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Article

Di- and Triheteronuclear Cu−Gd and Cu−Gd−Cu Complexes with Dissymmetric Double Bridge

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The study of the Cu−Gd interaction is simplified by the use of heteronuclear Cu−Gd complexes of low nuclearity, such as dinuclear Cu−Gd or trinuclear Cu−Gd−Cu complexes. In the large majority of cases published until now, this interaction presents the advantage of being ferromagnetic. Among the known examples, the complexes with the largest *J* values have been prepared with use of symmetric Schiff base compartmental ligands, so that the active cores of the molecules involve two phenoxo bridges between the copper and gadolinium ions. Keeping this remark in mind, we decided to synthesize simple complexes in which two different bridges link the copper and gadolinium ions. The structural determinations of a heterodinuclear Cu−Gd and a trinuclear Cu−Gd−Cu complex confirm the asymmetry of the central cores, involving phenoxo and hydroxo bridges. The magnetic studies evidence again the presence of ferromagnetic interactions. These results corroborate preponderance of the planarity of the $Cu-O_2-Gd$ core over the dissymmetry of the bridges.

Introduction

Ferromagnetic interactions between Cu(II) and Gd(III) ions have been evidenced in a large majority of heterodinuclear Cu−Gd complexes published until now.[1,2] Whereas the mechanism of ferromagnetic coupling was subject to debate, an interesting theoretical work has brought some advancement in the understanding of this phenomenon.[3] The first interpretation put forward by Gatteschi et al.[4] proposed spin polarization factors, owing to orbital interactions between the 6s Gd orbital and delocalization tails of the 3d Cu orbitals on the ligand. Kahn suggested,[5] according to the original Goodenough's work,[6] that a configuration interaction between states resulting from one-electron jump from the 3d Cu ion to the vacant 5d Gd orbitals was active. The authors of the recent article quoted above[3] confirm that the configuration interaction and polarization mechanisms are not contradictory but interconvertible by appropriate transformations of the magnetic orbitals. They demonstrate that "the involved orbitals are not genuine Cu(3d) and Gd(5d) atomic orbitals but molecular orbitals already containing a small tail of Gd-origin on the orbital located mainly on the [CuL] side as well as a slight mixing between 4f and 5d atomic orbitals of gadolinium. Within the C_{2v} symmetry, the system adopts an orthogonal orbital exchange pathway, with the main interaction concentrated between b_2 [Cu(II)L] and a_2 [Gd(III)] orbitals." Furthermore, they suppose that the factors at the

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origin of the few antiferromagnetic interactions are expected to result from the asymmetry of the donor atoms involved in the Cu−Gd bridging.

Because these authors have underlined that the Cu−Gd complexes prepared up to now do present a pseudo C_{2v} symmetry, we have directed the present work toward the preparation of a heterodinuclear Cu−Gd complex of different symmetry, with asymmetric bridges. An example of a trinuclear Cu−Gd−Cu complex possessing the same asymmetric bridge is also described. The magnetic properties of these complexes are reported.

Experimental Section

Materials. The starting copper complexes **1** and **2** were prepared according to an experimental process previously described for similar complexes.[7] $Gd(NO_3)_3 \cdot 5H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, NaN_3, and pyrrole carboxaldehyde (Aldrich) were used as purchased. High-grade solvents were used for preparing the complexes.

Caution! *The perchlorate and azide salts of metal complexes with organic ligands are potentially explosive. Although we worked without any incident, their handling necessitates extreme care.*

Complexes. [L^1Cupy]ClO_4 (1). To a stirred solution of ortho-vanillin (1.52 g, 1×10^{-2} mol) in methanol (50 mL) was first added copper perchlorate (3.7 g, 1×10^{-2} mol) dissolved in water (10 mL) and then pyridine (1.6 g, 2×10^{-2} mol). A few minutes later, a methanol solution (10 mL) of 1,2-diaminocyclohexane (1.14 g, 1×10^{-2} mol) was added at once with stirring at room temperature. Two hours later, the precipitate was filtered off, washed with cold methanol, and diethyl ether. Yield: 3.9 g (80%). Anal. Calcd for $C_{19}H_{24}ClCuN_3O_6$: C, 46.6; H, 4.9; N, 8.6. Found: C, 46.3; H, 4.7; N, 8.4. Characteristic IR absorptions (KBr): 3292, 3197, 3118, 2934, 1636, 1601, 1473, 1446, 1320, 1247, 1223, 1094, 1044, 974, 861, 743, 698, 623 cm^{-1}.

[L^2Cupy]ClO_4 (2). Using 1,2-diaminoethane instead of diaminocyclohexane yielded the corresponding complex. Yield: 3.2 g (73%). Anal. Calcd for $C_{15}H_{18}ClCuN_3O_6$: C, 41.4; H, 4.2; N, 9.6. Found: C, 41.1; H, 4.0; N, 9.4. Characteristic IR absorptions (KBr): 3320, 3259, 1641, 1605, 1471, 1446, 1295, 1248, 1227, 1093, 1044, 962, 851, 747, 700, 621, 442 cm^{-1}.

L^1CuN_3 (3). Sodium azide (0.1 g, 1.5×10^{-3} mol) was added to a suspension of [L^1Cupy]ClO_4 (0.49 g, 1×10^{-3} mol) in water (10 mL). After 30 min of stirring, the blue precipitate was filtered off, washed with isopropyl alcohol, diethyl ether, and dried. Yield: 0.30 g (85%). Anal. Calcd for $C_{14}H_{19}CuN_5O_2$: C, 47.6; H, 5.4; N, 19.8. Found: C, 47.3; H, 5.3; N, 19.4. Characteristic IR absorptions (KBr): 3296, 2926, 2036, 1628, 1601, 1451, 1347, 1331, 1146, 1046, 1027, 991, 909, 761, 682, 464 cm^{-1}.

