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A Genuine Example of a Discrete Bimetallic (Cu, Gd) Complex: Structural Determination and Magnetic Properties

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Since 1985,[1] increasing interest has been given to the magnetic properties of molecular complexes comprising simultaneously d and f transition metal ions. This interest has been essentially focused on the Cu(II), Gd(III) couple. However the complexes yet considered and structurally characterized[1−6] are not dinuclear but polynuclear with Cu_2Gd, Cu_4Gd, Cu_4Gd_2, or $(CuGd)_n$ cores so that they may support several types of magnetic interactions resulting from Cu−Gd, Cu−Cu or, eventually, Gd−Gd couplings. It may be noted that two recent papers[7,8] have described the synthesis and magnetic properties of several species supposed to be discrete dinuclear (Cu, Gd) complexes but, to our knowledge, the absence of long range interaction has not been supported by any structural study.

The present paper is devoted to a complex $LCuGd(NO_3)_3 \cdot Me_2CO$ (L being 1,2′-bis((3-methoxysalicylidene)diamino)-2-methylpropane and Me_2CO standing for acetone) which has been structurally characterized as a genuine example of a strictly dinuclear complex. Its magnetic behavior demonstrates undoubtedly the ferromagnetic nature of the (Cu, Gd) interaction which has been previously inferred from the experimental data related to polynuclear complexes[1−8] and supported by a theoretical study.[4]

Experimental Section

[(1,2-Bis((3-methoxysalicylidene)amino)-2-methylpropanato)copper(II)], LCu. This complex was obtained as previously described.[9] Anal. Calc. for $C_{20}H_{22}CuN_2O_4$ H_2O; C, 55.1; H, 5.5; N, 6.4. Found: C, 54.9; H, 5.5; N, 6.3.

$[CuLGd(NO_3)_3] \cdot Me_2CO$. Addition of $Gd(NO_3)_3 \cdot 5H_2O$ (0.25 g, 5.5 × 10^{-4} mol) to LCu (0.23 g, 5.5 × 10^{-4} mol) in acetone induced the formation of a precipitate which was filtered, washed with cold acetone and diethyl oxide. Yield: 0.36 g, 80% Anal. Calcd for $C_{20}H_{22}$ Cu Gd N_5 $O_{13} \cdot C_3H_6O$: C, 33.7; H, 3.4; N, 8.5 Found: C, 34.2; H, 3.4; N, 8.5. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): *m/z* = 699 (100), $[C_{20}H_{22}CuGdN_4O_{10}]^+$.

Materials and Methods. All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). Magnetic susceptibility data were collected on a powdered sample of the compound with use of a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants[10] (−337 × 10^{-6} emu mol^{-1}). Positive FAB mass spectra were recorded with a Nermag R10-10 spectrometer using 3-nitrobenzyl alcohol matrix. Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Crystal data are gathered in Table 1.

Table 1. Crystallographic Data for $[(C_{20}H_{22}N_2O_4)CuGd(NO_3)_3] \cdot C_3H_6O$

chem formula	$C_{23}H_{28}N_5O_{14}CuGd$	fw	819.29
crystal system	monoclinic	λ, Å	0.71073
space group	$P2_1/c$ (No. 14)	Z	4
a, Å	9.799(1)	D_c, g cm^{-3}	1.845
b, Å	18.926(3)	T, K	293
c, Å	16.012(1)	μ, mm^{-1}	3.025
β, deg	96.530(8)	R^a (obs)	0.0366
V, Å^3	2950.3(6)	wR2^b (obs, all)	0.0906, 0.1164

