

**Design and Magnetic Properties of a Magnetically Isolated Gd<sup>III</sup>Cu<sup>II</sup> Pair. Crystal Structures of [Gd(hfa)<sub>3</sub>Cu(salen)], [Y(hfa)<sub>3</sub>Cu(salen)], [Gd(hfa)<sub>3</sub>Cu(salen)(Meim)], and [La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] [hfa = Hexafluoroacetylacetonato, salen = *N,N'*-Ethylenebis(salicylideneaminato), Meim = 1-Methylimidazole]**

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The crystal structures of three compounds have been determined at room temperature, namely [Gd(hfa)<sub>3</sub>Cu(salen)] (**1**), [Y(hfa)<sub>3</sub>Cu(salen)] (**2**), and [Gd(hfa)<sub>3</sub>Cu(salen)(Meim)] (**3**), and the crystal structure of a fourth compound, [La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] (**4**), has been determined at  $-100$  °C; hfa = hexafluoroacetylacetonato, salen = *N,N'*-ethylenebis(salicylideneaminato), and Meim = 1-methylimidazole. [La(hfa)<sub>3</sub>Ni(salen)] (**5**), isomorphous with **1**, has also been synthesized. **1** crystallizes in the monoclinic system, space group  $P2_1/n$ , with  $a = 17.292(5)$  Å,  $b = 22.370(5)$  Å,  $c = 19.658(6)$  Å,  $\beta = 90.07(2)^\circ$ , and  $Z = 8$ . **2** crystallizes in the triclinic system, space group  $P\bar{1}$ , with  $a = 12.207(3)$  Å,  $b = 13.019(1)$  Å,  $c = 13.011(6)$  Å,  $\alpha = 82.87(4)^\circ$ ,  $\beta = 83.55(3)^\circ$ ,  $\gamma = 70.91(3)^\circ$ ,  $Z = 2$ . **3** crystallizes in the monoclinic system, space group  $P2_1/n$ , with  $a = 16.521(9)$  Å,  $b = 20.381(5)$  Å,  $c = 12.758(6)^\circ$ ,  $\beta = 93.22(6)^\circ$ , and  $Z = 4$ . **4** crystallizes in the monoclinic system, space group  $P2_1/n$ , with  $a = 12.826(2)$  Å,  $b = 23.067(8)$  Å,  $c = 13.081(3)$  Å,  $\beta = 91.37(2)^\circ$ , and  $Z = 4$ . The structures of **1**, **2**, and **4** consist of dimers of binuclear units in which the metal ions are bridged by the oxygen atoms of the salen ligand, with rather short Cu–Cu intermolecular separations (3.630(3) Å for **1**, 4.251(2) Å for **2**, and 3.620(2) Å for **4**). The Gd<sup>III</sup> ion in **1** and the Y<sup>III</sup> ion in **2** have a square antiprismatic environment, while the La<sup>III</sup> ion in **4** is nine-coordinate with a water molecule in the La<sup>III</sup> coordination polyhedron. In compounds **1**, **2**, and **4** the Cu<sup>II</sup> ion has a square planar environment. The Gd–Cu distances are 3.198(2) and 3.231(2) Å for **1**, the Y–Cu distance is 3.257(1) Å for **2**, and the La–Cu distance is 3.381(2) Å for **4**. The structure of **3** consists of perfectly isolated binuclear species, the Meim ligand occupying a peripheral apical position in the copper coordination sphere. The magnetic properties of **1** and **3** have been investigated. They have revealed Gd<sup>III</sup>–Cu<sup>II</sup> ferromagnetic interactions. The ground state of **3** is an  $S = 4$  state, stabilized by  $5.68\text{ cm}^{-1}$  with respect to the  $S = 3$  excited state. The situation is more complicated for **1**, due to the presence of Cu–Cu intermolecular interactions.

## Introduction

The mechanism of the interaction between two magnetic 3d ions within a polynuclear species is nowadays rather well understood.<sup>1</sup> The factors governing the nature, antiferro- or ferromagnetic, and the magnitude of this interaction to some extent can be controlled, so that it is now possible to design such species exhibiting predictable magnetic properties.<sup>2</sup> Perhaps, the most difficult situation is that where at least one of the two interacting ions possesses a first-order orbital momentum, for instance the case for the Co<sup>II</sup> ion in octahedral surroundings. In such a case, the Heisenberg–Dirac–Van Vleck phenomenological spin Hamiltonian is no longer appropriate to describe the spectrum of the low-lying states.<sup>1</sup>

When a lanthanide(III) ion, noted Ln<sup>III</sup>, is involved in the interaction, the situation is much less advanced as far as the understanding of the interaction phenomenon is concerned. This is obviously true when Ln<sup>III</sup> has an orbital contribution. It is also true for Gd<sup>III</sup> with a  $^8S_{7/2}$  single-ion ground state. Our main

interest in the field of Ln<sup>III</sup> molecular chemistry deals with one-, two-, or three-dimensional compounds containing both 4f and 3d ions. We recently reported several compounds of this type exhibiting rather unexpected magnetic properties.<sup>3–8</sup> In order to analyze these properties in a thorough manner, it appeared necessary to investigate model compounds containing perfectly isolated 4f–3d pairs. This paper focuses on the Gd<sup>III</sup>Cu<sup>II</sup> pair.

Gatteschi is the first to have pointed out that the Gd<sup>III</sup>–Cu<sup>II</sup> intramolecular interaction was ferromagnetic, apparently irrespective of the structural details of the compounds. He deduced this information from the study of Cu<sup>II</sup>Gd<sup>III</sup>Cu<sup>II</sup> trinuclear species.<sup>9–11</sup> The fitting of the magnetic susceptibility data led to rather large Cu<sup>II</sup>–Cu<sup>II</sup> antiferromagnetic interaction parameters, so that the values of the Gd<sup>III</sup>–Cu<sup>II</sup> interaction parameters might not be very accurate. Subsequently, other

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Cu<sup>II</sup>Gd<sup>III</sup>Cu<sup>II</sup> trinuclear species with ferromagnetic Gd<sup>III</sup>–Cu<sup>II</sup> interactions were reported.<sup>12,14</sup> In a series of extended compounds of the type Gd<sub>2</sub>[Cu(pba)]<sub>3</sub>·nH<sub>2</sub>O with pba = 1,3-propanediyl(oxamato), not only was the Gd<sup>III</sup>–Cu<sup>II</sup> interaction found to be ferromagnetic<sup>3–5</sup> but long-range ferromagnetic orderings were observed at very low temperatures.<sup>15</sup> These compounds are the first molecular-based ferromagnets involving Ln<sup>III</sup> ions.

