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Influence of Anionic Ligands (X) on the Nature and Magnetic Properties of Dinuclear $LCuGdX_3 \cdot nH_2O$ Complexes (LH_2 Standing for Tetradentate Schiff Base Ligands Deriving from 2-Hydroxy-3-methoxybenzaldehyde and X Being Cl, N_3C_2, and CF_3COO)

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The monometallic precursor L^1Cu (L^1H_2 standing for 1,3-bis((3-methoxysalicylidene)amino)-2,2′-dimethylpropane) reacts with $GdCl_3 \cdot 6H_2O$ to afford a dinuclear complex which crystallizes in the orthorhombic space group $Pca2_1$ (No. 29) in a cell having the dimensions $a = 9.0246(11)$ Å, $b = 16.5198(14)$ Å, $c = 20.286(2)$ Å, and $Z = 4$. Analysis of the structural data shows that it may be formulated as $[L^1CuCl_2Gd(H_2O)_4]Cl \cdot 2H_2O$. The cationic dinuclear unit possesses a CuO_2Gd bridging core which is almost planar. The complex displays a ferromagnetic interaction (10.1 cm^{-1}) which is the largest yet reported for a structurally characterized dinuclear (Cu−Gd) complex. Lower magnetic interactions are observed for neutral $L^1CuGdX_3 \cdot H_2O$ complexes (X = N_3C_2, CF_3COO). Consideration of the magnetic and structural data obtained for various dinuclear (Cu−Gd) complexes leads to a correlation between the magnitude of the magnetic interaction and the exponential of the dihedral angle between the two halves of the CuO_2Gd bridging core.

Introduction

In recent papers,[1,2] we have described the structures and magnetic properties of perfectly insulated dinuclear (Cu, Gd) complexes. We have also developed a general route allowing the nature of the 3d and 4f ions to be varied[3−6] without destroying the strictly dinuclear nature of the resulting complexes. The synthetic process relies on stepwise complexation of Schiff base ligands deriving from 2-hydroxy-3-methoxybenzaldehyde (L^iH_2 in Figure 1) to obtain mononuclear species (L^iCu) and dinuclear complexes, successively. The latter complexes correspond to the overall formulation $L^iCuLnX_3D_n$, X standing for a monoanionic species and D for a neutral molecule generally issued from the solvent. Cu(II) and Gd(III) occupy the inner and outer coordination site of L^i, respectively (cf. Figure 1). In previous work[1−6] it has been made a general use of nitrato anions (X = NO_3), each of them contributing to the electroneutrality and also to the completion of the coordination sphere of the 4f ions which eventually may include neutral molecules D. To highlight the influence exerted by the auxiliary ligands X on the nature and properties of $L^iCuLnX_3D_n$, we have considered four complexes: $L^1CuGdCl_3(H_2O)_6$ (**1**); $L^2CuGdCl_3(H_2O)_6$ (**1′**); $L^1CuGd(N_3C_2)_3(H_2O)$ (**2**); $L^1CuGd(CF_3COO)_3(H_2O)$ (**3**). The reference complex $L^1Cu(C_3H_6O)\,Gd(NO_3)_3$ (**4**) has been previously described.[2] The possibility of replacing NO_3 by more voluminous chelating anions has now been initiated by the study of $L^1Cu(O_2COMe)Gd(thd)_2$ (**5**) (thd standing for the anionic form of tetramethylheptanedione).[7]

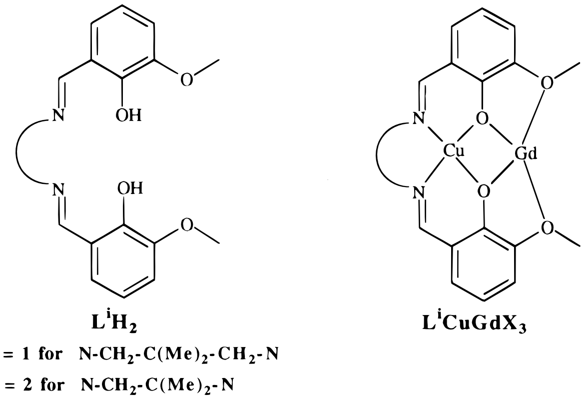

Figure 1. Schematic representation of the L^1H_2 and L^2H_2 ligands and of the L^iCuGd core in the **1**, **1′** and **2**−**5** complexes.