L^3Cu (4). [L^1Cupy]ClO_4 (0.49 g, 1×10^{-3} mol) and pyrrole carboxaldehyde (0.1 g, 1×10^{-3} mol) were mixed in methanol (15 mL). After the addition of NaOH (0.08 g, 2×10^{-3} mol), the solution was boiled with stirring for 20 min. Cooling yielded a red precipitate that was filtered off and washed with methanol and diethyl ether. Recrystallization from dichloromethane produced the desired complex. Yield: 0.23 g (61%). Anal. Calcd for $C_{19}H_{21}CuN_3O_2$: C, 59.0; H, 5.5; N, 10.9. Found: C, 58.3; H, 5.1; N, 10.5. Characteristic IR absorptions (KBr): 2935, 1633, 1600, 1471, 1440, 1319, 1295, 1260, 1245, 1082, 1029, 973, 856, 729 cm^{-1}.

[L^4Cu] (5). This complex was obtained through the experimental process described for L^3Cu (**4**), using of [L^2Cupy]ClO_4. Yield: 0.19 g (55%). Anal. Calcd for $C_{15}H_{15}CuN_3O_2$: C, 54.1; H, 4.5; N, 12.6. Found: C, 53.8; H, 4.3; N, 12.3. Characteristic IR absorptions (KBr): 2908, 1637, 1598, 1470, 1437, 1386, 1301, 1238, 1214, 1080, 1034, 978, 855, 729, 610, 471 cm^{-1}.

[$Cu(L^1)(\mu\text{-}OH)Gd(NO_3)_3(H_2O)$] (6). A methanolic solution (5 mL) of L^1CuN_3 (0.17 g, 5×10^{-4} mol) and $Gd(NO_3)_3 \cdot 6H_2O$ (0.22 g, 5×10^{-4} mol) was stirred at room temperature for 1 h, yielding a blue solution. Two days later, crystals were collected by filtration and air-dried. Yield: 0.12 g (35%). Anal. Calcd for $C_{14}H_{22}CuGdN_5O_{13}$: C, 24.4; H, 3.2; N, 10.2. Found: C, 24.1; H, 3.2; N, 10.4. Characteristic IR absorptions (KBr): 3380, 3325, 2952, 1634, 1506, 1471, 1384, 1302, 1217, 1172, 1033, 962, 813, 790, 747, 658, 478 cm^{-1}.

[$Cu_2(\mu\text{-}Cl)(L^4)_2(\mu\text{-}OH)_2Gd(H_2O)_2$]$(Cl)_2$ (7). A methanolic solution (5 mL) of L^4Cu (0.33 g, 1×10^{-3} mol) and $GdCl_3 \cdot 6H_2O$ (0.19 g, 5×10^{-4} mol) was stirred at room temperature for 1 h, yielding a green solution that was filtered off. Slow solvent evaporation yielded crystals that were collected by filtration and dried. Yield: 0.11 g (22%). Anal. Calcd for $C_{30}H_{38}Cl_3Cu_2GdN_6O_8$: C, 36.0; H, 3.8; N, 8.4. Found: C, 35.6; H, 3.6; N, 8.1. Characteristic IR absorptions (KBr): 3326, 2941, 1645, 1625, 1473, 1416, 1376, 1307, 1229, 1152, 1072, 1040, 1025, 968, 859, 766, 742, 598, 464 cm^{-1}.

{$(CuL^4)_2(\mu\text{-}OH)_2Gd(H_2O)_2(NO_3)_3$} (8). An acetone solution (5 mL) of L^4Cu (0.11 g, 3.3×10^{-4} mol) and $Gd(NO_3)_3 \cdot 6H_2O$ (0.15 g, 3.3×10^{-4} mol) was stirred at room temperature for 1 h, yielding a green precipitate that was filtered off, washed with diethyl ether and dried. Yield: 0.08 g (44%). Anal. Calcd for $C_{30}H_{38}Cu_2GdN_9O_{17}$: C, 33.3; H, 3.5; N, 11.7. Found: C, 33.5; H, 3.3; N, 11.4. Characteristic IR absorptions (KBr): 3404, 2944, 1642, 1623, 1472, 1411, 1384, 1302, 1280, 1224, 1072, 1040, 966, 859, 739, 641, 599, 458 cm^{-1}.

Physical Measurements. Elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France, for carbon, hydrogen, and nitrogen. IR spectra were recorded on a GX system 2000 Perkin-Elmer spectrophotometer; samples were run as KBr pellets. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. All samples were 3 mm diameter pellets molded from ground crystalline samples. Magnetic susceptibility measurements were performed in the 2−300 K range in a 0.1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.[8] Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibilities have been computed by exact calculations of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry[9] and with the *MAGPACK* program package[10] in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program *MINUIT*.[11]

Crystallographic Data Collection and Structure Determination for 5, 6, and 7. Crystals of **5**, **6**, and **7** were kept in the mother liquor until they were dipped into oil, glued on a glass fiber, and quickly cooled down to 180 K. The selected crystals of **5** (red, 0.40 × 0.10 × 0.05 mm^3), **6** (pink, 0.05 × 0.12 × 0.25 mm^3), and **7** (blue, 0.125 × 0.125 × 0.025 mm^3) were mounted on a Stoe Imaging Plate Diffractometer System (IPDS) using a graphite

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Table 1. Crystallographic Data for Complexes **5**, **6**, **7**

