

# The first $A_2B_2$ -heterometal ferrimagnetic chain. Structures and magnetic properties of polymeric $[Gd_2Cu_2]_n$ and the corresponding monomer

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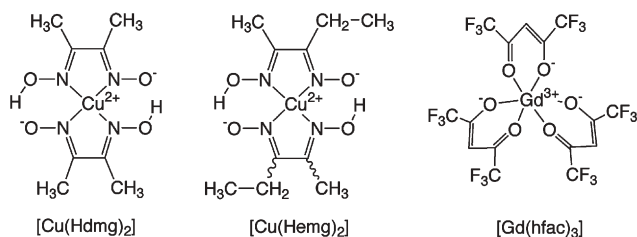
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One-dimensional polymeric complexes consisting of alternating dicopper(II) and digadolinium(III) units exhibited ferrimagnetic behavior which was ascribable to antiferromagnetic coupling across the oximate N–O bridges between the high-spin homodinuclear units.

Discrete oligonuclear complexes with bridging ligands are of increasing interest for the development of molecule-based magnets.<sup>1,2</sup> To exploit adjustable and short bridging ligands, we focused on oximate coordination compounds towards the rational synthesis of oligonuclear complexes, where the N–O groups can bridge in heterometallic systems.<sup>3</sup> Recently single-chain magnets have been developed in manganese(III)–nickel(II) coordination polymers using the N–O bridge of pyridine-2-aldoximate.<sup>4</sup> We applied bis(dimethylglyoximate)copper(II) (abbreviated as  $[Cu(Hdmg)_2]$ ) to the preparation of 3d–4f bimetallic ferro- or ferrimagnetic materials, and have reported the centrosymmetrical pentanuclear complex  $[Cu(dmg)_2\{Gd(hfac)_2\}_4(AcO)_4](Ph_4P)_2$  ( $[Gd_4Cu]$ ) and several lanthanide analogs showing ground state high-spin multiplicity.<sup>5</sup> The acetate anions were available as a cap as well as a bridge for the four peripheral Gd ions. In this communication we will report the structural and magnetic characterizations of the unique poly- and oligonuclear complexes which were obtained in the absence of acetate anions.



After deprotonation of  $[Cu(Hdmg)_2]$  in basic media, the resultant anionic oxygen atoms were planned for trapping with gadolinium(III) hexafluoroacetylacetonate  $[Gd(hfac)_3]$ .<sup>6</sup> Introduction of ethyl groups in place of methyl groups led to a remarkable steric effect. Practically the same procedures using  $[Cu(Hdmg)_2]$  and  $[Cu(Hemg)_2]$  gave different types of compounds (Hemg = ethylmethylglyoximate); polynuclear

$\{[Cu(dmg)(Hdmg)]_2\{Gd(hfac)_2(CH_3OH)\}_2\}_n$  ( $[Gd_2Cu_2]_n$ )<sup>†</sup> and tetranuclear  $\{[Cu(emg)(Hemg)(CH_3OH)]_2\{Gd(hfac)_2(CH_3OH)\}_2\}$  ( $[CuGd_2Cu]$ ).<sup>‡</sup> These structures were determined by means of single-crystal X-ray diffraction<sup>§</sup> and elemental analyses. The oxime groups were partially deprotonated,<sup>7</sup> as suggested by IR spectra, and the formal charges of the metal ions as well as the ligands were confirmed from magnetic measurements (see below).