Experimental Section

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N) were carried out by the Service de Microanalyze du Laboratoire de Chimie de Coordination, Toulouse, France. Fourier transform infrared spectroscopy on KBr pellets was performed on a Perkin-Elmer 1725 X FT-IR instrument. Electronic spectra were obtained with a Cary 2390 spectrometer, using dmso as solvent. Magnetic susceptibility data were collected on powdered samples of the different compounds with use of a SQUID-based sample magnetometer on a QUANTUM Design model MPMS instrument at 0.1 T. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.[8]

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Synthesis of the Ligands and Complexes. The mononuclear precursors $L^1Cu{\cdot}2H_2O$,[2] $L^2Cu{\cdot}H_2O$,[2] and $L^1Cu(C_3H_6O)Gd(NO_3)_3$[2] were obtained according to published procedures.

$[L^1CuCl_2Gd(H_2O)_4]Cl{\cdot}2H_2O$ (1). $L^1Cu{\cdot}2H_2O$ (0.47 g, 1 mmol) and $GdCl_3{\cdot}6H_2O$ (0.37 g, 1 mmol) were mixed together in MeOH (10 mL). The mixture was stirred and set aside until crystals appeared. They were filtered off, washed with methanol, diethyl ether, and dried. Yield: 0.6 g, 75%. Anal. Calcd for $C_{21}H_{36}Cl_3CuGdN_2O_{10}$: C, 31.4; H, 4.5; N, 3.5. Found: C, 31.2; H, 4.4; N, 3.4. Mass spectrum (FAB^+, 3-nitrobenzyl alcohol matrix): *m*/*z* = 661 (100), $[L^1CuGdCl_2]^+$.

$[L^2CuGdCl_3{\cdot}6H_2O]$ (1′). A similar procedure, starting with $L^2Cu{\cdot}H_2O$, gave the desired product in a 70% yield. Anal. Calcd for $C_{20}H_{34}Cl_3CuGdN_2O_{10}$: C, 30.4; H, 4.3; N, 3.5. Found: C, 30.0; H, 4.2; N, 3.3. Mass spectrum (FAB^+, 3-nitrobenzyl alcohol matrix): *m*/*z* = 647 (100), $[L^2CuGdCl_2]^+$.

$[L^1CuGd(N_3C_2)_3{\cdot}H_2O]$ (2). $L^1Cu(C_3H_6O)Gd(NO_3)_3$ (0.3 g, 0.36 mmol) and NaN_3C_2 (0.1 g, 1.1 mmol) were mixed in MeOH (10 mL) until a light green precipitate appeared. It was filtered off, washed with a little amount of methanol and diethyl ether, and dried. Yield: 0.1 g, 34%. Anal. Calcd for $C_{27}H_{26}CuGdN_{11}O_5$: C, 40.3; H, 3.2; N, 19.1. Found: C, 39.9; H, 3.0; N, 18.7. Mass spectrum (FAB^+, 3-nitrobenzyl alcohol matrix): *m*/*z* = 721 (100), $[L^1CuGd\ (N_3C_2)_2]^+$.

$L^1CuGd(CF_3COO)_3{\cdot}H_2O$ (3). To a MeOH solution (10 mL) of $L^1Cu{\cdot}2H_2O$ (0.47 g, 1 mmol) and $GdCl_3{\cdot}6H_2O$ (0.37 g, 1 mmol) was added a MeOH solution (10 mL) of CF_3COOH (0.4 g, 3.5 mmol) and NEt_3 (0.35 g, 3.5 mmol). The mixture was stirred and set aside until a precipitate appeared. It was filtered off and washed with water, acetone, and diethyl ether. Yield: 0.22 g, 23%. Anal. Calcd for $C_{27}H_{26}Cu\ F_9GdN_2O_{11}$: C, 34.3; H, 2.8; N, 3.0. Found: C, 34.4; H, 2.6; N, 2.9. Mass spectrum (FAB^+, 3-nitrobenzyl alcohol matrix): *m*/*z* = 815 (100), $[L^1CuGd(CF_3COO)_2]^+$.