	5	**6**	**7**
formula	$C_{15}H_{15}CuN_3O_2$	$C_{28}H_{44}Cu_2Gd_2N_{10}O_{26}$	$C_{30}H_{32}Cl_3Cu_2GdN_6O_8$
fw	332.84	1378.30	995.3
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12$
a, Å	6.8203(8)	7.9420(10)	14.760(3)
b, Å	9.3735(11)	11.8453(16)	15.749(3)
c, Å	11.8514(13)	13.2253(15)	8.1992(17)
α, deg	71.426(13)	106.596(15)	90
β, deg	74.148(13)	106.306(13)	90
γ, deg	71.865(13)	99.418(15)	90
V, Å^{-3}	669.67(13)	1103.4(3)	1929.3(7)
Z	2	1	2
ρ_{calcd}, g cm^{-3}	1.651	2.074	1.713
λ, Å	0.71073	0.71073	0.71073
T, K	180(2)	180	180(2)
μ(Mo Kα), mm^{-1}	1.638	4.02	3.052
R, $I > 2\sigma(I)$	0.0270	0.0654	0.0819
Rw, $I > 2\sigma(I)$	0.0326	0.0743	0.1663

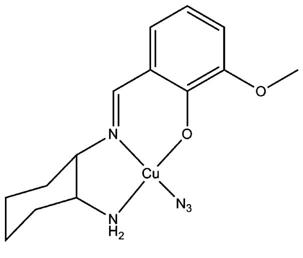
monochromator (λ = 0.71073 Å) and equipped with an Oxford Cryosystems cooler device. The data were collected at 180 K. The unit cell determination and data integration were carried out using the *Xred* package.[12] 6708 reflections were collected for **5**, of which 2461 were independent (Rint = 0.0432), 10 970 reflections for **6**, of which 4057 were independent (Rint = 0.118) and 18 084 reflections for **7**, of which 3529 were independent (Rint = 0.313).

The structures were solved by direct methods and refined by least-squares procedures using *WINGX*[13,14] or *CRYSTALS*.[15] Refinements were carried out through full-matrix least-squares on F^2 with *SHELXL-97*[16] (software package *WinGX*). Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[17] The hydrogen atoms were included in calculated positions and refined as riding atoms using *SHELX* default parameters, except for the water and hydroxo hydrogen atoms of **7** that were not localized due to the low quality of the structure. All non-hydrogen atoms were refined anisotropically. The figures were drawn with Zortep[18] and Cameron.[19] Crystal data collection and refinement parameters are collated in Table 1.

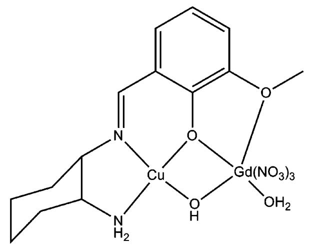
Results

Syntheses. The complexes under study appear in Chart 1 that shows a clear presentation of the ligands used in the present work. The synthesis of **6** and **7** is not straightforward, but both synthetic processes make use of copper complexes isolated through a similar preparative method previously described.[7,20] It is worth mentioning that this experimental process yielding copper complexes of a half-unit ligand L^i operates thanks to the template effect of the copper ions. It has not yet been described with 3d ions other than copper. The initial step yields [L^{i}CuPy]ClO$_4$ complexes where the copper ion is linked to three donor atoms from the half-unit ligand, the fourth equatorial position being occupied by a pyridine nitrogen atom. Unfortunately, the [L^{i}CuPy]ClO$_4$ precursors do not react with gadolinium ions to produce the expected Cu−Gd complexes. Because these precursors are cationic species in solution, the approach of a positive gadolinium ion seems to be prevented. To overcome this difficulty, we have changed the pyridine ligand for a ligand more tightly linked to the copper ion: reaction of sodium azide with [L^{1}CuPy]ClO$_4$ yields the new L^{1}CuN$_3$ complex. The structure of the equivalent complex with a ligand L^i prepared from salicylaldehyde instead of orthovanillin has been determined.[21] Then, reaction of L^{1}CuN$_3$ with gadolinium nitrate allows us to isolate **6**. The infrared and analytical data do agree with the presence of copper and

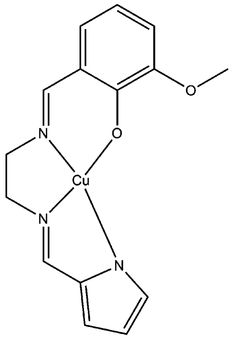
Chart 1. Schematic Representation of the Main Complexes with Their Ligand and Complex Numberings



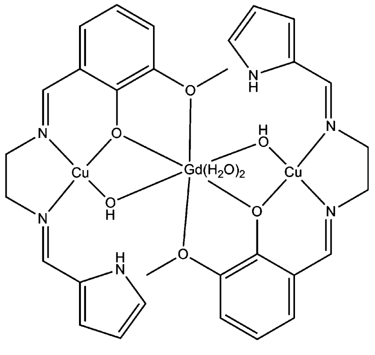
L^{1}CuN$_3$ **(3)**



[Cu(L^1)(μ-OH)Gd(NO$_3$)$_3$(H$_2$O)] **(6)**



L^{4}Cu **(5)**



[Cu$_2$(μ-Cl)(L^4)$_2$(μ-OH)$_2$Gd(H$_2$O)$_2$](Cl)$_2$ **(7)**

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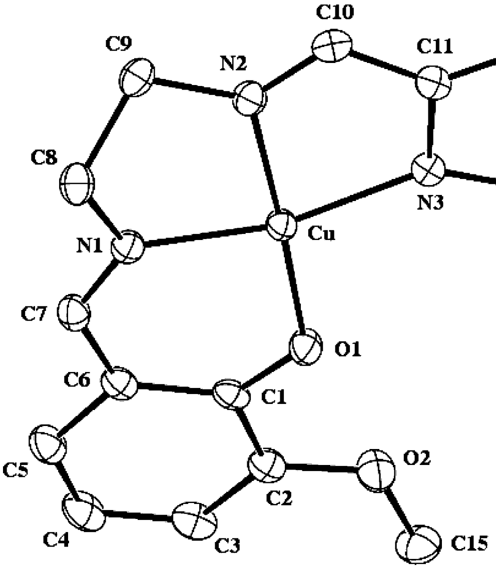