Fig. 1 shows the chain structure of  $[Gd_2Cu_2]_n$ , running along the b-axis. Each half of the repeating unit is crystallographically independent. The Gd ions are octacoordinate and a methanol molecule is coordinated in place of a hfac ligand. The lost anion charge is compensated-for by an oximate oxygen atom (O3). Two Gd ions are related with an inversion symmetry and doubly-bridged by oximate oxygen atoms (O3 and O3\*) with Gd1–O3 and Gd1–O3\* distances of 2.435(5) and 2.381(5) Å, respectively. The interatomic Gd–Gd distance is 4.0234(5) Å. Similar oxo-bridged digadolinium(III) structures have been reported<sup>5,8</sup> and ferromagnetic coupling ( $2J/k_B = +0.052$  K) was observed through the oxo bridge.<sup>8</sup>

The Gd1 and Cu1 ions in  $[Gd_2Cu_2]_n$  are separated by 4.044(1) Å and doubly-bridged by the oximate N–O groups. The Gd1–O1 distance is 2.357(6) Å. The geometry of the bridging ligands in heterometallic Gd/Cu complexes has been well investigated in connection with their magnetic exchange couplings.<sup>5,9,10</sup> In oximate-bridged Gd/Cu systems, bent structures of Gd–O–N–Cu bridges favor antiferromagnetic interactions.<sup>10</sup> The torsion angles of Gd1–O1–N1–Cu1 and Gd1–O3–N3–Cu1 in  $[Gd_2Cu_2]_n$  are  $-62.6(6)$  and  $55.8(6)^\circ$ , respectively. Another Gd–Cu pathway is a singly-bridged Gd1\*–O3–N3–Cu1 linkage, where the torsion angle is  $-94.3(6)^\circ$  with a Gd1\*–Cu1 distance of 4.611(1) Å.

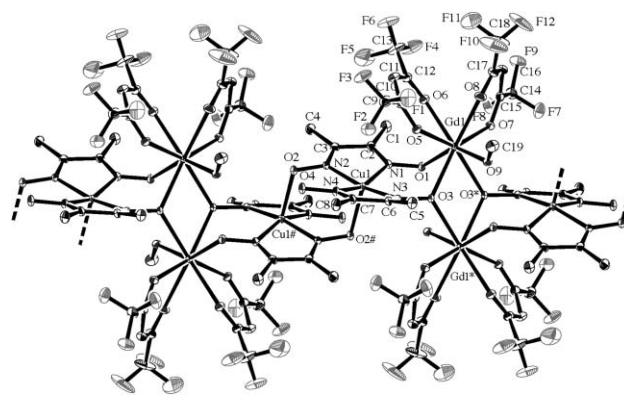


Fig. 1 Ortep drawing of  $[Gd_2Cu_2]_n$  with thermal ellipsoids at the 50% level. Two repeating units are shown. Hydrogen atoms and solvated methanol molecules are omitted.

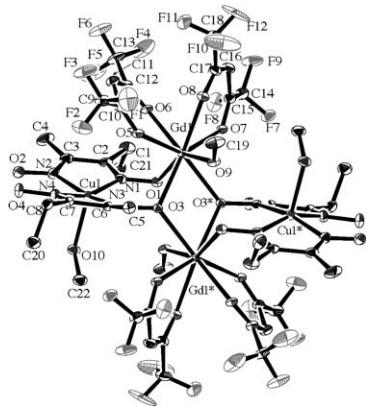
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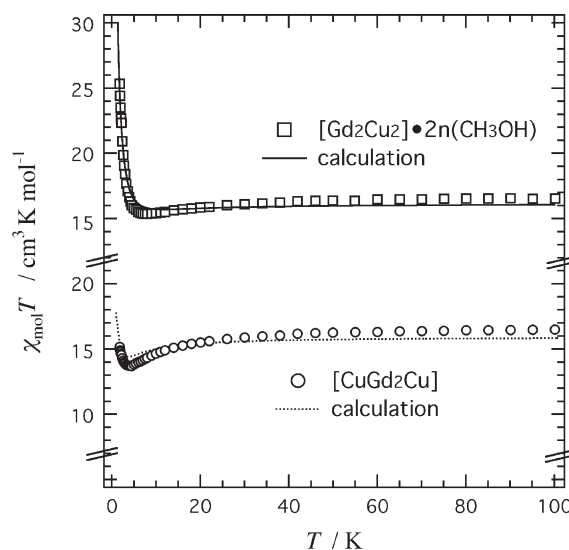
The [Cu(dm<sub>g</sub>)(Hdm<sub>g</sub>)] moieties in [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub> form a sandwich dimer, correlated with an inversion of symmetry. The CuI ion is pentacoordinate and a neighboring oximate oxygen atom is located in the axial position with a CuI–O2<sup>#</sup> distance of 2.246(5) Å. The two copper ions are separated by 3.889(1) Å. The starting material [Cu(Hdm<sub>g</sub>)<sub>2</sub>] has a quite similar dimeric structure, where, very interestingly, the ground triplet state has been characterized with  $2J/k_B = +43$  K.<sup>11</sup> Although the nominal charge of the ligands in [Cu(dm<sub>g</sub>)(Hdm<sub>g</sub>)<sub>2</sub>]<sup>2-</sup> is different from that of the ferromagnetic dimer [Cu(Hdm<sub>g</sub>)<sub>2</sub>], ferromagnetic coupling is assumed to take place as well in the present complex.