Just after the completion of this work, an important paper appeared reporting the magnetic properties of the first structurally characterized isolated Gd<sup>III</sup>Cu<sup>II</sup> pair.<sup>16</sup> The *S* = 4 parallel spin state was found to be stabilized by 4*J* = 28 cm<sup>-1</sup> with respect to the *S* = 3 antiparallel spin state, the interaction Hamiltonian being defined as  $-J_{\text{Gd}} \cdot \mathbf{S}_{\text{Cu}}$ . Other ferromagnetically coupled Gd<sup>III</sup>Cu<sup>II</sup> binuclear compounds were synthesized, but their crystal structures were not solved.<sup>17,18</sup> For completeness, let us also mention that some Gd<sup>III</sup>Cu<sup>II</sup> polynuclear species were structurally characterized, but their magnetic properties either were not investigated or were not conclusive as to the nature of the Gd<sup>III</sup>–Cu<sup>II</sup> interaction.<sup>19–22</sup>

This paper describes the crystal structures of [Gd(hfa)<sub>3</sub>Cu(salen)] (1), [Y(hfa)<sub>3</sub>Cu(salen)] (2), [Gd(hfa)<sub>3</sub>Cu(salen)(Meim)] (3), and [La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] (4), with hfa = hexafluoroacetylacetonato, salen = *N,N'*-ethylenebis(salicylideneaminato), and Meim = 1-methylimidazole. [La(hfa)<sub>3</sub>(Ni(salen))] (5) which is isomorphous with 1 was also synthesized. The structure of compound 1 reveals that the Gd<sup>III</sup>Cu<sup>II</sup> pairs are not perfectly isolated, but are associated in dimers of pairs with rather short intermolecular Cu–Cu separations. To avoid this, an Meim ligand was added in the copper coordination sphere, which afforded perfectly isolated pairs in compound 3. The magnetic properties of 3 were studied in a thorough manner.

## Experimental Section

**Syntheses.** The starting materials [Cu(salen)], [Ni(salen)], and [Ln(hfa)<sub>3</sub>]<sub>2</sub>H<sub>2</sub>O (Ln = La, Gd, Y) were obtained according to standard procedures.<sup>23,24</sup> 1-Methylimidazole is commercially available. [Gd(hfa)<sub>3</sub>Cu(salen)] (1) was prepared as follows: A 132 mg (0.4 mmol) sample of [Cu(salen)] dissolved in 50 mL of hot chloroform was slowly added to a solution of 326 mg (0.4 mmol) of [Gd(hfa)<sub>3</sub>]<sub>2</sub>H<sub>2</sub>O in chloroform under continuous stirring. The solution turned pink and subsequently red in the course of the reaction. It was then heated under

reflux for 1 h. Slow evaporation afforded well-shaped dark red small single crystals. Anal. Calcd for C<sub>31</sub>H<sub>17</sub>N<sub>2</sub>O<sub>8</sub>F<sub>18</sub>CuGd (1): C, 33.60; H, 1.55; N, 2.53; F, 30.86; Cu, 5.73; Gd, 14.19. Found: C, 33.84; H, 1.78; N, 2.45; F, 30.12; Cu, 5.49; Gd, 14.00. [Y(hfa)<sub>3</sub>Cu(salen)] (2), [La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] (4), and [La(hfa)<sub>3</sub>Ni(salen)] (5) were obtained in a similar fashion, using [Y(hfa)<sub>3</sub>]<sub>2</sub>H<sub>2</sub>O and [La(hfa)<sub>3</sub>]<sub>2</sub>H<sub>2</sub>O instead of [Gd(hfa)<sub>3</sub>]<sub>2</sub>H<sub>2</sub>O and using [Ni(salen)] instead of [Cu(salen)]. Anal. Calcd for C<sub>31</sub>H<sub>17</sub>N<sub>2</sub>O<sub>8</sub>F<sub>18</sub>CuY (2): C, 35.81; H, 1.65; N, 2.69; F, 32.88; Cu, 6.11; Y, 8.55. Found: C, 35.59; H, 1.75; N, 2.71; F, 32.45; Cu, 6.01; Y, 8.46. Calcd for C<sub>31</sub>H<sub>19</sub>N<sub>2</sub>O<sub>6</sub>F<sub>18</sub>CuLa (4): C, 33.61; H, 1.73; N, 2.53; F, 30.87; Cu, 5.74; La, 12.54. Found: C, 33.52; H, 1.98; N, 2.48; F, 30.41; Cu, 5.53; La, 12.29. Calcd for C<sub>31</sub>H<sub>17</sub>N<sub>2</sub>O<sub>8</sub>F<sub>18</sub>NiLa (5): C, 34.32; H, 1.60; N, 2.58; F, 31.52; Ni, 5.41; La, 12.80. Found: C, 34.15; H, 1.72; N, 2.54; F, 31.15; Ni, 5.21; La, 12.59. [Gd(hfa)<sub>3</sub>Cu(salen)Meim] (3) was synthesized as [Gd(hfa)<sub>3</sub>Cu(salen)] except that 0.085 mL (0.8 mmol) of 1-methylimidazole was added to the solution before the slow evaporation. The solution turned violet at once. Slow evaporation afforded very small green single crystals. Anal. Calcd for C<sub>35</sub>H<sub>23</sub>N<sub>4</sub>O<sub>8</sub>F<sub>18</sub>CuGd (3): C, 35.32; H, 1.95; N, 4.71; F, 28.73; Cu, 5.34; Gd, 13.21. Found: C, 35.42; H, 2.12; N, 4.79; F, 28.42; Cu, 5.19; Gd, 13.04.