Figure 1. Zortep plot of **5** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for the L^4Cu unit: Cu O1 1.894(1), Cu N1 1.939(2), Cu N2 1.951(2), Cu N3 1.960(2),. N1CuO1 94.17(7), N2 Cu O1 177.09(6), N2 Cu N1 83.35(7), O1 Cu N3 99.92(6), N1 Cu N3 165.78(7), N2 Cu N3 82.51(7).

gadolinium ions in a 1:1 ratio. The structural determination (vide infra) confirms that (i) the N_3^- azido anion has been exchanged for a hydroxo one, and (ii) one copper and one gadolinium ion are linked by an asymmetrical double bridge including one phenoxo and one hydroxo anion.

In the second synthetic process, $[L^2CuPy]ClO_4$ has been reacted with pyrrole carboxaldehyde in the presence of sodium hydroxide to yield the neutral complex L^4Cu, **5**, as a result of (i) the Schiff base condensation between L^2 and pyrrole carboxaldehyde, yielding a second imine function and (ii) deprotonation of the pyrrole function. Such a reaction is effective for preparing dissymmetric Schiff base ligands.[22] The pyrrole nitrogen atom cannot bridge copper to a second metal ion: then **5** has only two oxygen atoms (phenoxo and methoxy) able to coordinate a second metal ion. Because of this low coordination number, the reaction of neutral copper **5** with gadolinium ions was expected to yield at least a trinuclear $(\mathbf{5})_2GdX_3$ compound following complexation of the gadolinium ion by the phenoxo and methoxy oxygen atoms of each **5**. Although the analytical data agree with a 2:1 Cu/Gd ratio, the structural determination (vide infra) indicates that the resulting complex is not as simple as expected.

Description of the Structures. The unit cell of **5** contains two neutral $[L^4Cu]$ entities arranged in a head-to-tail orientation. One of these molecules is illustrated in Figure 1 with atom labeling. The bond lengths and angles involving the copper ion are collated in the figure caption. The copper ion is linked to the three nitrogen and to the oxygen atoms of the dideprotonated L^4 ligand. The deviation of N1−Cu−N3 from 180° reflects the strain in the ligand resulting from chelation of the copper ion. The phenoxo oxygen atom is responsible for the dimerization of these $[L^4Cu]$ entities, yielding pentacoordinate copper ions, with intermolecular Cu···O(phenoxo) contacts of 2.751(2) Å, creating a $Cu-O_2-Cu$ core with angles of 87.0(1) and 93.0(1)°. The five membered copper-diamino rings are not planar as usual, with gauche λ and δ conformations, respectively.

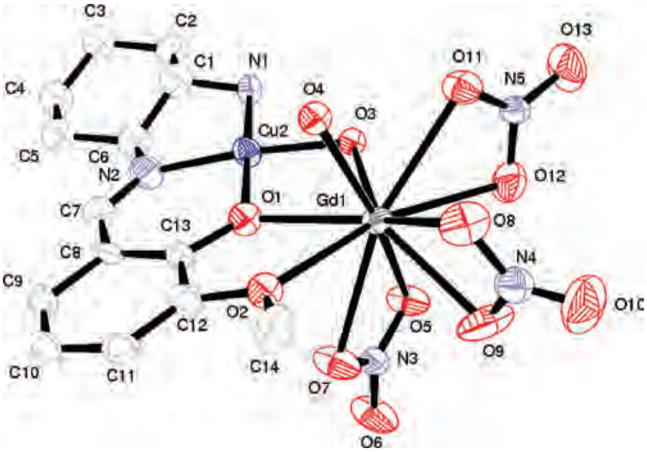

Figure 2. Ortep plot of **6** at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for the $L^1Cu(OH)Gd(NO_3)_3(H_2O)$ unit: Cu O1 1.912(10), Cu N1 1.987(11), Cu N2 1.926(12), Cu O3 1.924(2), Gd O1 2.357(10), Gd O2 2.605(10), Gd O3 2.331(9), Gd O4 2.361(9), Gd O5 2.506(9), Gd O7 2.562(10), Gd O8 2.474(10), Gd O9 2.503(12), Gd O11 2.604(10), Gd O12 2.531(11),. O1CuO3 82.4(4), CuO3Gd 106.5(4), O1GdO3 65.2(3), GdO1Cu 105.9(4).