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

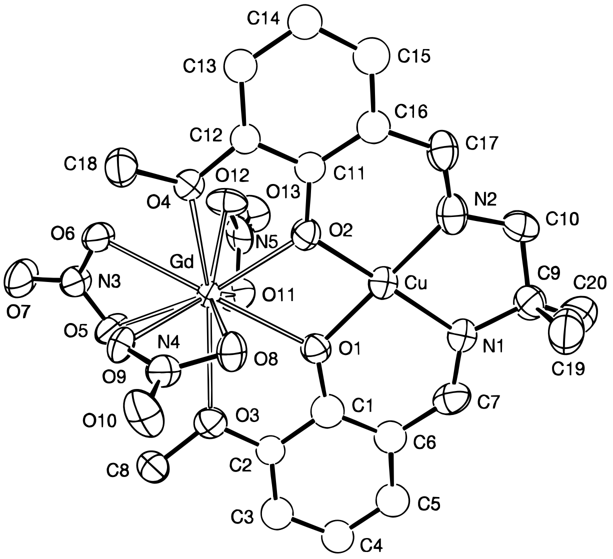

Figure 1. Ortep plot for $LCuGd(NO_3)_3 \cdot Me_2CO$. Selected bond lengths (Å) are as follows: Gd···Cu = 3.428(1), Gd−O(1) = 2.398(5), Gd−O(2) = 2.337(5), Gd−O(3) = 2.626(5), Gd−O(4) = 2.614(5), Gd−O(5) = 2.529(5), Gd−O(6) = 2.524(5), Gd−O(8) = 2.487(5), Gd−O(9) = 2.461(5),Gd−O(11) = 2.491(6), Gd−O(12) = 2.452(5),Cu−O(1) = 1.879(5), Cu−N(1) = 1.942(6), Cu−O(2) = 1.904(5), Cu−N(2) = 1.918(7). Selected bond angles (deg) are as follows: Gd−O(1)−Cu: 105.9(2), Gd−O(2)−Cu: 107.4(2).

Results and Discussion

Description of the Structure. The unit cell contains four discrete entities $[LCuGd(NO_3)_3]$ and intervening acetone molecules. A view of the dinuclear unit is represented in Figure 1 with selected bond distances and angles appearing in the figure caption. Significant atomic coordinates are given in Table 2.

The central region of the structure is occupied by the copper(II) and gadolinium(III) ions which are bridged one to the other via the two phenolic oxygen atoms of the ligand L. The four atoms of the GdO_2Cu network roughly form a plane, the deviations from the least-squares plane ranging from 0.0767(3) to 0.1090(9) Å. The two Gd−O(*i*)−Cu angles differ with values of 105.9(2)° (*i* = 1) and 107.4(2)° (*i* = 2). The related Gd−O(*i*) and Cu−O(*i*) distances are also clearly different. The

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Table 2. Selected Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters ($Å^2 \times 100$)

atom	x/a	y/b	z/c	U_{eq}/U_{iso}
Gd	0.20552(3)	0.07813(2)	0.25161(2)	3.49(1)[a]
Cu	0.29325(9)	0.24352(5)	0.32671(5)	4.95(2)[a]
O(1)	0.2977(5)	0.1504(3)	0.3676(3)	5.0(1)[a]
O(2)	0.1840(5)	0.2004(3)	0.2346(3)	4.9(1)[a]
O(3)	0.2578(5)	0.0182(3)	0.3997(3)	5.4(1)[a]
O(4)	0.0357(5)	0.1276(3)	0.1277(3)	4.9(1)[a]
O(5)	0.2737(6)	−0.0499(3)	0.2384(3)	6.3(2)[a]
O(6)	0.1669(7)	−0.0054(3)	0.1283(3)	6.6(2)[a]
O(7)	0.2202(8)	−0.1160(3)	0.1297(4)	8.5(2)[a]
O(8)	0.0054(5)	0.1091(3)	0.3270(3)	5.3(1)[a]
O(9)	0.0002(5)	0.0067(2)	0.2672(3)	4.8(1)[a]
O(10)	−0.1523(6)	0.0327(3)	0.3493(5)	8.9(2)[a]
O(11)	0.4604(6)	0.0683(4)	0.2625(4)	8.3(2)[a]
O(12)	0.3595(6)	0.1124(3)	0.1481(4)	6.9(2)[a]
O(13)	0.5831(7)	0.1038(4)	0.1652(5)	9.6(2)[a]
N(1)	0.3805(6)	0.2905(3)	0.4266(4)	5.2(2)[a]
N(2)	0.2695(7)	0.3381(3)	0.2844(5)	6.0(2)[a]
N(3)	0.2209(7)	−0.0586(3)	0.1641(4)	5.3(2)[a]
N(4)	−0.0518(7)	0.0471(3)	0.3153(4)	5.1(2)[a]
N(5)	0.4692(7)	0.0967(4)	0.1899(5)	7.0(2)[a]
C(1)	0.3419(9)	0.1306(4)	0.4469(5)	6.1(2)
C(2)	0.3236(8)	0.0584(4)	0.4636(4)	4.7(2)
C(3)	0.3700(8)	0.0312(4)	0.5439(5)	5.9(2)
C(4)	0.4345(9)	0.0754(4)	0.6053(5)	6.0(2)
C(5)	0.4472(9)	0.1463(4)	0.5890(5)	6.2(2)
C(6)	0.4036(8)	0.1758(4)	0.5103(5)	5.7(2)
C(7)	0.4132(8)	0.2517(5)	0.4956(5)	6.4(2)[a]
C(8)	0.2135(9)	−0.0519(4)	0.4209(5)	6.3(2)[a]
C(9)	0.3752(8)	0.3679(4)	0.4215(5)	6.6(2)[a]
C(10)	0.353(1)	0.3914(4)	0.3314(5)	7.0(2)[a]
C(11)	0.1239(7)	0.2370(4)	0.1666(4)	4.5(2)
C(12)	0.0462(7)	0.1967(4)	0.1071(4)	4.2(2)
C(13)	−0.0151(7)	0.2271(4)	0.0332(4)	4.9(2)
C(14)	0.0005(8)	0.2996(4)	0.0197(5)	5.2(2)
C(15)	0.0782(8)	0.3393(5)	0.0825(5)	6.0(2)
C(16)	0.1375(8)	0.3098(4)	0.1546(5)	5.2(2)
C(17)	0.2045(8)	0.3581(4)	0.2122(5)	5.8(2)[a]
C(18)	−0.0753(9)	0.0880(4)	0.0828(5)	6.0(2)[a]
C(19)	0.252(1)	0.3951(5)	0.4643(6)	8.6(3)[a]
C(20)	0.509(1)	0.3994(6)	0.4651(6)	9.8(4)[a]