## Crystallographic Data Collection and Structure Determination.

Reflections were collected at room temperature with the  $\omega$ - $2\theta$  mode up to Bragg angles of 25° for compounds 1, 3, and 4 and 23° for compound 2. Monochromatized Mo radiation was used ( $\lambda = 0.71069$  Å). Lattice constants were determined from 25 reflections conveniently distributed in reciprocal space. Direct methods were used to locate the first atoms. Subsequent Fourier series and refinements were computed to locate all the other atoms. Form factors were taken from the *International Tables of Crystallography*. Computations were carried out using the CRYSTALS package.<sup>25</sup> Absorption corrections were made using DIFABS.<sup>26</sup> Hydrogen atoms were not found. Reliability factors were defined as  $R = \sum(|F_o| - |F_c|)/\sum|F_o|$  and  $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ . Crystallographic data for compounds 1–4 are summarized in Table 1. For compounds 1–3 tiny crystals were used because larger crystals were not unique. The crystal size problem, together with the very large number of variable parameters in the case of 1, and the disorder of the fluorine atoms led to poor *R* factors. Detailed crystallographic data are given as Supporting Information. Let us note here that compound 1 crystallizes in a monoclinic space group with  $\beta = 90.07(2)^\circ$ . An orthorhombic space group was ruled out because criteria of equivalent reflections are not satisfied, and observed systematic absences are not compatible with such a space group. For compounds 1 and 2, the fluorine atoms were found to be disordered and equally distributed between two positions, and consequently their temperature factors were refined isotropically while those of all other atoms were refined anisotropically. For compound 3, 12 among 18 fluorine atoms were found to be equally distributed between two positions. [La(hfa)<sub>3</sub>Ni(salen)] (5) was found to be isostructural with 1 from systematic extinctions and approximate lattice parameters ( $a = 17.2(1)$  Å,  $b = 22.41(6)$  Å,  $c = 19.7(3)$  Å,  $\beta = 90.4(9)^\circ$ ). The atomic coordinates for compounds 1–4 are given as Supporting Information, and selected bond lengths are given in Table 2.

**Magnetic Measurements.** These were carried out with a Quantum Design MPMS-5S SQUID magnetometer working down to 1.9 K in the dc mode. It was verified that the magnetic susceptibilities for 1 and 3, measured at 1 kOe, were equal to the zero-field susceptibilities. The diamagnetic corrections were obtained by measuring the diamagnetic susceptibilities of [La(hfa)<sub>3</sub>Ni(salen)] (5) and Meim. These were found to be equal to  $-630 \times 10^{-6}$  and  $-40 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>, respectively.

## Description of the Structures

**[Gd(hfa)<sub>3</sub>Cu(salen)] (1).** The monoclinic unit cell contains  $4 \times 2$  [Gd(hfa)<sub>3</sub>Cu(salen)] molecules related by a pseudo center of symmetry located at  $x = -0.047$ ,  $y = 0.1864$ ,  $z = 0.2546$ .

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**Table 1.** Crystal Data for Compounds 1–4

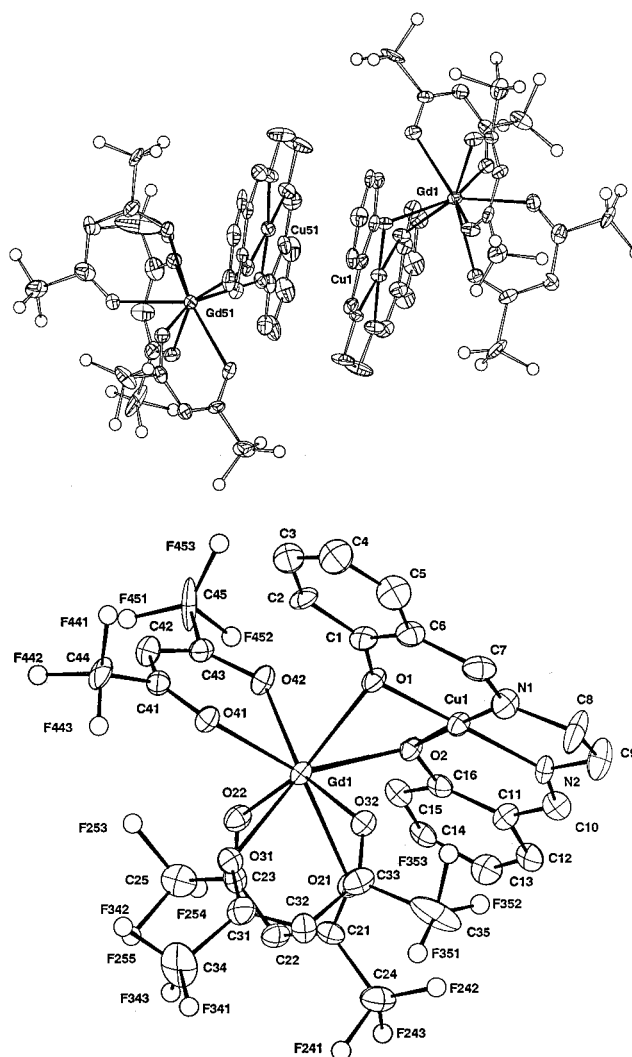
	1	2	3	4
empirical formula	GdCuC <sub>31</sub> H <sub>17</sub> N <sub>2</sub> O <sub>8</sub> F <sub>18</sub>	YCuC <sub>31</sub> H <sub>17</sub> N <sub>2</sub> O <sub>8</sub> F <sub>18</sub>	GdCuC <sub>35</sub> H <sub>24</sub> N <sub>4</sub> O <sub>8</sub> F <sub>18</sub>	LaCuC <sub>31</sub> H <sub>19</sub> N <sub>2</sub> O <sub>9</sub> F <sub>18</sub>
fw	1108.23	1039.89	1191.35	1107.92
<i>a</i> (Å)	17.292(5)	12.207(3)	16.521(9)	12.826(2)
<i>b</i> (Å)	22.370(5)	13.019(5)	20.381(5)	23.067(8)
<i>c</i> (Å)	19.658(6)	13.011(6)	12.758(6)	13.081(3)
$\alpha$ (deg)	90	82.87(4)	90	90
$\beta$ (deg)	90.07(2)	83.55(3)	93.22(6)	91.37(2)
$\gamma$ (deg)	90	70.91(3)	90	90
<i>V</i> (Å <sup>3</sup> )	7604(3)	1933(20)	4289(9)	3869(2)
<i>Z</i>	8	2	4	4
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
<i>T</i>	room	room	room	–100 °C
radiation ( $\lambda$ (Å))	Mo K $\alpha$ (0.710 69)	Mo K $\alpha$ (0.710 69)	Mo K $\alpha$ (0.710 69)	Mo K $\alpha$ (0.710 69)
$\rho_{\text{calc}}$	1.94	1.77	1.85	1.91
$\mu$ (cm <sup>–1</sup> )	24.32	21.85	21.65	17.80
<i>R</i> <sup>a</sup>	0.058	0.068	0.070	0.054
<i>R</i> <sub>w</sub> <sup>b</sup>	0.062	0.070	0.081	0.059

