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# A General Route to Strictly Dinuclear Cu(II)/Ln(III) Complexes. Structural Determination and Magnetic Behavior of Two Cu(II)/Gd(III) Complexes

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Starting from a single precursor, bis(3-methoxysalicylaldehydato)copper (II), which contains an $O_4Cu$ chromophore, three routes to discrete dinuclear Cu(II)/Ln(III) complexes (Ln = Pr, Eu, Gd, Yb) are described. The pairs of chromophores occurring in the resulting complexes are either $O_4Cu/O_4Ln$ or $O_2N_2Cu/O_4Ln$, the coordination sphere of the Ln ions being completed, in both cases, with six oxygen atoms afforded by three nitrato ions. Two Cu/Gd complexes involving either two tridentate ligands (**2**) or one hexadentate ligand (**7**) have been structurally characterized. They crystallize in the monoclinic space groups $P2_1/n$ (No. 14) (**2**) and $P2_1/c$ (No. 14) (**7**). The cell parameters are $a = 9.7185(7)$ Å, $b = 16.7839(12)$ Å, $c = 14.8868(8)$ Å, $\beta = 97.445(5)°$, and $Z = 4$ (**2**) and $a = 9.7656(9)$ Å, $b = 19.889(2)$ Å, $c = 15.870(2)$ Å, $\beta = 95.512(9)°$, and $Z = 4$ (**7**) respectively. The magnetic properties of six Cu/Ln complexes have been determined. A quantitative analysis of the magnetic properties of the Cu/Gd complexes shows that the interaction is of the ferromagnetic type with a $J$ constant varying from 4.8 to 7.0 cm$^{-1}$. The decrease of the interaction parallels the variation of the dihedral angle between the two halves (OCuO and OGdO) of the bridging core.

## Introduction

In a recent Note[1] we described the structure and magnetic properties of a discrete (Cu/Gd) complex, $L^3CuGd(NO_3)_3$ **(6)** (cf. Figure 1). It was obtained by reacting $Gd(NO_3)_3$ with the preformed mononuclear species $L^3Cu$.[2] Owing to the increasing interest[3−11] given to the magnetic behavior of molecular complexes comprising simultaneously d and f transition metal ions, it seemed desirable to develop a general route allowing the nature of the d and f ions to be varied without destroying the strictly dinuclear nature of the resulting complexes. Hereafter, we present the first step toward that goal since we report on a process which, starting from a single mononuclear precursor $L^1_2Cu$, gives access to various dinuclear complexes comprising the Cu(II)/Gd(III), Cu(II)/Yb(III), Cu(II)/Eu(III), and Cu(II)/Pr(III) couples. Particular attention has been paid to the (Cu/Gd) complexes which display magnetic properties amenable to a rather simple analysis based on a spin-only Hamiltonian. Indeed Gd(III), with a $^8S_{7/2}$ single-ion ground state, does not possess a first-order orbital moment. Two complexes have been structurally characterized as discrete dinuclear (Cu/Gd) complexes and their magnetic properties determined.