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

copper gadolinium separation of 3.428(1) Å has to be compared to the values previously reported[1,2] for polynuclear Cu/Gd complexes (from 3.30(1) to 3.37(5) Å).

The copper (II) ion completes its coordination sphere with two imino nitrogen atoms from L. The four atoms of the N_2O_2 chromophore are almost coplanar since they are alternately displaced from the mean plane by less than 0.03 Å. The copper(II) ion is pulled out the equatorial plane by 0.1077(9) Å in spite of the absence of any apical ligand. The bond lengths to Cu(II) are within the usual range observed for copper coordinated to Schiff bases.[11]

The gadolinium ion is decacoordinated. In addition to the two phenolic oxygens, the rare earth achieves its environment with two methoxy oxygen atoms from L and six oxygen atoms coming from three bidentate nitrato ions. The range of the Gd−O bond lengths is rather large (from 2.337(5) to 2.626(5) Å) with significant differences between the phenolic, methoxy and nitrato oxygen atoms. The shortest Gd−O bonds (2.367 Å mean) are related to the phenolic oxygen while the largest bonds (2.620 Å mean) involve the methoxy oxygen.

It may be noted that the separations between metal ions belonging to neighbouring molecules are large (Gd···Cu = 7.730(1) Å, Gd···Gd = 9.084 (1) Å, and Cu···Cu = 8.010(1) Å) and preclude any significant intermolecular interaction.

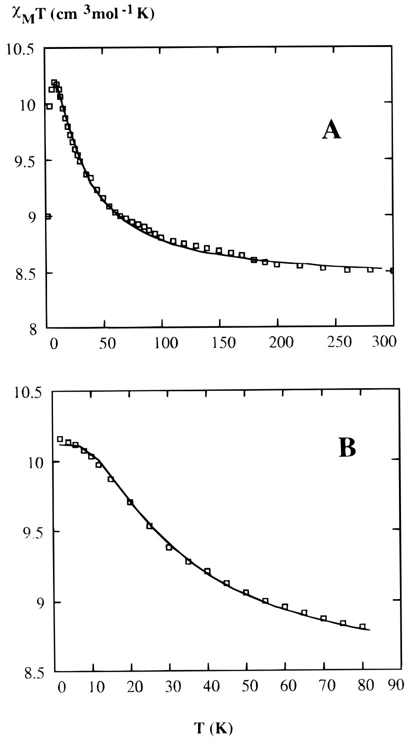

Figure 2. Experimental (◇) temperature dependence of $\chi_M T$ for $LCuGd(NO_3)_3{\cdot}Me_2CO$, at 0.5 (A) and 0.05 T (B). The full lines correspond to the best data fits (see text).