X-ray Data Collection and Structure Determination of 1. The crystal was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. The data were collected at 20 ± 1 °C using Mo Kα radiation with a graphite monochromator (λ = 0.710 73 Å) to a maximum 2θ value of 54°. The crystal quality was monitored by scanning three standard reflections every 2 h. No significant variation was observed during the data collection. After corrections for Lorentz and polarization effects,[9] absorption corrections from ψ scans were applied.[10] The structure was solved by using the Patterson method[11] and refined by full-matrix least squares.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found on a difference Fourier and introduced in calculations with a riding model, except those bonded to water molecules which were allowed to vary isotropically. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation.[13] Refinement was on F_o^2 for all reflections. Weighted *R* factors R_w and goodness of fit *S* were based on F_o^2; conventional *R* factors were based on F_o ($F_o > 4\sigma(F_o)$), with F_o set to zero for negative F_o^2. The calculations were performed on a MicroVAX 3400 and a PC computer using the programs MOLEN,[9] SHELXS-97,[11] SHELXL-97,[12] and ZORTEP.[14]

The crystallographic data are summarized in Table 1. Atomic coordinates are given in Table 2.

Table 1. Crystallographic Data for $[L^1CuCl_2Gd(H_2O)_4]Cl{\cdot}2H_2O$ (**1**)

chem formula	$C_{21}H_{36}Cl_3CuGdN_2O_{10}$	fw	803.67
space group	$Pca2_1$ (No. 29)	T	293(2) K
a	9.0246(11) Å	λ	0.710 73 Å
b	16.5198(14) Å	ρ_{calcd}	1.765 g cm^{-3}
c	20.286(2) Å	μ_{calcd}	31.61 cm^{-1}
V	3024.3(5) Å^3	R^a (all, obsd)	0.03414, 0.0210
Z	4	R_w^b (all, obsd)	0.0553, 0.0513

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 100) for $[L^1CuCl_2Gd(OH_2)_4]Cl{\cdot}2H_2O$ (**1**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{eq}{}^a$
Gd	0.63872(2)	0.28121(1)	0.25000(1)	3.26(1)
Cu	0.41061(6)	0.20928(3)	0.37746(2)	3.77(1)
Cl(1)	0.1399(1)	0.26647(6)	0.30898(6)	4.56(2)
Cl(2)	0.7076(2)	0.15061(8)	0.44882(6)	5.95(3)
Cl(3)	0.3479(1)	0.42564(7)	0.10663(5)	4.72(2)
O(1)	0.5147(3)	0.1715(2)	0.2972(1)	3.58(6)
O(2)	0.5101(3)	0.3088(2)	0.3478(1)	3.80(6)
O(3)	0.6911(3)	0.1497(2)	0.1968(1)	4.33(6)
O(4)	0.6438(3)	0.4222(2)	0.2835(2)	4.61(7)
O(5)	0.6327(3)	0.3310(2)	0.1395(2)	5.92(9)
O(6)	0.8092(3)	0.2415(2)	0.3317(2)	5.58(8)
O(7)	0.8865(3)	0.3094(3)	0.2131(2)	5.83(9)
O(8)	0.3902(3)	0.2985(3)	0.2139(2)	8.2(1)
O(9)	0.9964(4)	0.4006(2)	0.1146(2)	6.6(1)
O(10)	0.7821(4)	0.3144(3)	0.0281(2)	7.4(1)
N(1)	0.3292(3)	0.1006(2)	0.3951(2)	3.67(7)
N(2)	0.3134(4)	0.2654(2)	0.4521(2)	4.36(8)
C(1)	0.5412(4)	0.,0958(2)	0.2807(2)	3.41(8)
C(2)	0.6375(4)	0.0795(2)	0.2271(2)	3.75(8)
C(3)	0.6724(5)	0.0028(3)	0.2076(2)	4.8(1)
C(4)	0.6122(5)	−0.0623(2)	0.2408(3)	5.4(1)
C(5)	0.5152(5)	−0.0487(3)	0.2914(2)	4.7(1)
C(6)	0.4795(4)	0.0286(2)	0.3132(2)	3.62(8)
C(7)	0.3732(4)	0.0367(2)	0.3658(2)	3.86(8)
C(8)	0.7846(5)	0.1389(3)	0.1396(2)	5.5(1)
C(9)	0.2066(5)	0.0888(3)	0.4428(2)	5.3(1)
C(10)	0.2199(4)	0.1354(3)	0.5063(2)	4.4(1)
C(11)	0.1968(5)	0.2250(3)	0.4922(3)	5.4(1)
C(12)	0.0913(5)	0.1099(3)	0.5507(3)	6.3(1)
C(13)	0.3647(5)	0.1211(5)	0.5415(3)	8.7(2)
C(14)	0.4964(4)	0.3817(2)	0.3718(2)	3.54(8)
C(15)	0.5667(4)	0.4467(2)	0.3400(2)	4.06(9)
C(16)	0.5577(6)	0.5245(3)	0.3619(2)	6.2(1)
C(17)	0.4748(7)	0.5425(3)	0.4189(3)	7.0(2)
C(18)	0.4027(6)	0.4804(3)	0.4509(2)	6.4(1)
C(19)	0.4133(5)	0.4007(3)	0.4285(2)	4.55(9)
C(20)	0.3269(5)	0.3406(3)	0.4637(2)	4.6(1)
C(21)	0.7127(5)	0.4860(3)	0.2454(3)	6.5(1)