Fig. 2 shows the molecular structure of [CuGd<sub>2</sub>Cu], which can be regarded as a prototype of [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub>. The core structure is practically the same as that of [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub> but the magnetic coupling is cut off since the CuI ion is coordinated with an additional methanol molecule (C22O10) as a cap. The Gd1–Gd1\*, Gd1–CuI and Gd1\*–CuI separations are 3.9855(4), 3.939(3) and 4.7848(8) Å, respectively, within a molecule. As we expected *cis-trans* isomerism in the [Cu(Hem<sub>g</sub>)(em<sub>g</sub>)] moiety, we actually observed disorder of the Me group at C3 and Et group at C2, or the Et group at C3 and Me group at C2. Population analysis indicates that the former is a major isomer (56%). The ethyl groups in [Cu(Hem<sub>g</sub>)(em<sub>g</sub>)] are bent in the same direction with respect to the copper basal plane, and accordingly this steric hindrance prevents dimerization of [Cu(Hem<sub>g</sub>)(em<sub>g</sub>)]. Instead, a methanol ligand from the solvent occupies the axial position.

The magnetic properties were investigated on a SQUID magnetometer down to 1.8 K for both compounds. The theoretical high temperature limit of the spin-only  $\chi_{\text{mol}}T$  value should be 16.5 cm<sup>3</sup> K mol<sup>-1</sup> for a Gd<sub>2</sub>Cu<sub>2</sub> unit, with  $S_{\text{Gd}} = 7/2$  and  $S_{\text{Cu}} = 1/2$ . As Fig. 3 shows, the experimental  $\chi_{\text{mol}}T$  values at 100 K were close to the calculated ones, being in good agreement with the Gd<sub>2</sub>Cu<sub>2</sub> spin quantities. Upon cooling, the  $\chi_{\text{mol}}T$  values initially decreased but subsequently increased again. This behavior is characteristic of ferrimagnetic compounds. The ground state of [CuGd<sub>2</sub>Cu] is expected to be  $S_{\text{total}} = 6$  from Gd–Gd ferromagnetic coupling and Gd–Cu antiferromagnetic coupling. The X-ray crystal structure analysis revealed that the detailed geometries of the present compounds were compatible with the observed magnetic interactions.



**Fig. 2** Ortep drawing of [CuGd<sub>2</sub>Cu] with thermal ellipsoids at the 50% level. Hydrogen atoms are omitted. Only a major *trans*-isomer is drawn with respect to the position of the methyl and ethyl groups at C2 and C3.

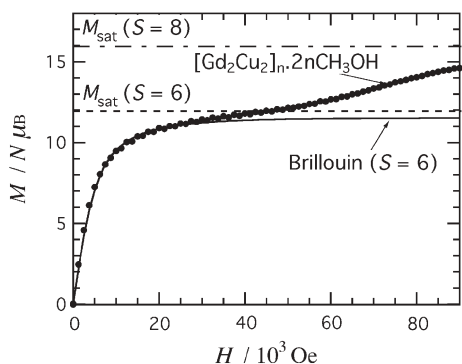


**Fig. 3** Temperature dependence of  $\chi_{\text{mol}}T$  for [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub>·2*n*(CH<sub>3</sub>OH) (top) and [CuGd<sub>2</sub>Cu] (bottom) measured at 500 Oe. The solid and broken lines represent the corresponding theoretical fits.