The molecular plot of $[Cu(L^1)(\mu\text{-}OH)Gd(NO_3)_3(H_2O)]$, **6**, represented in Figure 2 confirms the dinuclear nature of this structure. The copper and gadolinium ions are connected by an asymmetric double bridge involving the phenoxo oxygen atom of the L^1 ligand and the hydroxo oxygen atom. The basal plane of the copper ion involves the three donor atoms brought by the half-unit ligand (N_2O) and the hydroxo anion. A long axial bond (Cu−O11 = 2.657(9) Å) supplements the copper coordination sphere. The gadolinium ion is 10-coordinate, with two oxygen donor atoms originating from the L^1 ligand (methoxy and phenoxo), one from the hydroxo anion, one from a water molecule, and six oxygen atoms from three chelating nitrato anions. The Gd−O(hydroxo) bond length (2.331(8) Å) is slightly shorter than the Gd−O(phenoxo) (2.357(10) Å) and the Gd−Ow (2.361(9) Å) ones. The Gd···Cu distance within the dinuclear complex equals 3.417(2) Å. These dinuclear complex molecules are associated by pairs of different enantiomers (*S*,*S* and *R*,*R*) through a Cu···O11 contact (2.657(9) Å) connecting a copper ion and an oxygen atom of a chelating nitrato anion. This contact induces an elongation of the Gd−O11 bond (2.604(10) Å), in comparison to the other Gd−O(nitrato) bond lengths, characterized by a mean value of 2.515(10) Å. The five membered copper-diamino rings are not planar, the (*S*,*S*) and (*R*,*R*) enantiomers having a gauche δ and a gauche λ deformation, respectively. The diaminocyclohexyl rings have a chair conformation. The dihedral angle between the planes containing the two bridging oxygen atoms and each metal ion (copper and gadolinium, respectively) is practically planar and equal to 0.3(1)°.

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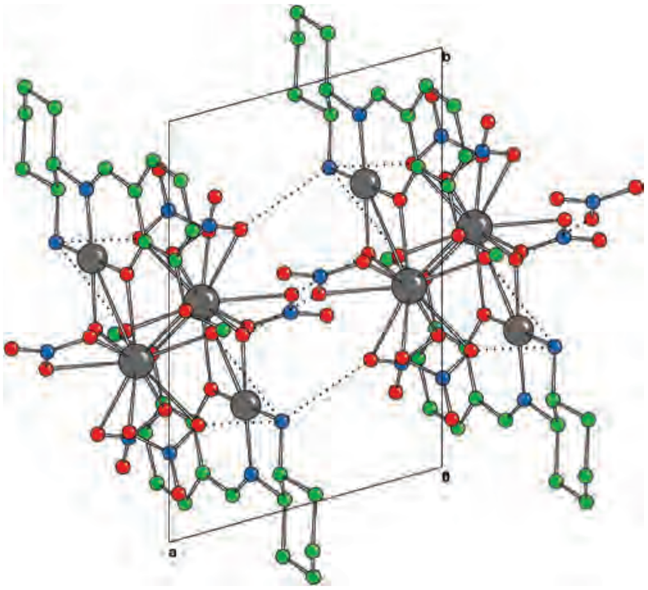

Figure 3. View of two molecules of **6** in the *ab* plane, showing intra- and intermolecular hydrogen bonds, and how 1D chains of hydrogen bonded molecules develop in the *a* direction. Hydrogen atoms are omitted for clarity. (O3···O5′, 2.90(2) Å; H33···O5′, 2.18(1) Å; O3−H33···O5′, 146.7(7)°; N1···O12′, 3.25(2) Å; H12···O12′, 2.53(2) Å; N1−H12···O12′, 142.6(9)°, N1···O4″, 3.21(2) Å; H13···O4″, 2.535(8) Å; N1−H13···O4″, 136.66(8)°; N1···O8″, 3.42(2) Å; H13···O8″, 2.71(2) Å; N1−H13···O8″, 141.15(8)°; symmetry operations: ′ = 1 − *x*, 1 − *y*, 1 − *z*; ″ = −*x*, 1 − *y*, 1 − *z*).

Intermolecular hydrogen interactions operate between the oxygen atoms O3 (hydroxo) and O5 (nitrato) and also between the nitrogen atom N1 (diaminocyclohexyl fragment of L^1) and the oxygen atom O12 (nitrato) leading to 1D chains of dinuclear molecules running parallel to *c*. Weaker hydrogen interactions also operate intramolecularly between N1 and, on the one hand the oxygen atom O4w, and, on the other hand, the oxygen atom O8(nitrato). A fragment of the crystal packing of **6** is displayed in Figure 3, and the characteristic interatomic distances and angles are collated in the Figure caption.

Although the structural determination of **7**, $[Cu_2(\mu\text{-}Cl)(L^4)_2(\mu\text{-}OH)_2Gd(H_2O)_2](Cl)_2$ is of lower quality (Figure 4), it is clear that the reaction of the L^4Cu complex with gadolinium induces formation of a novel heteronuclear Cu−Gd complex. The splitting of the Cu−N(pyrrole) bond is followed by protonation of the pyrrole nitrogen atom and replacement of the Cu−N bond by a Cu−O bond, the oxygen atom originating from a hydroxo anion that bridges the copper and gadolinium cations. An asymmetric hydroxo-phenoxo double bridge is present, as in **6**; however, the gadolinium coordination sphere includes two such bridges, yielding a trinuclear Cu−Gd−Cu entity. The gadolinium ion is eight-coordinate to four oxygen atoms from two L^2 ligands (methoxo and phenoxo), two oxygens from hydroxo anions, and two from water molecules. The chloride ions do not participate in the gadolinium coordination sphere but one of them is involved in a Cu−Cl−Cu bridge through weak Cu−Cl axial bonds (2.742(3) Å, yielding five-coordinate copper ions. The dihedral angle (21.0(3)°) between the planes containing the two bridging oxygen atoms and each metal ion, copper and gadolinium, respectively, is larger than in **6**. The angle between the two planes containing the gadolinium ion and the oxygen atoms of each double bridge, respectively, equals 71.8(2)°.