^{a} U_{eq} = one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

Structural and Spectroscopic Data for Complex 1. A molecular plot of $L^1CuGdCl_3(H_2O)_6$ (**1**) is represented in Figure 2, while significant bond lengths and angles appear in Table 3. The central part of the structure is occupied by Cu(II) and Gd(III) ions which are bridged by two phenolato oxygen atoms afforded by L^1. This network occurs in all the dinuclear complexes involving the ligand L^1H_2 and the Cu and Gd metal ions. However, in complex **5**[7] there is a triple bridge between the Cu and Gd centers via two phenolato oxygens from L^1 and two oxygens from the monomethyl carbonate anion while each tetramethylheptanedione ligand acts as a chelating reagent toward Gd.

In **1**, the Cu−Gd separation of 3.5121(5) Å is somewhat shorter than in **4**[2] (3.5231(4) Å) but longer than in **5**[7] (3.4727(4) Å). The dihedral angle between the planes O(1)-CuO(2) and O(1)GdO(2) is markedly smaller in **1** with a value of 1.7(2)° compared to those in **4** and **5** with values of 16.6(2) and 19.1(2)°, respectively.

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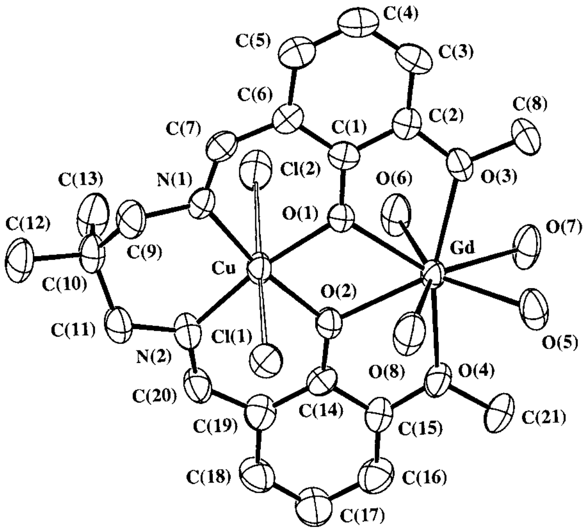

Figure 2. Plot for the $[L^1CuCl_2Gd(H_2O)_4]$ cationic entity with ellipsoids drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[L^1CuCl_2Gd(H_2O)_4]Cl \cdot 2H_2O$

Cu−O(1)	1.981(2)	Cu−N(1)	1.972(3)
Cu−O(2)	1.967(3)	Cu−N(2)	1.981(3)
Cu−Cl(1)	2.965(11)	Cu−Cl(2)	3.1965(15)
Gd−O(1)	2.335(2)	Gd−O(5)	2.388(3)
Gd−O(2)	2.344(2)	Gd−O(6)	2.354(3)
Gd−O(3)	2.471(3)	Gd−O(7)	2.404(3)
Gd−O(4)	2.427(3)	Gd−O(8)	2.377(3)
Gd−O(1)−Cu	108.65(11)	Gd−O(2)−Cu	108.81(11)
O(1)−Cu−O(2)	78.19(10)	O(1)−Gd−O(2)	64.31(9)
c[a]	1.7(2)		

[a] Dihedral angle between the CuO(1)O(2) and GdO(1)O(2) planes.