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|. \quad ^b R_w = \sum w(|F_o| - |F_c|)^2 / \sum w F_o^2.$$

**Table 2.** Selected Bond Lengths (Å) for Compounds 1–4

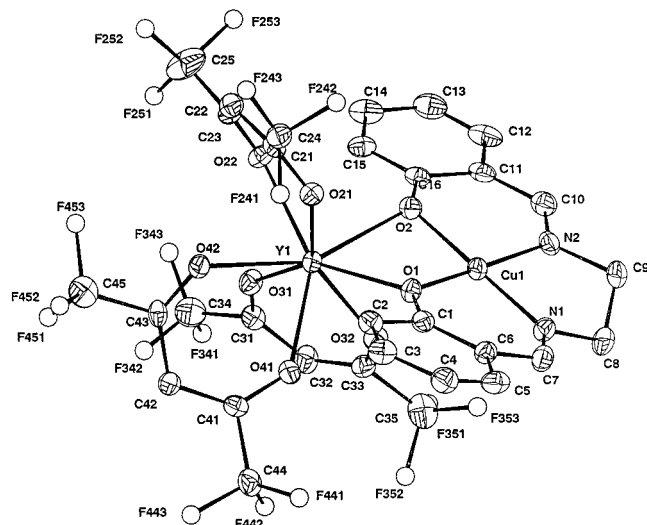
Compound 1			
Gd1–O1	2.48(1)	Gd51–O51	2.45(1)
Gd1–O2	2.41(1)	Gd51–O52	2.46(1)
Gd1–O21	2.42(1)	Gd51–O71	2.34(1)
Gd1–O22	2.37(1)	Gd51–O72	2.37(1)
Gd1–O31	2.37(1)	Gd51–O81	2.35(1)
Gd1–O32	2.37(1)	Gd51–O82	2.36(1)
Gd1–O41	2.34(1)	Gd51–O91	2.40(1)
Gd1–O42	2.38(1)	Gd51–O92	2.35(1)
Cu1–O1	1.89(1)	Cu51–O51	1.90(1)
Cu1–N1	1.89(1)	Cu51–N51	1.91(2)
Cu1–O2	1.924(9)	Cu51–O52	1.90(1)
Cu1–N2	1.919(1)	Cu51–N52	1.91(1)
Compound 2			
Y1–O1	2.326(6)	Y1–O2	2.413(6)
Y1–O21	2.344(7)	Y1–O22	2.361(7)
Y1–O31	2.281(7)	Y1–O32	2.418(7)
Y1–O41	2.294(7)	Y1–O42	2.352(7)
Cu1–O1	1.918(6)	Cu1–N1	1.921(9)
Cu1–O2	1.937(7)	Cu1–N2	1.927(9)
Compound 3			
Gd1–O1	2.38(2)	Gd1–O2	2.39(2)
Gd1–O21	2.37(2)	Gd1–O22	2.44(2)
Gd1–O31	2.41(2)	Gd1–O32	2.41(2)
Gd1–O41	2.38(2)	Gd1–O42	2.37(1)
Cu1–O1	1.91(2)	Cu1–N1	2.03(2)
Cu1–O2	2.01(2)	Cu1–N2	1.96(3)
Cu1–N3	2.13(4)		
Compound 4			
La1–O1	2.591(7)	La1–O2	2.578(7)
La1–O3	2.618(9)	La1–O4	2.551(8)
La1–O5	2.522(9)	La1–O6	2.505(9)
La1–O7	2.519(8)	La1–O8	2.493(8)
La1–O9	2.522(8)	Cu1–O1	1.897(8)
Cu1–N1	1.95(1)	Cu1–O2	1.928(7)
Cu1–N2	1.93(1)		

Because of this pseudosymmetry, the atomic parameters were refined in two blocks. The atom labeling for the molecule containing the atoms Gd1 and Cu1 is the same as that for the molecule [Y(hfa)<sub>3</sub>Cu(salen)] shown in Figure 2. In the following, the structural information for the molecule containing the metal atoms noted Gd51 and Cu51 will be given in parentheses. The assembly of the two molecules of the asymmetric unit is shown in Figure 1. For the sake of clarity, the disordered fluorine atoms are not represented. Within each molecule the metal atoms are doubly bridged by the oxygen atoms of the salen ligand. The intramolecular Gd–Cu distance is equal to 3.198(2) Å (3.231(2) Å). The copper atom and its two oxygen and two nitrogen neighbors form a plane. The deviations from



**Figure 1.** Top: View of two [Gd(hfa)<sub>3</sub>Cu(salen)] molecules related through a pseudo center of symmetry in compound 1. Bottom: View of one of the [Gd(hfa)<sub>3</sub>Cu(salen)] binuclear units in compound 1 with the atom-labeling scheme. Thermal ellipsoids are drawn at 20% probability. Open circles correspond to fluorine atoms.

this mean plane are 0.013 Å for Cu1, 0.008 Å for O1, –0.014 Å for O2, –0.014 Å for N1, and 0.008 Å for N2 (0.058 Å for Cu51, 0.053 Å for O51, –0.023 Å for O52, –0.024 Å for N51, and 0.052 Å for N52). The bridging network GdO1O2Cu has a butterfly shape; taking O1O2 as the hinge, the GdO1O2 and



**Figure 2.** View of the [Y(hfa)<sub>3</sub>Cu(salen)] binuclear unit in compound 2. Thermal ellipsoids are drawn at 20% probability. Open circles correspond to fluorine atoms.

