The best fit is obtained for $z_0 = 3.8 \times 10^{-8}$ s and $\Delta/k_B = 28.5$ K. These

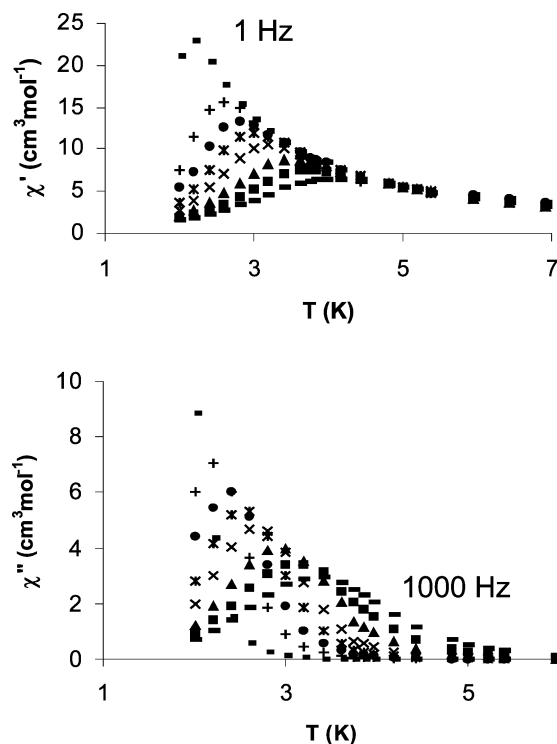


Figure 5. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities against temperature measured in a 3 G ac magnetic field oscillating at different frequencies (from 1 to 1000 Hz) for **3**.

values are comparable to the values reported in the literature for the Mn₁₂ cluster ($z_0 = 2.7 \times 10^{-7}$ s, $\Delta/k_B = 62$ K), the Fe₈ cluster ($z_0 = 2 \times 10^{-7}$ s, $\Delta/k_B = 23$ K), and the tetranuclear (Cu, Tb)₂ species ($z_0 = 2.7 \times 10^{-8}$ s, $\Delta/k_B = 21$ K), but different from the $\Delta/k_B = 322$ K found for (Pc₂Tb) entities ($z_0 = 0.6 \times 10^{-7}$ s).

Eventually, the Cole–Cole plot (Figure S1) shows a symmetrical shape with an α parameter of 0.17 similar to the one found in a previously described single chain magnet (SCM).¹⁸ This result indicates that a single relaxation time is involved in the present relaxation process. It allows us to tell that we are dealing with a new example of SCM while it excludes spin-glass or superparamagnetic behavior. Comparison of the (Cu₂, Gd) and (Cu₂, Tb) entities underlines the anisotropy importance necessary to get convenient relaxation times.

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

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