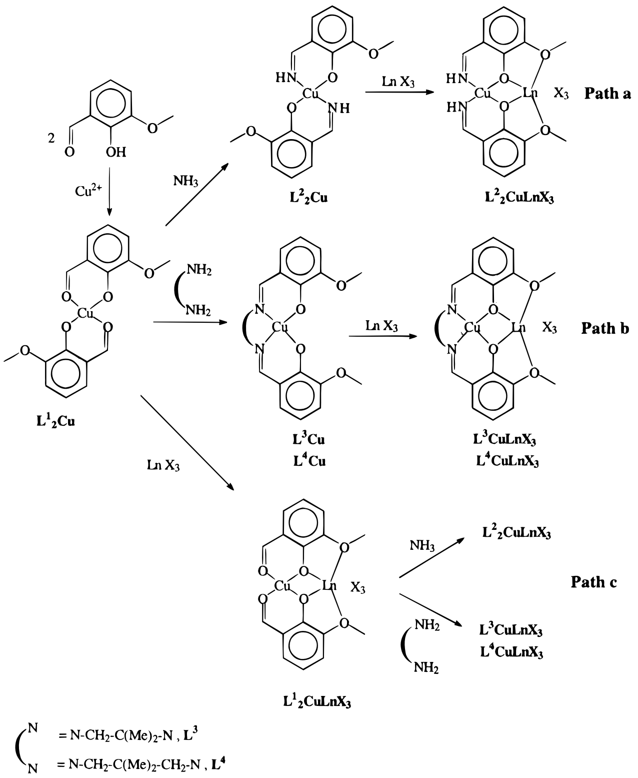

**Figure 1.** Schematic representation of the three synthetic pathways. Solvent ($H_2O$, MeOH, $OCMe_2$) is omitted.

## Experimental Section

**Bis(3-methoxysalicylaldehydato)copper(II), $L^1_2Cu$.** An ethanolic solution (40 mL) of 3-Methoxysalicylaldehyde (3.05 g, 20 mmol), Cu(OH)$_2$ (1 g, 10 mmol), and NaOH (0.4 g, 10 mmol) was boiled during

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15 min. After cooling, the solution gave a precipitate, which was filtered off and washed with ethanol and diethyl ether. Yield: 2.9 g, 80%. Anal. Calcd for $C_{16}H_{14}CuO_6$: C, 52.5; H, 3.8. Found: C, 52.5; H, 3.7.

**Path a: Bis(3-methoxysalicylaldiminato)copper(II), $L^2_2Cu$.** An ethanolic solution (40 mL) of $L^1_2Cu$ (3.7 g, 10 mmol) and an aqueous solution (30%) of ammonium hydroxide (5 mL) was boiled during 10 min. After cooling, the solution gave a precipitate, which was filtered off and washed with ethanol and diethyl ether. Yield: 3.1 g, 85%. Anal. Calcd for $C_{16}H_{16}CuN_2O_4{\cdot}2H_2O$: C, 48.0; H, 5.0; N, 7.0. Found: C, 48.0; H, 5.0; N, 6.8.

**[$L^2_2Cu(H_2O)Gd(NO_3)_3$].** Addition of a slight excess of $Ln(NO_3)_3{\cdot}6H_2O$ (1.2 mmol) (Ln stands for Gd (**2**), Yb (**3**), Eu (**4**), or Pr (**5**)) to $L^2_2Cu$ (0.40 g, 1 mmol) in acetone (20 mL) and warming induced the formation of a precipitate, which was filtered off and washed with acetone and diethyl ether. Yield: 0.56 g, 80%. Anal. Calcd for $C_{16}H_{16}CuGdN_5O_{13}{\cdot}H_2O$: C, 26.5; H, 2.5; N, 9.6. Found: C, 26.6; H, 2.2; N, 9.3. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 645$ (100), $[C_{16}H_{16}CuGdN_4O_{12}]^+$. A hot methanolic solution of $L^2_2Cu$ was added to a hot methanolic solution of $Gd(NO_3)_3{\cdot}6H_2O$ in a tube. Upon standing at room temperature, the mixture provided crystals, which were collected by filtration and air-dried. Microanalytical data confirm the presence of methanol instead of water and support the formula **[$L^2_2Cu(MeOH)Gd(NO_3)_3$] (2).** Anal. Calcd for $C_{16}H_{16}CuGdN_5O_{13}{\cdot}MeOH$: C, 27.6; H, 2.7; N, 9.5. Found: C, 27.3; H, 2.4; N, 9.2.

**[$L^2_2Cu(H_2O)Yb(NO_3)_3$] (3).** Yield: 0.63 g, 86%. Anal. Calcd for $C_{16}H_{16}CuYbN_5O_{13}{\cdot}H_2O$: C, 25.9; H, 2.4; N, 9.5. Found: C, 25.7; H, 2.2; N, 9.2. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 661$ (100), $[C_{16}H_{16}CuN_4O_{12}Yb]^+$.

**[$L^2_2Cu(H_2O)Eu(NO_3)_3$] (4).** Yield: 0.61 g, 85%. Anal. Calcd for $C_{16}H_{16}CuEuN_5O_{13}{\cdot}H_2O$: C, 26.7; H, 2.5; N, 9.7. Found: C, 27.0; H, 2.4; N, 9.7. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 640$ (100), $[C_{16}H_{16}CuEuN_4O_{12}]^+$.