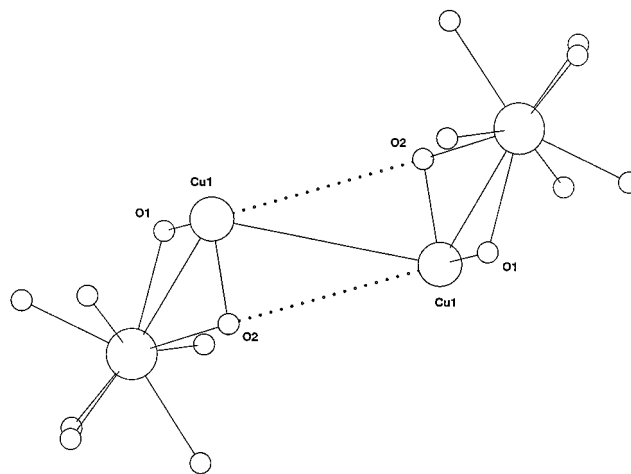
CuO1O2 planes form a dihedral angle of 133.0° (130.4°), the O1–O2 distance being equal to 2.544 Å (2.545 Å).

The gadolinium environment is a distorted square antiprism of oxygen atoms, two belonging to the salen ligand and six belonging to the hfa ligands. The upper square consists of O1, O21, O42, and O41 (O51, O71, O92, and O91), and the lower square, of O2, O22, O31, and O32 (O52, O72, O81, and O82). The average O–O distances are 2.750 Å (2.744 Å) within the upper plane and 2.797 Å (2.766 Å) within the lower plane; the average interplane O–O distance is 3.200 Å (3.210) Å. The dihedral angle between upper and lower planes is 10.1° (10.2°).

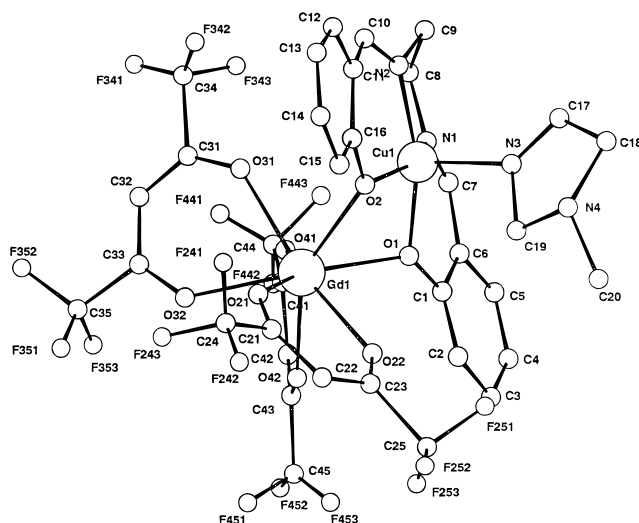
Due to the occurrence of the pseudo center of symmetry, the two least-squares planes Cu1O1O2N1N2 and Cu51O51–O52N51N52 are nearly parallel, the dihedral angle between them being 2.6°. The Cu1–Cu51 distance is equal to 3.630(3) Å. The Gd1–Cu1–Cu51 angle is equal to 114.4°. The copper atom of the first molecule is located neither above the copper atom nor above the salen oxygen atoms of the second molecule. The Cu–O distances involving the two molecules of the asymmetric unit are 3.619(11) and 4.377(11) Å for Cu1–O51 and Cu1–O52, respectively, and 4.400(12) and 3.578(11) Å for Cu51–O1 and Cu51–O2, respectively.

**[Y(hfa)<sub>3</sub>Cu(salen)] (2).** The unit cell contains two molecules related through a center of symmetry. The molecule shown in Figure 2 is very close to what was found for compound 1, yttrium replacing gadolinium. The intramolecular Y–Cu distance is equal to 3.275 Å, and the O1–O2 distance between bridging oxygen atoms is equal to 2.668 Å. The YCuO1O2 bridging network has again a butterfly shape, the dihedral angle between YO1O2 and CuO1O2 planes being equal to 27.2°. The copper atom and its O1, O2, N1, and N2 neighbors form a plane. The deviations from this mean plane are 0.030 Å for Cu, –0.053 Å for O1, 0.037 Å for O2, 0.040 Å for N1, and –0.053 Å for N2. The yttrium atom is surrounded by eight oxygen atoms, forming a distorted square antiprism. The upper plane consists of the O1, O21, O41, and O42 atoms with O–O distances of 2.824, 2.881, 2.725, and 2.922 Å, respectively. The lower plane consists of O2, O22, O31, and O32 with O–O distances of 3.162, 2.859, 2.730, and 2.736 Å, respectively. The mean interplane O–O distance is 2.916 Å. The dihedral angle between those two mean planes is 0.89°.

The Cu–Cu separation between two units related through a symmetry center is equal to 4.251(2) Å, which is significantly larger than in 1. The sequence of Y–Cu–Cu–Y atoms makes



**Figure 3.** Schematic representation of the association of two [Y(hfa)<sub>3</sub>Cu(salen)] molecules related through an inversion center in compound 2.



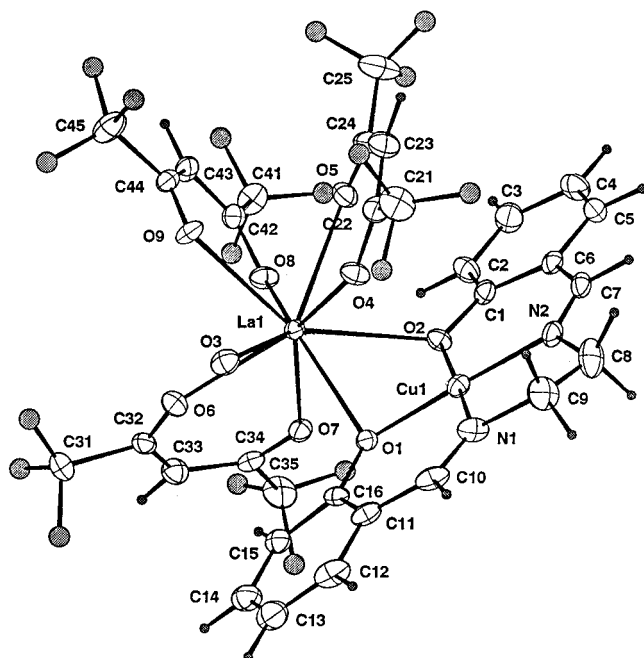
**Figure 4.** View of the [Gd(hfa)<sub>3</sub>Cu(salen)(Meim)] binuclear unit in compound 3.

a broken line with YCuCu angles of 107.2° (see Figure 3). The two least-squares planes of copper surroundings are parallel, and the axis joining the two copper atoms makes an angle of 36° with the normal to those planes.