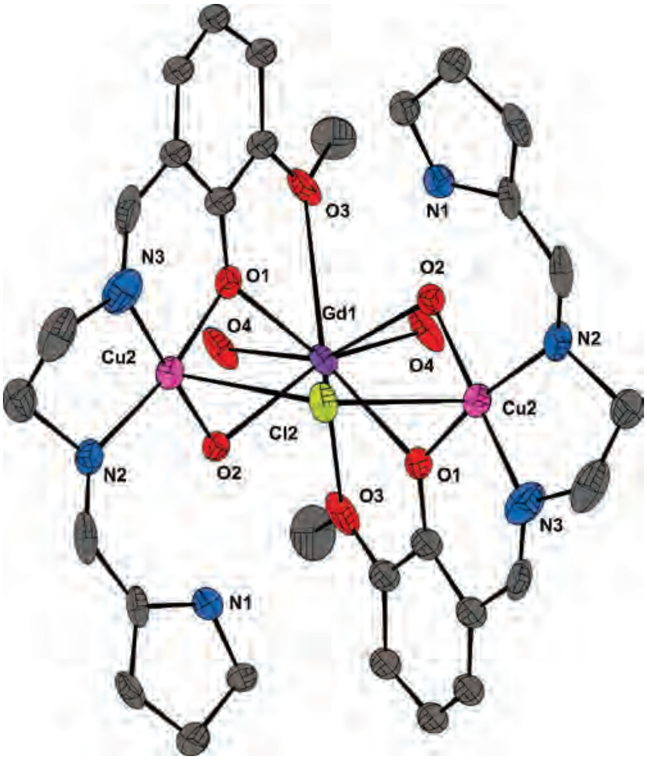

Figure 4. Cameron plot of **7** at the 20% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for the $\{[L^4Cu(OH)]_2ClGd(H_2O)_2\}Cl_2$ complex: Cu O1 1.949(11), Cu N2 2.002(15), Cu N3 1.87(2), Cu O2 1.966(11), Cu Cl 2.742(3), Gd O1 2.325(11), Gd O2 2.305(10), Gd O3 2.714(13), Gd O4 2.425(9), O1CuO2 81.8(4), CuO2Gd 103.1(5), O1GdO2 67.2(4), GdO1Cu 103.0(5).

Intermolecular hydrogen interactions operate between the oxygen atom O4w and the μ-Cl2 anion (O4···Cl2′ = 3.15(1) Å), leading to 1D chains of trinuclear complex cations running parallel to the *c* axis. Intramolecular hydrogen interactions also operate between O4w and, on the one hand Cl1 (O4···Cl1″ = 3.00(2) Å and, on the other hand, the oxygen atom O2(hydroxo) (O4···O2‴ = 3.17(1) Å). A third intramolecular hydrogen interaction operates between the nitrogen atom N1 (pyrrole fragment of L^4) and O2 (hydroxo) (N1···O2 = 2.769 Å and N1−H1a···O2 = 157.0(2)°). A fragment of the crystal packing of **7** is displayed in Figure 5.

Magnetic Properties. The magnetic susceptibility of dinuclear Cu−Gd **6** and trinuclear Cu−Gd−Cu **7** and **8** have been measured in the 2−300 K temperature range in a 0.1 T applied magnetic field. The thermal variation of the $\chi_M T$ versus *T* plot of **6** is similar to what was observed for previously reported Cu−Gd dinuclear complexes (Figure 6).[23] χ_M is the molar magnetic susceptibility of the dinuclear complex, corrected for the diamagnetism of the ligands.[8] At 300 K, $\chi_M T$ is equal to 8.10 cm^3 K mol^{-1}, which is attributable to one Cu^{II} and one Gd^{III} uncoupled cation (8.25 cm^3 K mol^{-1}). Upon lowering the temperature, $\chi_M T$ increases, reaching a maximum value of 9.77 cm^3 K mol^{-1} at 8 K,

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[23] Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *Inorg. Chem.* **2000**, *39*, 165.

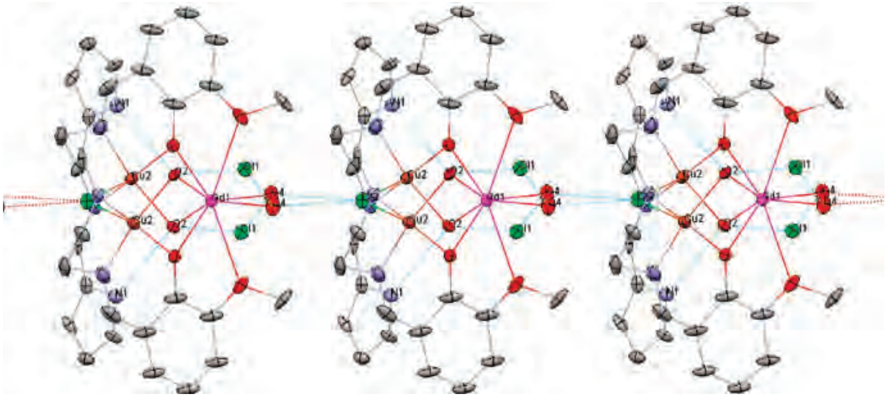

Figure 5. Mercury view of three molecules of **7** along the *b* axis, showing intra- and intermolecular hydrogen bonds, and how 1D chains of hydrogen bonded molecules develop in the *c* axis direction. Hydrogen atoms are omitted for clarity.

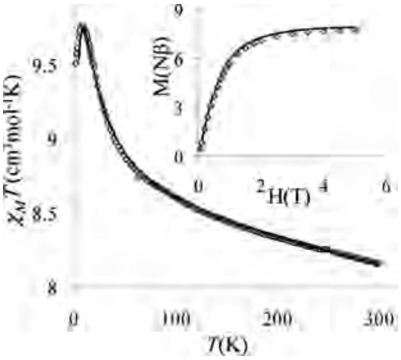

Figure 6. Thermal variation of the χ_MT product for **6**. The full line corresponds to the best data fit (text). The inset shows the field dependence of the magnetization for **6**.