Magnetic Study. The temperature dependence of the magnetic susceptibility in the range 2−300 K is shown in Figure 2A in the $\chi_M T$ vs T form, the applied magnetic field being equal to 0.5 T. At 300K, $\chi_M T$ is equal to 8.6 cm^3 K mol^{-1} which roughly corresponds to the value expected for the two uncoupled metal ions. When the temperature is lowered, $\chi_M T$ increases, reaches a maximum of 10.2 cm^3 K mol $^{-1}$ at 10 K, and then decreases to 9.0 cm^3 K mol $^{-1}$ at 2 K. The behavior observed in the 300−10 K range is indicative of a ferromagnetic interaction between the Gd(III) and Cu(II) ions. The maximum value of 10.2 compares well with the value (10.0 cm^3 K mol^{-1}) expected for the spin state $S = 4$ resulting from ferromagnetic coupling between Gd(III) ($S = {}^7/_2$) and Cu(II) ($S = {}^1/_2$), both ions having g values of 2.0. The decrease of χ_MT observed below 10 K is most likely attributable to saturation effects. The two other conceivable explanations, zero field splitting of the $S = 4$ ground state and/or antiferromagnetic interaction between neighbouring molecules are not consistent with a second set of data (Figure 2B) obtained with a field of 0.05 T. In this instance the experimental results can be analyzed on the basis of a spin only expression derived from a spin Hamiltonian $H = -JS_{Cu}{\cdot}S_{Gd}$. In principle the two low lying spin levels, $E(4) = 0$ and $E(3) = 4J$ have different g values,[12] $g_4 = (7g_{Gd} + g_{Cu})/8$ and $g_3 = (9g_{Gd} - g_{Cu})/8$. Finally the experimental data may be fitted using the expression

$$\chi_M T = \frac{4N\beta^2}{k}\left[\frac{15{g_4}^2 + 7{g_3}^2 3^{-4J/kT}}{9 + 7e^{-4J/kT}}\right]$$

In the 10−300 K temperature range, a satisfactory fit of the high field data is obtained for the following set of parameters: $g_{Cu} = 2.11$, $g_{Gd} = 2.01$, and $J = 7.0(1)$ cm^{-1} with an agreement factor $R = 4.4 \times 10^{-4}$ ($R = \sum(\chi_{obs}T - \chi_{calc}T)^2/\sum(\chi_{obs}T)^2$). Rather

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similar values of the parameters are deduced from the second data set ($2 \leq T \leq 80$ K, $H = 0.05$ T): $g_{\mathrm{Cu}} = 2.07$, $g_{\mathrm{Gd}} = 2.00$, and $J = 6.8(1)$ cm^{-1}. In this last instance the value of the agreement factor R is improved up to 1.4×10^{-5}.

Finally the main result of the present work is to afford an unambiguous example of a strictly dinuclear (Gd, Cu) complex. The analysis of the magnetic data using a simple approach comprising only an isotropic exchange points to a ferromagnetic interaction which must be attributed to nothing but the Gd, Cu couple. The stabilization of the $S = 4$ state in $\mathrm{GdO_2Cu}$ systems has been related[4] to the coupling between the Gd(III)−Cu(II) ground configuration and the Gd(II)−Cu(III) charge transfer excited configuration, an electron being transferred from the singly occupied 3d copper orbital to an empty 5d gadolinium orbital. The corresponding J value has been estimated[4] at 4.8 cm^{-1} while the experimental values[1,2,4] extend from 1.2 to 7.4 cm^{-1}. A somewhat higher value of 11.4 cm^{-1} has been reported[8] for a complex $\mathrm{L'CuGd(NO_3)(H_2O)_3}$ [L′ being *N*,*N*′-bis(3-hydroxysalicylidene)-1,2-propanediamine], the structure of which has not been solved.

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Supporting Information Available: Tables giving details of the experimental X-ray diffraction study, atomic coordinates, thermal parameters, all bond lengths and angles, and least-squares planes calculations for $\mathrm{[(C_{20}H_{22}N_2O_4)CuGd(NO_3)_3]\ C_3H_6O}$ (11 pages). Ordering information is given on any current masthead page.

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