**[Gd(hfa)<sub>3</sub>Cu(salen)(1-Meim)] (3).** The structure again consists of Gd<sup>III</sup>Cu<sup>II</sup> binuclear units (see Figure 4), in which the metal ions are doubly bridged by the oxygen atoms of the salen ligand. The additional Meim ligand occupies the apical position in the copper coordination sphere, with an apical Cu–N bond length of 2.13(4) Å. The equatorial plane consists of the oxygen and nitrogen atoms of salen. The deviations of these atoms from the least-squares equatorial plane are 0.087 Å for O1, –0.084 Å for O2, –0.085 Å for N1, and 0.083 Å for N2. The copper atom is displaced from this equatorial plane toward the apical position by 0.382 Å. The Gd–Cu distance is equal to 3.252(4) Å, and the dihedral angle between the GdO1O2 and CuO1O2 planes is equal to 140.43°.

The gadolinium environment is again a distorted square antiprism. The average O–O distances are 2.83 Å for the upper plane, 2.87 Å for the lower plane, and 2.87 Å for the edges joining these two planes. The dihedral angle between upper and lower planes is 0.9°. These planes are puckered with respective averaged distances to planes of 0.24 and 0.18 Å.

**[La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] (4).** The monoclinic unit cell contains 2 × 2 [La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] molecules related by a center of symmetry (see Figure 5). The intramolecular La–



**Figure 5.** View of the  $[\text{La}(\text{hfa})_3(\text{H}_2\text{O})\text{Cu}(\text{salen})]$  binuclear unit in compound **4**. Thermal ellipsoids are drawn at 20% probability. Open circles correspond to fluorine atoms.

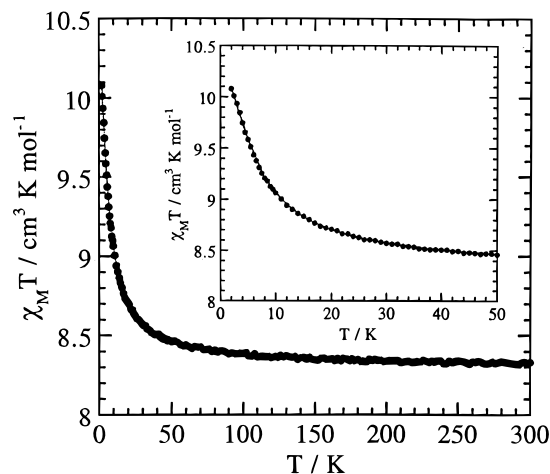
Cu distance is equal to  $3.381(2)$  Å. As for **1** and **2**, the copper atom and its four nearest neighbors form a plane. On the other hand, a water molecule is bound to the La atom, which consequently is surrounded by nine oxygen atoms instead of eight for compounds **1**–**3**. The occurrence of this water molecule in the  $\text{La}^{\text{III}}$  coordination polyhedron results in a somewhat different space filling although the envelope wrapped around the molecule encloses about the same volume. This is responsible for a different unit cell which nevertheless maintains a close relationship with that of compound **1**. As a matter of fact, the  $a$  and  $c$  lattice parameters for **4** are half-diagonals of the  $ac$  base of the unit cell of **1**.

The two symmetry-related least-squares planes of copper surroundings are parallel with a Cu–Cu separation of  $3.621(2)$  Å, which is very close to the value found for **1**. The LaCuCu angle is equal to  $123^\circ$ .

### Magnetic Properties

Let us first consider the compound  $[\text{Gd}(\text{hfa})_3\text{Cu}(\text{salen})\text{Meim}]$  (**3**), the structure of which consists of well-isolated  $\text{Gd}^{\text{III}}\text{Cu}^{\text{II}}$  units. Figure 6 shows the  $\chi_{\text{M}}T$  versus  $T$  curve,  $\chi_{\text{M}}$  being the molar magnetic susceptibility corrected for core diamagnetism and  $T$  being the temperature. At room temperature,  $\chi_{\text{M}}T$  is equal to  $8.33(1)$   $\text{cm}^3 \text{K mol}^{-1}$ , which corresponds to what is expected for isolated  $\text{Gd}^{\text{III}}$  and  $\text{Cu}^{\text{II}}$  ions, remains almost constant as  $T$  is lowered to ca. 100 K, increases as  $T$  is lowered further, and attains a value of  $10.08$   $\text{cm}^3 \text{K mol}^{-1}$  at 2 K.

The profile of the curve indicates that the  $\text{Gd}^{\text{III}}\text{—Cu}^{\text{II}}$  interaction is ferromagnetic, with an  $S = 4$  ground state and an  $S = 3$  excited state. Using  $-J\mathbf{S}_{\text{Gd}} \cdot \mathbf{S}_{\text{Cu}}$  as the interaction Hamiltonian results in a septet–nonet energy gap of  $4J$ . The ratio between the  $\chi_{\text{M}}T$  values at 2 and 300 K is equal to 1.21, which closely corresponds to the ratio  $(\chi_{\text{M}}T)_{\text{LT}}/(\chi_{\text{M}}T)_{\text{HT}}$  between low-temperature and high-temperature limits of  $\chi_{\text{M}}T$  for such a ferromagnetically coupled  $\text{Gd}^{\text{III}}\text{Cu}^{\text{II}}$  pair  $[(\chi_{\text{M}}T)_{\text{LT}}/(\chi_{\text{M}}T)_{\text{HT}} = 40/33]$  if the local Zeeman factors  $g_{\text{Gd}}$  and  $g_{\text{Cu}}$  are assumed to be equal]. The theoretical expression for  $\chi_{\text{M}}T$  is



**Figure 6.** Experimental (●) and calculated (—)  $\chi_{\text{M}}T$  versus  $T$  curves for compound **3**. The insert is an expanded view of the low-temperature data.

$$\chi_{\text{M}}T = \frac{4N\beta^2}{k} \frac{7g_3^2 + 15g_4^2 \exp(4J/kT)}{7 + 9 \exp(4J/kT)}$$

where  $g_3$  and  $g_4$  are the Zeeman factors associated with the  $S = 3$  and  $S = 4$  low-lying states, respectively;  $g_3$  and  $g_4$  are related to the local Zeeman factors through<sup>1</sup>