**[$L^2_2Cu(H_2O)Pr(NO_3)_3$] (5).** Yield: 0.60 g, 85%. Anal. Calcd for $C_{16}H_{16}Cu_5PrNO_{13}{\cdot}H_2O$: C, 27.1; H, 2.5; N, 9.9. Found: C, 26.7; H, 2.1; N, 9.7. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 628$ (100), $[C_{16}H_{16}CuPrN_4O_{12}]^+$.

**Path b: (1,2-Bis((3-methoxysalicylidene)amino)-2-methylpropanato)copper(II), $L^3Cu$, and [$L^3CuGd(NO_3)_3$]$\cdot$OCMe$_2$ (6).** These complexes were obtained as previously described.[1]

**(1,3-Bis((3-methoxysalicylidene)amino)-2,2′-dimethylpropanato)-copper(II)], $L^4Cu$.** An ethanolic solution of $L^1_2Cu$ (3.7 g, 10 mmol) and 1,2-diamine-2,2′-dimethylpropane (1 g, 10 mmol) was boiled during 10 min. After cooling, the solution gave a precipitate, which was filtered off and washed with ethanol and diethyl ether. Yield: 3.5 g, 80%. Anal. Calcd for $C_{21}H_{24}CuN_2O_4{\cdot}2H_2O$: C, 53.9; H, 6.0; N, 6.0 Found: C, 54.1; H, 6.1; N, 5.9.

**[$L^4Cu(C_3H_6O)Gd(NO_3)_3$] (7).** Addition of a slight excess of $Gd(NO_3)_3{\cdot}6H_2O$ (0.5 g, 1.1 mmol) to $L^4Cu$ (0.47 g, 1 mmol) in acetone and warming induced the formation of a precipitate, which was filtered off and washed with acetone and diethyl ether. Yield: 0.64 g, 90%. Anal. Calcd for $C_{21}H_{24}CuGdN_5O_{13}{\cdot}C_3H_6O$: C, 34.6; H, 3.6; N, 8.5. Found: C, 34.6; H, 3.5; N, 8.2. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 713$ (100), $[C_{21}H_{24}CuGdN_4O_{10}]^+$.

A few milligrams each of $L^4Cu$ and $Gd(NO_3)_3$. $6H_2O$ were deposited in a tube with acetone. The solution kept at room temperature provided crystals, which were collected by filtration and air-dried.

**Path c: [$L^1_2CuGd(NO_3)_3$]$\cdot C_3H_6O$ (1).** Addition of $Gd(NO_3)_3{\cdot}6H_2O$ (0.5 g, 1.1 mmol) to 0.37 g of $L^1_2Cu$ (1 mmol) in acetone and warming, induced the formation of a precipitate, which was filtered off and washed with acetone and diethyl ether. Yield: 0.64 g, 90%. Anal. Calcd for $C_{16}H_{14}CuGdN_3O_{15}{\cdot}C_3H_6O$: C, 29.7; H, 2.6; N, 5.5. Found: C, 29.6; H, 2.5; N, 5.2. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): $m/z = 647$ (50), $[C_{16}H_{14}CuGdN_2O_{12}]^+$.

Compounds **2**, **6**, and **7** can be prepared by addition of the appropriate diamine (1,2-diamine-2-dimethylpropane or 1,2-diamine-2,2′-dimethylpropane) or an excess of ammonia to an ethanolic solution of $L^1_2CuGd(NO_3)_3$ (0.61 g, 1 mmol). After gentle boiling, the precipitates which appeared were filtered off and washed with ethanol and diethyl ether. Their microanalyses were identical to those of the similar complexes prepared by path b.