We should not overestimate the Gd–Gd interaction. A ferromagnetic example was reported for oxo-bridged Gd–Gd interactions but the magnetic coupling was very weak.<sup>8</sup> In the antiferromagnetic case, couplings between Gd ions are reported to be as small as  $2J/k_B = -0.06$  K.<sup>12</sup> The  $\chi_{\text{mol}}T$  minimum in the present study indicates that the antiferromagnetic coupling is operative between nearest neighbors before two Gd spins are aligned parallel, *i.e.*,  $|J_{\text{Gd-Cu}}| \gg |J_{\text{Gd-Gd}}|$ . Thus, the copper glyoximate moieties play the role of a ferrimagnetic coupler like [Gd<sub>4</sub>Cu];<sup>5</sup> the Gd spins are indirectly aligned as Gd(↑)–Cu(↓)–Gd(↑). The [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub> polymer is not a simple system consisting of alternating  $S = 7$  and  $S = 1$  species.

We describe first the magnetic properties of tetranuclear [CuGd<sub>2</sub>Cu] as a “monomer,” and then those of polymeric [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub> will be treated as a system perturbed from the monomer. To simplify the model, interactions between Gd ions are neglected and Gd–Cu relations are considered uniform. Thus, the susceptibility data of [CuGd<sub>2</sub>Cu] are analyzed according to the Heisenberg spin Hamiltonian  $H = -2J(S_{1(\text{Gd})} \cdot S_{3(\text{Cu})} + S_{1(\text{Gd})} \cdot S_{4(\text{Cu})} + S_{2(\text{Gd})} \cdot S_{3(\text{Cu})} + S_{2(\text{Gd})} \cdot S_{4(\text{Cu})})$ . We applied the Kambe vector coupling method,<sup>13</sup> giving an analytical expression as  $\chi_{\text{mol}} = (Ng^2\mu_B^2/3k_B T)(A/B)$  where  $A$  and  $B$  are functions of  $J/k_B T$ .<sup>¶</sup> The best fit curve is superposed in Fig. 3 (bottom) with optimized parameters  $2J/k_B = -0.74(6)$  K and  $g = 1.97(1)$  for the monomer. Assuming that the  $g$  value is 2.00, the purity is estimated to be 97%. The negative  $J$  value implies the ground ferrimagnetic state [Cu(↓)Gd(↑)Gd(↑)Cu(↓)] with  $S_{\text{total}} = 6$ , and a minimum is reproduced on the calculated curve.

The  $\chi_{\text{mol}}T$  value of [Gd<sub>2</sub>Cu<sub>2</sub>]<sub>n</sub>·2*n*(CH<sub>3</sub>OH) exceeded the spin-only value expected from  $S_{\text{total}} = 6$  (21 cm<sup>3</sup> K mol<sup>-1</sup>), indicating the presence of ferromagnetic coupling beyond the monomer unit. The magnetic properties of the polymer can be analyzed by introducing a  $zJ'/k_B$  factor into the expression available for the monomer, that is,  $\chi_{\text{mol}} = (Ng^2\mu_B^2/3k_B(T - zJ'))(A/B)$ . A calculated curve is superposed in Fig. 3 (top) using best fit parameters of  $2J/k_B = -1.3(2)$  K,  $g = 1.98(1)$  and  $zJ'/k_B = +0.55(5)$  K. The positive  $J'$  value implies ferromagnetic coupling between the



**Fig. 4** Magnetization curve of  $[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$  measured at 2.0 K. The solid line represents a Brillouin function with  $S = 6$ . The broken lines indicate the theoretical saturation magnetization with  $S = 6$  and 8.

monomeric “[CuGd<sub>2</sub>Cu]” units. Owing to the crystal symmetry, a one-dimensional uniform ferromagnetic structure is expected, where ferromagnetic coupling occurs at every neighboring Cu–Cu interaction. Therefore, the proposed exchange coupling model of  $[\text{Gd}(\uparrow)\text{Gd}(\uparrow)\text{Cu}(\downarrow)\text{Cu}(\downarrow)]_n$  is plausible.