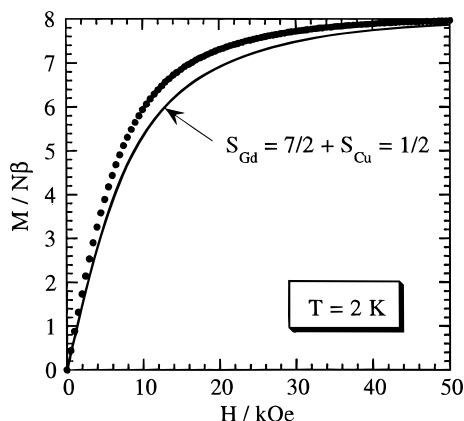
$$g_3 = (9g_{\text{Gd}} - g_{\text{Cu}})/8$$

$$g_4 = (7g_{\text{Gd}} + g_{\text{Cu}})/8$$

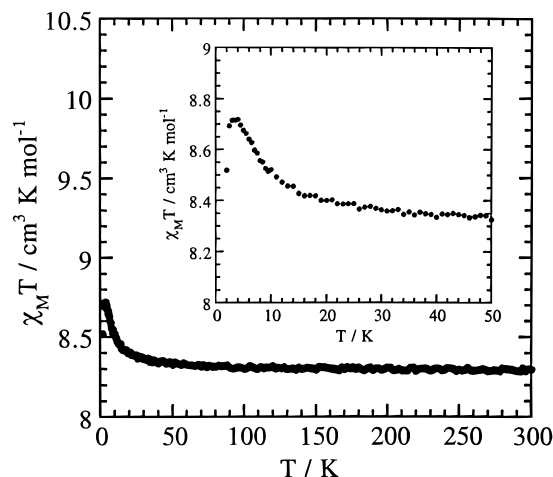
Least-squares fitting of the experimental data leads to  $J = 1.42$   $\text{cm}^{-1}$ ,  $g_{\text{Gd}} = 2.00$ ,  $g_{\text{Cu}} = 2.10$ . The agreement factor defined as  $\Sigma[(\chi_{\text{M}}T)^{\text{calc}} - (\chi_{\text{M}}T)^{\text{obs}}]^2 / \Sigma[(\chi_{\text{M}}T)^{\text{obs}}]^2$  is then equal to  $2.58 \times 10^{-6}$ , which indicates an excellent agreement between observed and calculated values.

The field dependence of the magnetization at 2 K was also measured. The  $M$  versus  $H$  curve is shown in Figure 7. The saturation magnetization is close to  $8N\beta$ . This curve is compared to the sum of the Brillouin functions for isolated  $\text{Gd}^{\text{III}}$  and  $\text{Cu}^{\text{II}}$  ions. For any value of the field, the experimental magnetization is higher than anticipated for noninteracting ions, which confirms the ferromagnetic nature of the interaction. The experimental magnetization is very close, but slightly below the Brillouin function for an  $S = 4$  pair state. This result agrees with the fact that the populations of the  $S = 4$  and  $S = 3$  states at 2 K are 0.894 and 0.106, respectively.

Let us now consider the compound  $[\text{Gd}(\text{hfa})_3\text{Cu}(\text{salen})]$  (**1**). The  $\chi_{\text{M}}T$  versus  $T$  curve is shown in Figure 8.  $\chi_{\text{M}}T$  is first constant and equal to  $8.30(2)$   $\text{cm}^3 \text{K mol}^{-1}$  as  $T$  is lowered from room temperature to ca. 50 K, increases as  $T$  is lowered further, reaches a maximum value of  $8.70(1)$   $\text{cm}^3 \text{K mol}^{-1}$  around 4 K, and then slightly decreases. This curve again reveals ferromagnetic interactions. However, the maximum value of  $\chi_{\text{M}}T$  at 4 K is lower than expected for a fully populated  $S = 4$  ground state. A comparison of Figures 5 and 7 points out the differences between the magnetic properties of compounds **1** and **3**. The ferromagnetic interaction is clearly more pronounced for **3**. The main structural difference between the two compounds is the presence of dimers of  $\text{Gd}^{\text{III}}\text{Cu}^{\text{II}}$  pairs in **1**, with rather short intermolecular Cu–Cu distances. Studying the magnetic properties of  $[\text{La}(\text{hfa})_3(\text{H}_2\text{O})\text{Cu}(\text{salen})]$  (**4**) might provide some insight into this  $\text{Cu}^{\text{II}}\text{—Cu}^{\text{II}}$  interaction. Indeed, the  $\text{La}^{\text{III}}$  ion is nonmagnetic. The EPR spectrum of  $[\text{La}(\text{hfa})_3(\text{H}_2\text{O})\text{Cu}(\text{salen})]$  is characteristic of a triplet state, with an axial zero-field splitting parameter  $D$  equal to  $2.48 \times 10^{-2}$   $\text{cm}^{-1}$ ,



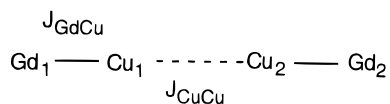
**Figure 7.** Field dependence of the magnetization for compound **3** at 2 K. The full line represents the theoretical magnetization curve for isolated Gd<sup>III</sup> and Cu<sup>II</sup> ions.



**Figure 8.**  $\chi_M T$  versus  $T$  curve for compound **1**. The insert is an expanded view of the low-temperature data. The scale of the main graph is the same as in Figure 6, facilitating comparison of the two curves.

and half-field transitions. On the other hand, the magnetic susceptibility follows a Curie law down to 2 K; the singlet–triplet energy gap is certainly smaller than  $\pm 0.2 \text{ cm}^{-1}$ .

The interpretation of the magnetic properties of [Gd(hfa)<sub>3</sub>-Cu(salen)] (**1**) in principle requires us to consider a dimer of pairs as



with intramolecular  $J_{\text{GdCu}}$  and intermolecular  $J_{\text{CuCu}}$  interaction parameters. The fitting of the experimental data with such a model does not lead to a unique set of parameters;  $J_{\text{GdCu}}$  and  $J_{\text{CuCu}}$  are strongly correlated, which is not surprising. However,  $J_{\text{GdCu}}$  is smaller for compound **1** than for **3**, of the order of  $0.4 \text{ cm}^{-1}$ .