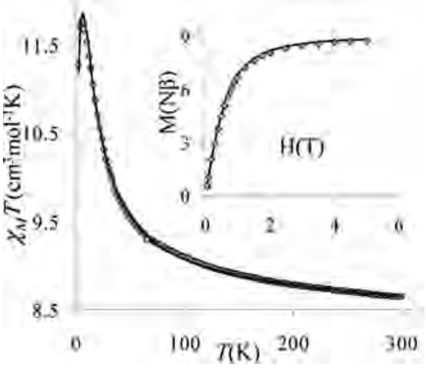

Figure 7. Thermal variation of the χ_MT product for **7**. The full line corresponds to the best data fit (text). The inset shows the field dependence of the magnetization for **7**.

which is followed by a slight decrease to 9.52 cm^3 K mol^{-1}at 2 K. The maximum value is not far from that expected (10 cm^3 K mol^{-1}) for a pair of ferromagnetically coupled Cu^{II} and Gd^{III} cations. A quantitative analysis using the Hamiltonian $H = -J(S_{Cu}\cdot S_{Gd})$ has been realized with the *MAGPACK* program.[10] To take into account possible intermolecular magnetic interactions mediated by the hydrogen contacts evidenced by the single crystal X-ray structure, a zj' spin−spin coupling constant (mean-field approximation formalism[24]) has been considered. The best fit leads to the parameter values $J = 8.4(1)$ cm^{-1}, $g = 2.00$, $zj' = -0.02(1)$ cm^{-1}. The agreement factor, $R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{obs}]^2 = 1 \times 10^{-4}$ is good.

Confirmation of the nature of the ground state and consequently of the nuclearity of **6** is afforded by the field dependence of the magnetization M at 2 K. The Brillouin function for an $S = 4$ spin state correctly fits the experimental values of M. (Figure 6, insert). Furthermore increasing the field up to 5 T results in a magnetization close to the saturation value of 8 Nβ units, consistent with an $S = 4$ ($g = 2$) system.

The thermal variation of the $\chi_M T$ versus T plot of the trinuclear Cu−Gd−Cu **7** is shown in Figure 7. χ_M is the molar magnetic susceptibility of the trinuclear complex, corrected for the diamagnetism of the ligands.[8] At 300 K, $\chi_M T$ is equal to 8.65 cm^3 K mol^{-1}, which is attributable to two Cu(II) and one Gd(III) uncoupled cation (8.63 cm^3 K mol^{-1}). Upon lowering the temperature, $\chi_M T$ increases reaching a maximum value of 11.77 cm^3 K mol^{-1} at 7 K, which is followed by a slight decrease to 11.26 cm^3 K mol^{-1} at 2 K. The maximum value corresponds to that expected (12.37 cm^3 K mol^{-1}) for a trinuclear complex with two ferromagnetic Cu−Gd interactions. A quantitative analysis using the Hamiltonian $H = -J(S_{Cu}\cdot S_{Gd} + S_{Cu}\cdot S_{Gd})$, and considering possible intermolecular magnetic interactions (zj'), leads to: $J = 4.4(1)$ cm^{-1}, $g = 2.0$, $zj' = -0.05(1)$ cm^{-1}. The agreement factor $R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{obs}]^2 = 1 \times 10^{-5}$ is excellent. The Brillouin function for a $S = {}^9/_2$ spin state correctly fits the experimental values of M (Figure 7, insert), with a magnetization value of 8.95 Nβ at 5 T, very close to the expected saturation value of 9 Nβ units.

In complete agreement with the analytical and infrared data, the magnetic data of complex **8**, $\{Cu(L^4)_2(\mu\text{-}OH)_2Gd(H_2O)_2(NO_3)_3\}$, which has not been structurally characterized, confirm its trinuclear character. A quantitative analysis leads to $J = 5.5(1)$ cm^{-1}, $g = 2.00$, and $zj' = -0.04(1)$ cm^{-1}, $R = 1.5 \times 10^{-5}$ (Figure S1 in the Supporting Information).

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[24] To take into account the inter-complex interaction, the following definition of the susceptibility has been used:

$$\chi'_M = \frac{\chi}{1 - \dfrac{2zJ'\chi}{Ng^2\beta^2}}$$

See for example O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

Discussion

Until now, the heterodinuclear Cu−Gd complexes with the highest interaction parameters *J* have been obtained by using compartmental Schiff base ligands having an inner N_2O_2 coordination site for the copper ion and an outer and larger O_2O_2 site prone to link a 4f lanthanide ion.[23] The copper and gadolinium ions are linked by a double phenoxo bridge. To obtain asymmetric Cu−Gd bridges, we have carried out the monocondensation of a diamine with ortho-vanillin, aiming to obtain a ligand providing a single phenoxo bridge (Chart 1), the other bridge being brought by an exogenous function X. The structural determination of **6** corroborated our expectation. The dinuclear Cu−Gd complex includes an asymmetric double bridge involving the phenoxo oxygen atom of the ligand and the less common μ-OH^- hydroxo anion. Such a OH^- bridge has been reported only once, in a tetranuclear Cu_2Dy_2 complex quite different from our dinuclear entity.[4] The main differences between **6** and the reported Cu_2Dy_2 complex are the nuclearity, dinuclear versus tetranuclear, and the OH^- binding mode, which links two dysprosium and one copper ion in a μ_3 fashion,[4] whereas it bridges the copper and gadolinium ions of **6** in a μ_2 mode. From the magnetic point of view, this difference may be very important. Unfortunately, the azido ligand, which is also able to bridge two metal ions, has been disconnected during the reaction and replaced by the hydroxo anion. To the best of our knowledge, no Cu−Gd complex including a mixed phenoxo-azido bridge has been reported yet.