The gadolinium ion is eight-coordinated in **1**. In addition to the two anionic oxygens from the phenolate groups of L^1, Gd(III) completes its coordination sphere with six neutral oxygen donors, two from the OMe side arms and four from water molecules. The two longest Gd−O bonds involve the OMe side arms (2.427(3) and 2.471(3) Å) while the two shortest ones are from the phenolate oxygens (2.344(2) and 2.335(2) Å). The four Gd−O(water) bonds have lengths varying from 2.354(3) to 2.404(3) Å. These Gd−O bonds are shorter than in other related complexes.[1,2,7]

In **1**, the copper is surrounded by six donor atoms. The equatorial N_2O_2 donors afforded by L^1 are nearly coplanar, the largest deviation from the mean plane being equal to 0.029 Å. The axial positions are occupied by chloride ions at 2.920(1) and 3.175(1) Å from the equatorial plane.

The two uncoordinated water molecules are involved in a hydrogen bond network which also includes the three chloride ions and the four water molecules coordinated to Gd(III). This network turns above and below the CuO_2Gd bridging core but does not lead to short internuclear contacts. The separations between metal ions belonging to neighboring molecules are large: 8.2566(8) Å for Cu···Cu, 8.5215 (3) Å for Gd···Gd, and 7.5248(6) Å for Cu···Gd.

Finally, it may be emphasized that, in contrast to what happens in **4**, the auxiliary anionic ligands (X = Cl) in **1** do not participate in the gadolinium coordination sphere. Two of them are linked to the copper ion while the third one is uncoordinated. The resulting dinuclear unit is not neutral but cationic and is best represented by the formula $[L^1CuCl_2Gd(H_2O)_4]^+$. The large value of λ_{max} (696 nm) in a dmso solution is consistent with a firm coordination of the two chloride ions in axial positions of the copper ion. Smaller values ($\lambda_{max} = 610$ nm) are observed for complexes **1′** and **2**−**4**; they most probably point out loose apical binding of neutral molecules (H_2O, MeOH, dmso), or at least pentacoordination. Conversely, in complexes **1′** and **2**−**4**, the anionic ligands (Cl, N_3C_2, CF_3COO, and NO_3, respectively) do not bind to the copper center but are involved in the coordination sphere of the gadolinium ion in addition to the O_4 donor set afforded by the main L^1 ligand. From literature data, N_3C_2[15] and CF_3COO[16] may act as bidentate ligands to reach 8[17] or 10 coordinance,[2] as in **4**. FAB^+ spectra give signals at *m*/*z* = 661 (100) (**1**), 647 (100) (**1′**), 721 (100) (**2**), and 809 (100) (**3**) with *m*/*z* values and isotopic features attributable to $[L^iCuGdX_2]^+$ cations, respectively (X = Cl, N_3C_2, or CF_3COO and *i* = 1, 2). Nevertheless, complexes **1**, **1′**, and **2**−**5** have a ferromagnetic behavior (vide infra) which can be attributed to nothing but intramolecular Cu···Gd interactions mediated by both phenolato oxygens of the ligand L^i.

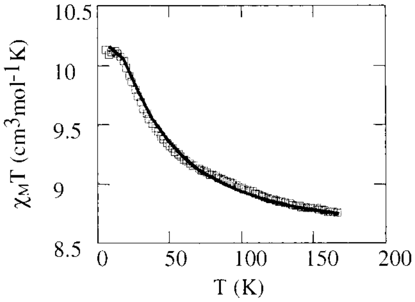

Figure 3. Thermal dependence of $\chi_M T$ for $[L^1CuCl_2Gd(H_2O)_4]Cl \cdot 2H_2O$ (**1**) at 0.1 T. The full line corresponds to the best data fit.