We measured the magnetization curve of the present complexes, affording further evidence of the antiferromagnetic Gd–Cu coupling described above. Fig. 4 shows the result for  $[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$ . The magnetization showed a plateau around  $H = 5 \times 10^4$  Oe, this magnetization value being close to the theoretical saturation value of  $S_{\text{total}} = 6$ . The magnetization subsequently started to increase again to reach the theoretical maximum of the ferromagnetic limit ( $S_{\text{total}} = 8$ ). This behavior clearly supports the notion that the ground state is ferrimagnetic and the antiferromagnetic coupling is weak, so that the Zeeman energy gives rise to a spin-flip to give an excited  $[\text{Gd}(\uparrow)\text{Gd}(\uparrow)\text{Cu}(\uparrow)\text{Cu}(\uparrow)]_n$  state. The  $M$ – $H$  curve of  $[\text{CuGd}_2\text{Cu}]$  also showed a similar spin-flip, although the plateau is rather ambiguous.

In summary, we have reported the structural and magnetic characterization of  $[\text{Gd}_2\text{Cu}_2]_n$  and  $[\text{CuGd}_2\text{Cu}]$ . Although ferromagnetic coupling between Gd and Cu ions has often been observed and reported,<sup>9</sup> the present complexes have antiferromagnetic couplings due to their bent Cu–N–O–Gd structure. As a result, the  $[\text{Cu}(\text{dmg})_2]$  core plays the role of ferrimagnetic coupler between the Gd spins. To the best of our knowledge,  $[\text{Gd}_2\text{Cu}_2]_n$  is the first  $\text{A}_2\text{B}_2$ -type ferrimagnetic chain. This report will provide a promising strategy for the rational construction of discrete and polymeric coordination compounds based on 3d–4f heterometallic systems.

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## Notes and references

† The following procedure is typical.  $\text{Cu}(\text{Hdmg})_2$  (14.7 mg, 0.050 mmol) was dissolved in methanol (0.5 mL) containing KOH (0.10 mmol). The resultant solution was combined with a methanol solution (2 mL) containing  $\text{Gd}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  (106 mg, 0.13 mmol) and  $\text{Gd}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  (31.6 mg, 0.07 mmol) at room temperature. After addition of a methanol solution (1 mL) containing  $\text{Ph}_4\text{PCl}$  (0.1 mmol), brown plates of  $[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$  were precipitated from the clear filtrate at room temperature for a few days. They were suitable for X-ray and magnetic

studies. The yield was 32%. Found: C, 26.85; H, 2.54; N, 6.14.  $[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$  requires: C, 26.21; H, 3.04; N, 5.82%. IR (KBr) 1660, 1558, 1531, 1490, 1261, 1205, 1144 and  $1099 \text{ cm}^{-1}$ .

‡ According to a procedure similar to that of  $[\text{Gd}_2\text{Cu}_2]_n$ , black plates of  $[\text{CuGd}_2\text{Cu}]$  were prepared using  $[\text{Cu}(\text{Hemg})_2]$  instead of  $[\text{Cu}(\text{Hdmg})_2]$ . The yield was 27%. Found: C, 27.68; H, 2.74; N, 6.02.  $[\text{CuGd}_2\text{Cu}]$  requires: C, 27.66; H, 2.74; N, 5.87%. IR (KBr) 1658, 1531, 1489, 1255, 1211, 1149, 1078 and  $800 \text{ cm}^{-1}$ .