The gadolinium ion is 10-coordinate in dinuclear **6**, whereas it is 8-coordinate in trinuclear **7**. This difference may originate from the presence in **6** of nitrato anions, which are good chelators. On the other hand, the copper ions are pentacoordinate in **6** and **7**, with axial Cu−O(nitrato) or Cu−Cl(chloro) bonds larger than 2.6 Å.

The electroneutrality of **4** is a factor favoring the preparation of a 3d−4f entity. Because the outer coordination site of **4** includes only two oxygen atoms, the use of gadolinium chloride associated to the presence of the deprotonated pyrrole nitrogen atom, which is unable to act as a bridge toward a second metal ion, favors the formation of a trinuclear Cu−Gd−Cu complex. The structural determination of **7** does agree with this assumption, but the net result is more complex than expected. In comparison with the starting complex **4**, inserting a gadolinium ion induces the splitting of the Cu−N bond and protonation of the free pyrrole nitrogen atom. The loss of a negative charge is balanced by the insertion of a hydroxo bridge between the copper and gadolinium ions. The gadolinium ion is 8-coordinate to two phenoxo and methoxo oxygen atoms from two different CuL^4H ligand complexes, two hydroxo anions, and two water molecules. The apical position of each copper ion is occupied by a bridging chloro ligand, as observed in previous structural determinations.[23] Surprisingly, the Cu−Gd bridges in the dinuclear and trinuclear **6** and **7** are quite similar. This result evidences the acidic character of gadolinium in protic solvents, as previously shown for a copper complex similar to **5**, but including an imidazole instead of the pyrrole ring.[22] In the later case, the imidazole nitrogen atom not involved in the copper coordination sphere was protonated without splitting of the Cu−N bond. In protic solvents, the solutions of positive ions are acidic:[25]

$$M(OH_2)^{n+} + H_2O \rightarrow M(OH)^{(n-1)+} + H_3O^+ \qquad (1)$$

These protons are picked up by the basic functions, pyrrole or azido N^{3-}, and the hydroxo group is involved in the Cu−Gd bridge. This behavior easily explains the failure to prepare Cu−Gd complexes with phenoxo-azido bridges. In spite of the absence of structural evidence, the reaction of gadolinium nitrate (instead of gadolinium chloride) with **4** yields again a trinuclear **8**, as evidenced by the infrared, analytical, and magnetic data. Indeed, the infrared spectrum of **8** clearly indicates that both ionic (1384 cm^{-1})[26] and bidentate nitrates (1472, 1302 cm^{-1})[27,28] are present.

Compared to the Cu−Gd complexes obtained with symmetrical Schiff base ligands,[23] these new Cu−Gd entities present a lower symmetry, due to the half-unit ligand, and more importantly to the dissymmetric phenoxo-hydroxo Cu−Gd bridges. Nevertheless, the magnetic studies do confirm that the Cu−Gd interaction is still ferromagnetic. Furthermore, the *J* value for **6** is among the largest values observed for dinuclear Cu−Gd complexes (8.4 cm^{-1}). Some years ago, the accumulated experimental data allowed us to put forward a magneto-structural correlation between the coupling strength and the $Cu-O_2-Gd$ dihedral angle of the dinuclear complexes.[23] Indeed, deviation of the $Cu-O_2-Gd$ core from planarity reduces the ferromagnetic interaction. The importance of this structural factor is confirmed by the experimental result found for dinuclear **6**, where a dihedral angle of 0.3(1)° between the CuOO and GdOO planes is associated with a *J* value of 8.4 cm^{-1}. This value compares well with the one obtained for a symmetrical double phenoxo bridge for which a 1.7(2)° dihedral angle is associated to a 10.1 cm^{-1} *J* value.[23] This result evidences the preponderance of the structural factor over the nature of the bridge, symmetric with two phenoxo bridges or non symmetric with phenoxo-hydroxo bridges.

Trinuclear **7** and **8** are characterized by *J* values lower than, or equal to, half the value found for dinuclear **6**, 4.4 and 5.5 cm^{-1}, respectively, in agreement with the presence of two copper ions around the gadolinium ion. The decrease of *J* for **7** may be explained by the increased dihedral angle. On the other hand, the 5.5 cm^{-1} *J* value for **8** would correspond to a dihedral angle close to 0−1°, as in **6**. This difference can be easily explained by the presence of nitrato anions unable to bridge the copper ions. Releasing this constraint favors a $Cu-O_2-Gd$ core closer to planarity.

Conclusion

Two different strategies have allowed us to synthesize dinuclear Cu−Gd and trinuclear Cu−Gd−Cu complexes

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characterized by an asymmetrical double phenoxo-hydroxo bridge. In both cases, the starting material is a monomeric copper complex, including a half-unit ligand resulting from the monocondensation of orthovanillin with a diamine, 1,2-diaminocyclohexane or 1,2-diaminoethane. These complexes, **1** and **2**, respectively, do not react with gadolinium salts. Further reaction with sodium azide or pyrrole carboxaldehyde yields neutral complexes, **3**−**5**, which do react with gadolinium ions to yield dinuclear Cu−Gd (**6**) or trinuclear Cu−Gd−Cu (**7**, **8**) complexes possessing asymmetrical phenoxo-hydroxo Cu−Gd double bridges. The acidic character of the gadolinium ions, and the use of starting complexes including only one phenoxo function are responsible for the formation of these asymmetrical bridges. In spite of these asymmetric bridges, ferromagnetic interactions operate in **6**−**8**. These results corroborate preponderance of the planarity of the Cu−O_2−Gd core over the dissymmetry of the bridges. The dominating role of a structural factor is a strong experimental argument in favor of a decisive contribution of the 5d gadolinium orbitals in the magnetism of the Cu−Gd complexes.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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