Magnetic Properties. The magnetic behavior of complex **1** is represented in Figure 3 in the form of the thermal variation of the $\chi_M T$ product, χ_M being the molar magnetic susceptibility corrected for diamagnetism. At 300 K, $\chi_M T$ is equal to 8.6 cm^3 K mol^{-1}, which roughly corresponds to the value expected for the two uncoupled metal ions. Lowering the temperature causes $\chi_M T$ to increase to 10.1 cm^3 K mol^{-1} at 5 K. That value compares well with that (10 cm^3 K mol^{-1}) expected for a $S = 4$ spin state resulting from ferromagnetic coupling between Cu(II) ($S = {}^1/_2$) and Gd(III) ($S = {}^7/_2$) and assuming $g_{Cu} = g_{Gd} = 2.0$. A quantitative analysis has been performed on the basis of an expression derived from the spin-only Hamiltonian $-JS_{Cu} \cdot S_{Gd}$. Taking into consideration the *g* values associated with the low lying levels $E(4) = 0$ and $E(3) = 4J$, $g_4 = (7g_{Gd} + g_{Cu})/8$, and $g_3 = (9g_{Gd} - g_{Cu})/8$,[18] we obtain the following theoretical expression:

$$\chi_M T = \frac{4N\beta^2}{k}\left[\frac{15{g_{(4)}}^2 + 7{g_{(3)}}^2 e^{-4J/kT}}{9 + 7e^{-4J/kT}}\right]$$

Least-squares fitting of the experimental data leads to $J = 10.1(4)$ cm^{-1}, $g_{Cu} = 2.08(2)$, and $g_{Gd} = 2.010(1)$. The excellent quality of the fit and the reliability of the model are certified by the value (4×10^{-5}) of the agreement factor $R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\sum[(\chi_M T)_{obs}]^2$. To take into account the constant $\chi_M T$ values at very low temperature, a Weiss constant of −0.1 K has been introduced in the theoretical expression given above.

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Table 4. *J* Values and Structural Parameters ($a-d$)[a] for Dinuclear Cu−Gd Complexes

compd	J (cm^{-1})	a	b	c	d	ref
Salen(MeIm)CuGd(hfa)$_3$[b]	1.42			39.6	3.252(4)	15
L^{1}Cu(O$_2$CoMe)Gd(thd)$_2$[b]	4.2	83.04(10)	65.07(8)	19.1(2)	3.4727(4)	7
L^{1}Cu(OCMe$_2$)Gd(NO$_3$)$_3$	4.8	78.29(9)	62.14(7)	16.6(2)	3.5231(4)	2
L$^3{}_2$Cu(HOMe)Gd(NO$_3$)$_3$[b]	6.8	79.31(8)	63.29(7)	12.5(2)	3.4842(3)	2
L^{2}Cu(OCMe$_2$)Gd(NO$_3$)$_3$[b]	7.2	81.8(2)	63.0(2)	12.9(2)	3.4275(9)	1
[L^{1}CuCl$_2$Gd(H$_2$O)$_4$]Cl•2H$_2$O	10.1	78.19(10)	64.31(9)	1.7(2)	3.5121(5)	this work

[a] a and b are respectively the O(1)−Cu−O(2) and O(1)−Gd−O(2) angles, c is the dihedral angle between the O(1)CuO(2) and O(1)GdO(2) planes, and d is the Cu···Gd separations ($a-c$) in deg and d in Å). [b] Salen = *N,N′*-ethylenebis(salicylideneaminato). MeIm = 1-methylimidazole. O$_2$COMe = monomethyl carbonate. L^1 and L^2 are described in the text. L^3 = 3-methoxysalicylaldiminato.

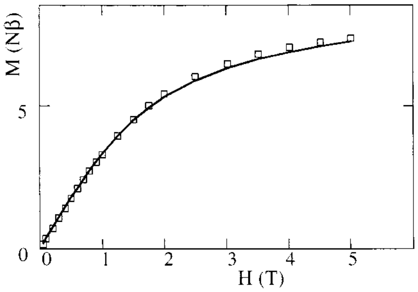

Figure 4. Field dependence of the magnetization for [L^{1}CuCl$_2$Gd(H$_2$O)$_4$]Cl•2H$_2$O (**1**). The full line corresponds to the Brillouin function for an $S = 4$ spin state.