§ Diffraction data of single crystals of  $[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$  and  $[\text{CuGd}_2\text{Cu}]$  were collected on a Rigaku R-axis RAPID diffractometer with graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The structures were solved by direct methods and expanded using Fourier techniques in the CrystalStructure program package (version 3.5.1, Rigaku/MS, The Woodlands, TX, USA, 2003). Numerical absorption correction was used. All of the hydrogen atoms were located at calculated positions. The thermal displacement parameters were refined anisotropically for non-hydrogen atoms. Full-matrix least-squares methods were applied using all of the unique reflection data. Selected crystallographic data are  **$[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$** :  $\text{C}_{20}\text{H}_{22}\text{CuF}_{12}\text{GdN}_4\text{O}_{10}$ ,  $M = 927.19$ , triclinic,  $P-1$ ,  $a = 10.556(7)$ ,  $b = 11.115(9)$ ,  $c = 14.15(1) \text{ \AA}$ ,  $\alpha = 71.78(6)$ ,  $\beta = 75.76(6)$ ,  $\gamma = 84.77(6)^\circ$ ,  $V = 1527(1) \text{ \AA}^3$ ,  $Z = 2$ ,  $d_{\text{calc}} = 2.015 \text{ g cm}^{-3}$ ,  $\mu = 2.983 \text{ mm}^{-1}$ ,  $T = 95 \text{ K}$ ,  $R(I > 2\sigma(I)) = 0.061$ ,  $R_w(\text{all data}) = 0.106$  for 7005 unique reflections ( $2\theta_{\text{max}} = 55^\circ$ ).  **$[\text{CuGd}_2\text{Cu}]$** :  $\text{C}_{22}\text{H}_{26}\text{CuF}_{12}\text{GdN}_4\text{O}_{10}$ ,  $M = 955.24$ , monoclinic,  $C2/c$ ,  $a = 26.50(1)$ ,  $b = 11.984(9)$ ,  $c = 23.72(2) \text{ \AA}$ ,  $\beta = 116.10(4)^\circ$ ,  $V = 6762(7) \text{ \AA}^3$ ,  $Z = 8$ ,  $d_{\text{calc}} = 1.876 \text{ g cm}^{-3}$ ,  $\mu = 2.699 \text{ mm}^{-1}$ ,  $T = 105 \text{ K}$ ,  $R(I > 2\sigma(I)) = 0.048$ ,  $R_w(\text{all data}) = 0.079$  for 7353 unique reflections ( $2\theta_{\text{max}} = 55^\circ$ ). Somewhat large final residual electron densities were found mainly near the metal ions. For  $[\text{CuGd}_2\text{Cu}]$ , a disorder model was applied for isomers having methyl and ethyl groups at C2 and C3, and a population analysis indicated that the *trans* isomer was the major one (56(2)%). Similarly, the trifluoromethyl C18F10F11F12 group had conformers around the C17–C18 bond, and accordingly the thermal displacement factors were somewhat large along the rotation track. The major conformer (58(4)%) is drawn in Fig. 2. CCDC 280386 and 280387 for  $[\text{Gd}_2\text{Cu}_2]_n \cdot 2n(\text{CH}_3\text{OH})$  and  $[\text{CuGd}_2\text{Cu}]$ , respectively. See <http://dx.doi.org/10.1039/b511361j> for crystallographic data in CIF or other electronic format.

¶  $A = 1224e^{14x} + 840e^{12x} + 546e^{10x} + 330e^{8x} + 180e^{6x} + 84e^{4x} + 30e^{2x} + 2022 + 2016e^{-2x} + 6e^{-6x} + 30e^{-8x} + 84e^{-10x} + 180e^{-12x} + 330e^{-14x} + 546e^{-16x}$  and  $B = 17e^{14x} + 15e^{12x} + 13e^{10x} + 11e^{8x} + 9e^{6x} + 7e^{4x} + 5e^{2x} + 67 + 63e^{-2x} + e^{-4x} + 3e^{-6x} + 5e^{-8x} + 7e^{-10x} + 9e^{-12x} + 11e^{-14x} + 13e^{-16x}$  with  $x = J/k_B T$ .

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