**Table 1.** Crystallographic Data for [$L^2_2Cu(MeOH)Gd(NO_3)_3$] (**2**) and [$L^4Cu(OCMe_2)Gd(NO_3)_3$] (**7**)

| | **2** | **7** |
|---|---|---|
| formula | $C_{17}H_{20}CuGdN_5O_{14}$ | $C_{24}H_{30}CuGdN_5O_{14}$ |
| mol wt | 739.17 | 833.33 |
| space group | $P2_1/n$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$, Å | 9.7185(7) | 9.7656(9) |
| $b$, Å | 16.7839(12) | 19.889(2) |
| $c$, Å | 14.8868(8) | 15.870(2) |
| $\beta$, deg | 97.445(5) | 95.512(9) |
| $V$, Å$^3$ | 2407.8(3) | 3068.1(5) |
| $Z$ | 4 | 4 |
| $F$(000) | 1448 | 1656 |
| $D_{\text{calcd}}$, g cm$^{-3}$ | 2.039 | 1.804 |
| $\lambda$, Å | 0.710 73 | 0.710 73 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 36.95 | 29.11 |
| data collct $T$, K | 293 | 293 |
| $R^a$ (all, obsd) | 0.033, 0.021 | 0.040, 0.026 |
| $R_w{}^b$ (all, obsd) | 0.060, 0.052 | 0.075, 0.065 |

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

**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[12] ($-279.3 \times 10^{-6}$ emu mol$^{-1}$ for **1**, $-259.5 \times 10^{-6}$ emu mol$^{-1}$ for **2**, $-257.5 \times 10^{-6}$ emu mol$^{-1}$ for **3**, $-295.5 \times 10^{-6}$ emu mol$^{-1}$ for **4**, $-299.5 \times 10^{-6}$ emu mol$^{-1}$ for **5**, and $-293.9 \times 10^{-6}$ emu mol$^{-1}$ for **7**). Positive FAB mass spectra were recorded with a Nermag R10-10 spectrometer using a 3-nitrobenzyl alcohol matrix.

**Single-Crystal X-ray Analysis.** Suitable crystals were obtained from methanol for **2** and acetone for **7**. Crystals were glued on a glass fiber. The accurate unit cell parameters for each compound were obtained by means of least-squares fits of 25 centered reflections. The data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å). A summary of the crystallographic data and data collection and refinement parameters is given in Table 1. Three standard reflections were monitored every 2 h and showed no significant variation over the data collection. Data were reduced in the usual way with the MolEN package.[13] An empirical absorption correction[14] was applied on the basis of $\psi$ scans. The structures of **2** and **7** were solved by the Patterson method[15] and refined by the full-matrix least-squares technique,[16] using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were introduced in calculations using a riding model, except those involved in hydrogen bonds in **2** (H bonded to N(1), N(2), and O(14) atoms), which were refined isotropically. Atomic scattering factors were taken from a standard source.[17] The fractional coordinates are given in Tables 2 (**2**) and 3 (**7**).

## Results and Discussion

The syntheses developed in the present work are schematized in Figure 1. In previous papers[18,19] we have shown that the

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**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 100$) for **2**

| | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Gd | 0.23421(1) | 0.75952(1) | 0.55871(1) | 2.61(1) |
| Cu | 0.58500(4) | 0.75351(2) | 0.53210(3) | 3.42(1) |
| O(1) | 0.4204(2) | 0.8185(1) | 0.5004(2) | 3.49(5) |
| O(2) | 0.4424(2) | 0.6822(1) | 0.5647(2) | 3.36(5) |
| O(3) | 0.1788(2) | 0.8433(1) | 0.4131(2) | 3.50(5) |
| O(4) | 0.2371(2) | 0.6202(1) | 0.6330(2) | 3.96(5) |
| O(5) | 0.1896(3) | 0.6619(2) | 0.4304(2) | 5.22(6) |
| O(6) | 0.0199(2) | 0.6834(2) | 0.5058(2) | 4.47(6) |
| O(7) | 0.0145(4) | 0.5815(2) | 0.4165(3) | 9.5(1) |
| O(8) | 0.2019(2) | 0.9025(1) | 0.5982(2) | 4.36(6) |
| O(9) | 0.0126(2) | 0.8384(1) | 0.5567(2) | 4.15(5) |
| O(10) | 0.0033(4) | 0.9614(2) | 0.5956(3) | 8.6(1) |
| O(11) | 0.1535(3) | 0.7685(2) | 0.7110(2) | 4.62(6) |
| O(12) | 0.3716(3) | 0.7858(2) | 0.7079(2) | 5.39(7) |
| O(13) | 0.2869(4) | 0.7935(3) | 0.8355(2) | 9.1(1) |
| O(14) | 0.6598(3) | 0.7763(2) | 0.6908(2) | 6.52(8) |
| N(1) | 0.7036(3) | 0.8406(2) | 0.5030(2) | 4.45(7) |
| N(2) | 0.7189(3) | 0.6680(2) | 0.5311(2) | 4.40(7) |
| N(3) | 0.0719(3) | 0.6397(2) | 0.4491(2) | 4.75(7) |
| N(4) | 0.0705(3) | 0.9028(2) | 0.5838(2) | 4.17(7) |
| N(5) | 0.2711(3) | 0.7829(2) | 0.7544(2) | 4.82(7) |
| C(1) | 0.4121(3) | 0.8783(2) | 0.4407(2) | 3.10(6) |
| C(2) | 0.2810(3) | 0.8953(2) | 0.3930(2) | 3.26(6) |
| C(3) | 0.2623(4) | 0.9576(2) | 0.3326(2) | 4.22(8) |
| C(4) | 0.3744(4) | 1.0045(2) | 0.3181(3) | 4.90(9) |
| C(5) | 0.5030(4) | 0.9890(2) | 0.3632(3) | 4.41(8) |
| C(6) | 0.5260(3) | 0.9243(2) | 0.4238(2) | 3.48(7) |
| C(7) | 0.6663(3) | 0.9054(2) | 0.4631(2) | 4.16(8) |
| C(8) | 0.0472(3) | 0.8474(2) | 0.3560(2) | 4.24(8) |
| C(9) | 0.4612(3) | 0.6079(2) | 0.5943(2) | 3.06(6) |
| C(10) | 0.3505(3) | 0.5710(2) | 0.6301(2) | 3.32(6) |
| C(11) | 0.3570(4) | 0.4932(2) | 0.6592(3) | 4.69(8) |
| C(12) | 0.4786(4) | 0.4491(2) | 0.6538(3) | 5.14(9) |
| C(13) | 0.5870(4) | 0.4834(2) | 0.6195(3) | 4.73(9) |
| C(14) | 0.5827(3) | 0.5636(2) | 0.5901(2) | 3.58(7) |
| C(15) | 0.7035(3) | 0.5961(2) | 0.5559(2) | 4.39(8) |
| C(16) | 0.1279(4) | 0.5899(2) | 0.6803(3) | 5.7(1) |
| C(17) | 0.7975(5) | 0.7791(3) | 0.7305(3) | 7.1(1) |

[a] Equivalent isotropic $U$ defined as $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

complexes $L^1{}_2M$ ($M^{2+}$ standing for $Ni^{2+}$ or $Cu^{2+}$) react with $NH_3$ to afford $L^2{}_2M$, which upon addition of alkali-metal ions yield dimetallic complexes of the $L^2{}_2MM'X$ type ($M'^{+}$ standing for $Na^+$, $Li^+$, or $K^+$ and $X^-$ for $ClO_4{}^-$ or $NO_3{}^-$). The key points of that process (path a in Figure 1) are the assembly of two imine molecules around $M^{2+}$ to form a trans-$MN_2O_2$ chromophore and then, in the presence of $Na^+$, $Li^+$, or $K^+$, the alteration of configuration from trans to cis with the concomitant creation of an external $O_4$ binding site. Subsequently we have demonstrated that this process may be used to prepare dimetallic (Cu/Ba) and (Cu/Ca) complexes.[20] Substituting $H_2NCH_2C(CH_3)_2NH_2$ for $NH_3$ (path b, in Figure 1) has led to the isolation of the first structurally characterized example of a discrete binuclear (Cu/Gd) complex.[1] Interestingly, we have found that the process of self-assembly and organization is not restricted to the complexes of the imino ligand $L^2H$ but may be applied to the complexes of the precursor $L^1H$. Then the resulting dinuclear species $L^1{}_2MLnX_3$ may be reacted with ammonia or a suitable diamine to obtain the $L^2{}_2MLnX_3$, $L^3MLnX_3$, and $L^4MLnX_3$ complexes (path c in Figure 1). Using these different processes we have prepared the following complexes: $L^1{}_2CuGdX_3$ (**1**), $L^2{}_2CuGdX_3$ (**2**), $L^2{}_2CuYbX_3$ (**3**), $L^2{}_2CuEuX_3$ (**4**), $L^2{}_2CuPrX_3$ (**5**), $L^3CuGdX_3$ (**6**), and $L^4CuGdX_3$ (**7**). In all cases, X stands for $NO_3$ and water or solvent molecules eventually present are omitted.