## Discussion and Conclusion

When we initiated this work, our goal was to design compounds containing perfectly isolated Ln<sup>III</sup>Cu<sup>II</sup> binuclear species in order to investigate the 4f–3d interaction in a thorough fashion. It also occurred to us that it would be interesting to have at our disposal isostructural Ln<sup>III</sup>M<sup>II</sup> compounds in which either the lanthanide(III) or the 3d ion would be diamagnetic. Such compounds with a single paramagnetic center should allow us to study the single-ion properties. This

information is indispensable for the analysis of the 4f–3d interaction in the case where Ln<sup>III</sup> carries a first-order orbital momentum.

We first considered the [Ln(hfa)<sub>3</sub>M(salen)] compounds where Ln may be any lanthanide atom and M<sup>II</sup> is either Cu<sup>II</sup> with a spin-doublet ground state or Ni<sup>II</sup> with a spin-singlet ground state. The determination of the crystal structures of three compounds of this family revealed that the Ln<sup>III</sup>M<sup>II</sup> binuclear units were not perfectly isolated within the lattice but formed dimers of Ln<sup>III</sup>M<sup>II</sup> pairs, with rather short Cu–Cu separations. The EPR spectra of [La(hfa)<sub>3</sub>(H<sub>2</sub>O)Cu(salen)] and [Y(hfa)<sub>3</sub>Cu(salen)], both containing a diamagnetic Ln<sup>III</sup> ion (here we incorporate Y<sup>III</sup> as a lanthanide(III) ion with a small ionic radius), present the typical features of triplet states. Therefore, the investigation of these [Ln(hfa)<sub>3</sub>M(salen)] and [Ln(hfa)<sub>3</sub>(H<sub>2</sub>O)M(salen)] compounds could not provide unambiguous and accurate information regarding the 4f–3d interaction. Hence, we added an apical ligand in the copper coordination sphere, which afforded well-isolated binuclear species.

It is well-known that the crystal structures of most of the rare earth element compounds change along the lanthanide series. In the present case, two modifications occur. For Ln = La, with the largest ionic radius, the space group is  $P2_1/n$ , and the Ln<sup>III</sup> ion is nine-coordinate. For Ln = Gd, the  $P2_1/n$  space group is retained but the content of the unit cell is changed and the Ln<sup>III</sup> ion is eight-coordinate. For Ln = Y, with a smaller ionic radius, the eight-coordination of Ln<sup>III</sup> is retained but the space group is  $P1$ .

[Gd(hfa)<sub>3</sub>Cu(salen)(Meim)] (**3**) is not the first compound containing perfectly isolated Gd<sup>III</sup>Cu<sup>II</sup> pairs. Another compound of this kind, of formula LGdCu(NO<sub>3</sub>)<sub>3</sub> with L = 1,2'-bis(3-methoxysalicylideneamino)-2-methylpropanato, was recently reported.<sup>16</sup> The ground nonet–excited septet energy gap was found to be equal to  $28 \text{ cm}^{-1}$  for LGdCu(NO<sub>3</sub>)<sub>3</sub> and  $5.68 \text{ cm}^{-1}$  for **3**. It is then interesting to compare the structures of the two compounds. Probably, the most pertinent difference between the two compounds concerns the GdO<sub>2</sub>Cu bridging network, which is almost planar for LGdCu(NO<sub>3</sub>)<sub>3</sub> and bent along the O–O direction for **3** with a dihedral angle of  $140.43^\circ$ . As a result of this bending, the Gd–Cu distance in **3** ( $3.254 \text{ \AA}$ ) is shorter than it is in LGdCu(NO<sub>3</sub>)<sub>3</sub> ( $3.428 \text{ \AA}$ ). Let us also mention that the Gd<sup>III</sup> ion is octacoordinated in **3** and decaordinated in LGdCu(NO<sub>3</sub>)<sub>3</sub>. It has been shown for Cu<sup>II</sup> dimers<sup>27,28</sup> and Cu<sup>II</sup>Ni<sup>II</sup> binuclear species<sup>29</sup> that bending the bridging network results in a decrease of the magnetic interaction. The same situation apparently holds for Gd<sup>III</sup>Cu<sup>II</sup> species. Let us note, however, that for Cu<sup>II</sup>Cu<sup>II</sup> and Cu<sup>II</sup>Ni<sup>II</sup> species the interaction is antiferromagnetic while for Gd<sup>III</sup>Cu<sup>II</sup> species, it is ferromagnetic.

The last point we wish to mention briefly concerns the mechanism of the Gd<sup>III</sup>–Cu<sup>II</sup> interaction. In a preceding paper,<sup>12</sup> we attributed the ferromagnetic character of this interaction to the coupling between the 4f–3d ground configuration and the excited configuration arising from the  $3d_{\text{Cu}} \rightarrow 5d_{\text{Gd}}$  electron transfer, according to a mechanism suggested first by Goodenough.<sup>30</sup> In such a mechanism,  $J$  is given by

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 (28) Charlot, M. F.; Kahn, O.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1410.  
 (29) Journaux, Y.; Kahn, O.; Morgenstern-Badarau, I.; Galy, J.; Jaud, J.; Bencini, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 6305.  
 (30) Goodenough, J. B. *Magnetism and the Chemical Bond*; Interscience, New York, 1963.

$$J = \sum_{i=1}^5 [\beta_{5d-3d}^2 \Delta / (4U^2 - \Delta^2)]_i$$

$\beta_{5d-3d}$  is a transfer integral involving the singly-occupied copper orbital and a 5d gadolinium orbital,  $\Delta$  is the energy gap between  $S = 3$  and  $S = 4$  excited states arising from the  $4f^7 5d^1$  electron-transfer configuration, and  $U$  is the energy cost of such a transfer. The summation applies to the five 5d gadolinium orbitals. The largest  $\beta_{5d-3d}$  integrals (in absolute values) probably involve the gadolinium 5d orbitals oriented along the Gd–O1 and Gd–O2 directions. If this is so, one easily understands why bending the bridging network results in a

decrease of those  $|\beta_{5d-3d}|$  integrals and therefore in a decrease of the Gd<sup>III</sup>–Cu<sup>II</sup> interaction.

In the near future, we intend to study other [Ln(hfa)<sub>3</sub>Cu(salen)(Meim)] binuclear compounds in which the Ln<sup>III</sup> ion will have an orbital contribution.

**Supporting Information Available:** Tables of detailed crystal data, atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, interatomic distances, and interatomic bond angles for compounds **1–4** and a figure showing the crystal packing for compound **3** (31 pages). Ordering information is given on any current masthead page.

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