Such a behavior can be due to slight interactions between heterodinuclear entities through the hydrogen bond network but seems to depend more probably on a partial saturation at low temperature of the large magnetic moment in the magnetic field, as observed before.[1] Nevertheless, the ferromagnetic interaction is definitively supported by the field dependence of the magnetization M at 4 K. In Figure 4, the experimental values correctly fit the Brillouin function for a S = 4 spin state. Applying the same analysis to the magnetic data collected for the three other complexes leads to the following values:

$$\mathbf{1'}\text{:}\quad J = 8.8(4)\ \text{cm}^{-1}\quad g_{\text{Cu}} = 2.10(1)\quad g_{\text{Gd}} = 2.010(1)\quad R = 2 \times 10^{-4}$$

$$\mathbf{2}\text{:}\quad J = 7.8(1)\ \text{cm}^{-1}\quad g_{\text{Cu}} = 2.09(1)\quad g_{\text{Gd}} = 1.992(1)\quad R = 1.1 \times 10^{-4}$$

$$\mathbf{3}\text{:}\quad J = 6.3(1)\ \text{cm}^{-1}\quad g_{\text{Cu}} = 2.08(1)\quad g_{\text{Gd}} = 1.980(1)\quad R = 1.8 \times 10^{-4}$$

Obviously the four complexes considered in the present paper display a ferromagnetic coupling between the two metal ions as do all the previously reported dinuclear (Cu,Gd) complexes, with fairly large J values.

The elements for a comparison of the structural and magnetic characteristics of the CuO$_2$Gd bridging network are reported in Table 4. It appears that the variations (Δ) of the angles O(1)-CuO(2) (a) and O(1)GdO(2) (b) and those of the Cu···Gd distance (d) are small ($\Delta a \leq 6\%$, $\Delta b \leq 3.2\%$, and $\Delta d \leq 8.0\%$) and probably unable to account for the large variation of the J constant (from 1.4 to 10.1 cm^{-1}).

From the magnetic properties of several polynuclear (Cu$_n$-Gd$_n$) complexes, it has been reported that the J_{CuGd} values and the Cu···Gd distances could be correlated by an exponential function.[19] Applied to complex **1**, this relationship leads to a value of J ≈ 3.1 cm^{-1}, which does not match the experimental value of 10.1 cm^{-1}. Obviously, clear-cut and pertinent differences between (Cu,Gd) complexes are afforded by the dihedral angle (c) between the two halves (OCuO and OGdO) of the bridging network. As previously suggested,[7,17] lowering the bending of the CuO$_2$Gd core causes the ferromagnetic interaction to increase. Within the framework of the present paper we wish to underline the interest of complex **1** which approaches the limiting case of no bending and displays the largest ferromagnetic interaction yet reported for structurally characterized (Cu,-Gd) complexes. Analysis of the data reported in Table 4 points out a satisfying correlation between the absolute value of the ferromagnetic coupling constant J and the dihedral angle (c):

$$|J| = A \exp(Bc)$$

with $A = 11.5$, $B = -0.054$, $|J|$ in cm^{-1}, and c in deg. The quality of the fit, obtained with a limited number of experimental data, implies that the correlation must remain a working hypothesis at this stage. It may be noted that application of the relation to trinuclear complexes is more difficult. From the c values calculated for (Cuapen)$_2$Gd(ClO$_4$)$_3$(H$_2$O)$_3$[20] and (Cusalen)$_2$-Gd(ClO$_4$)$_3$(H$_2$O)$_3$[20] we obtained J values of 4.3 and 3.3 cm^{-1}, respectively. If the first one is in correct agreement with the experimental value of 5.3 cm^{-1}, this is not the case for the second one (3.3 cm^{-1} instead of 7.4 cm^{-1}). Such a bad correlation is not really surprising if we remember the complexity of these systems, with nearly equal but opposite antiferromagnetic Cu−Cu and ferromagnetic Cu−Gd magnetic interactions.

Tentatively the decrease of J along the series **1**, **1′**, and **2**−**5** could be attrributed to an increase of the dihedral angle (c) originating in more important steric demands in the vicinity of the bridging network. These results also confirm that the L^{1}H$_2$ ligand is more appropriate than L^{2}H$_2$ to give the highest J values.

The stabilization of the ferromagnetic ($S = 4$) spin state in CuO$_2$Gd systems has been attributed[17] to the coupling between the Cu(II)−Gd(III) ground configuration and the Cu(II)−Gd(II) charge-transfer excited configuration, an electron being transferred from the singly occupied 3d copper orbital to an empty 5d gadolinium orbital according to a mechanism first suggested by Goodenough.[21] In this instance the influence exerted by the bending parameter may be related to change of the β_{5d-3d} transfer integrals.

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Supporting Information Available: X-ray crystallographic files including the structural data for [L^{1}CuCl$_2$Gd(H$_2$O)$_4$]Cl•2H$_2$O in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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