**Table 3.** Atomic Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 100$) for **7**

| | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Gd | 0.19861(2) | 0.07449(1) | 0.24674(1) | 3.29(1) |
| Cu | 0.28967(4) | 0.23681(2) | 0.32134(2) | 3.16(1) |
| O(1) | 0.1729(2) | 0.1933(1) | 0.2305(1) | 3.70(5) |
| O(2) | 0.2847(2) | 0.1444(1) | 0.3624(1) | 3.72(5) |
| O(3) | 0.0232(2) | 0.1139(1) | 0.1297(2) | 4.50(5) |
| O(4) | 0.2456(3) | 0.0158(1) | 0.3888(1) | 4.57(6) |
| O(5) | −0.0031(3) | 0.0036(1) | 0.2629(2) | 5.68(7) |
| O(6) | −0.0065(3) | 0.0994(2) | 0.3248(2) | 6.34(8) |
| O(7) | −0.1641(4) | 0.0261(2) | 0.3421(3) | 11.5(2) |
| O(8) | 0.1733(4) | −0.0064(2) | 0.1228(2) | 7.11(9) |
| O(9) | 0.2816(4) | −0.0462(2) | 0.2328(2) | 6.71(8) |
| O(10) | 0.2456(4) | −0.1089(2) | 0.1220(2) | 7.8(1) |
| O(11) | 0.4532(3) | 0.0707(2) | 0.2553(2) | 7.22(9) |
| O(12) | 0.3538(3) | 0.1108(2) | 0.1433(2) | 7.7(1) |
| O(13) | 0.5752(3) | 0.1106(2) | 0.1602(2) | 8.0(1) |
| O(14) | 0.5109(3) | 0.2444(2) | 0.2520(2) | 6.20(7) |
| N(1) | 0.2647(3) | 0.3261(1) | 0.2668(2) | 3.65(6) |
| N(2) | 0.3814(3) | 0.2693(1) | 0.4310(2) | 3.85(6) |
| N(3) | −0.0614(4) | 0.0431(2) | 0.3116(2) | 6.06(9) |
| N(4) | 0.2333(3) | −0.0554(2) | 0.1584(2) | 4.84(7) |
| N(5) | 0.4641(3) | 0.0977(2) | 0.1854(2) | 5.32(8) |
| C(1) | 0.1082(3) | 0.2219(2) | 0.1618(2) | 3.41(6) |
| C(2) | 0.0265(3) | 0.1803(2) | 0.1055(2) | 3.87(7) |
| C(3) | −0.0412(4) | 0.2060(2) | 0.0322(2) | 5.43(9) |
| C(4) | −0.0269(5) | 0.2733(2) | 0.0125(3) | 6.2(1) |
| C(5) | 0.0490(4) | 0.3151(2) | 0.0670(3) | 5.37(9) |
| C(6) | 0.1156(3) | 0.2898(2) | 0.1432(2) | 3.81(7) |
| C(7) | 0.1912(3) | 0.3376(2) | 0.1973(2) | 4.00(7) |
| C(8) | −0.0839(4) | 0.0736(2) | 0.0855(3) | 6.2(1) |
| C(9) | 0.3373(4) | 0.3851(2) | 0.3034(2) | 4.66(8) |
| C(10) | 0.3322(4) | 0.3912(2) | 0.3979(2) | 4.38(8) |
| C(11) | 0.4269(4) | 0.3398(2) | 0.4428(2) | 5.17(9) |
| C(12) | 0.3911(5) | 0.4601(2) | 0.4251(3) | 6.2(1) |
| C(13) | 0.1861(4) | 0.3846(2) | 0.4230(3) | 6.4(1) |
| C(14) | 0.3289(3) | 0.1205(2) | 0.4388(2) | 3.54(6) |
| C(15) | 0.3105(4) | 0.0520(2) | 0.4556(2) | 3.90(7) |
| C(16) | 0.3571(4) | 0.0239(2) | 0.5324(2) | 4.77(8) |
| C(17) | 0.4214(4) | 0.0638(2) | 0.5959(2) | 5.27(9) |
| C(18) | 0.4368(4) | 0.1309(2) | 0.5823(2) | 5.16(9) |
| C(19) | 0.3897(3) | 0.1609(2) | 0.5042(2) | 3.85(7) |
| C(20) | 0.4095(4) | 0.2316(2) | 0.4963(2) | 4.27(7) |
| C(21) | 0.2011(5) | −0.0509(2) | 0.4086(3) | 6.2(1) |
| C(22) | 0.6293(4) | 0.2312(2) | 0.2737(3) | 6.6(1) |
| C(23) | 0.6672(5) | 0.1900(3) | 0.3514(4) | 9.7(2) |
| C(24) | 0.7431(6) | 0.2558(4) | 0.2264(6) | 12.6(3) |

[a] Equivalent isotropic $U$ defined as $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structures of **2** and **7** have been determined by X-ray diffraction while that of complex **6** has been previously reported.[1]

The four $L^2{}_2CuLnX_3$ complexes display very similar mass spectra ($FAB^+$). In every case, we observe signals corresponding to the $[L^2{}_2CuLn(NO_3)_2]^+$ ions. They appear at $m/z = 645$ (Ln = Gd), 661 (Ln = Yb), 640 (Ln = Eu), and 628 (Ln = Pr), respectively. A second signal is observed at $m/z = 583$, 599, 578, and 566 for complexes **2**, **3**, **4**, and **5**, respectively. Seemingly, they correspond to $[L^2{}_2CuLn(NO_3)]$ ions, suggesting a change of the oxidation state from $Ln^{3+}$ to $Ln^{2+}$. A different spectral pattern characterizes complex **1** with signals at $m/z =$ 647, 388 and 366. They are attributable to $[L^1{}_2CuLn(NO_3)_2]^+$, $[L^1{}_2CuNa]^+$, and $[L^1{}_2CuH]^+$, respectively. However, it may be underlined that, for these five complexes, the most intense signal corresponds to the $[L^i{}_2CuLn(NO_3)_2]^+$ ion (i = 1, 2). Complexes **6** and **7** give similar spectra.[1]

The infrared spectra of **2**, **3**, **4**, and **5** are almost superimposable in the 400−3500 $cm^{-1}$ range. The bands characteristic of the coordinated ligand ($\nu_{CC}$, $\nu_{CN}$, $\nu_{CO}$) are observed at 1618($\pm$1) and 1560($\pm$3) $cm^{-1}$. Owing to the large electronic

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(20) Costes, J. P.; Laurent, J. P.; Chabert, P.; Commenges, G.; Dahan, F. *Inorg. Chem.* **1997**, *36*, 656.

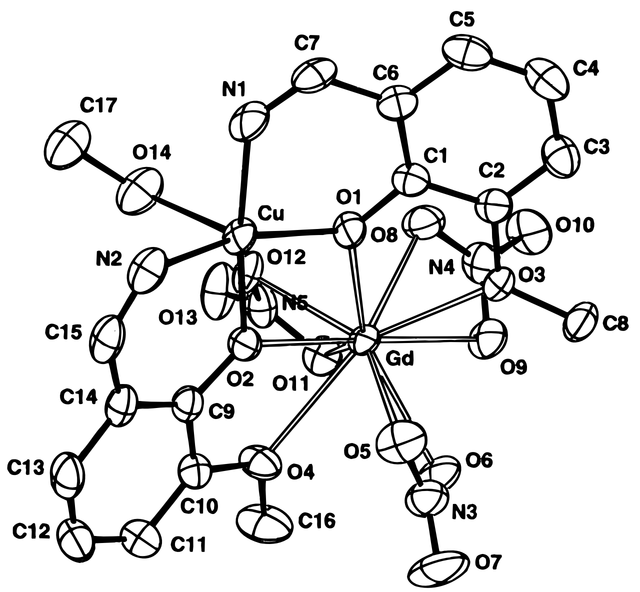

**Figure 2.** ORTEP plot for [$L^2{}_2Cu(MeOH)Gd(NO_3)_3$] (**2**) with ellipsoids drawn at the 50% probability level.

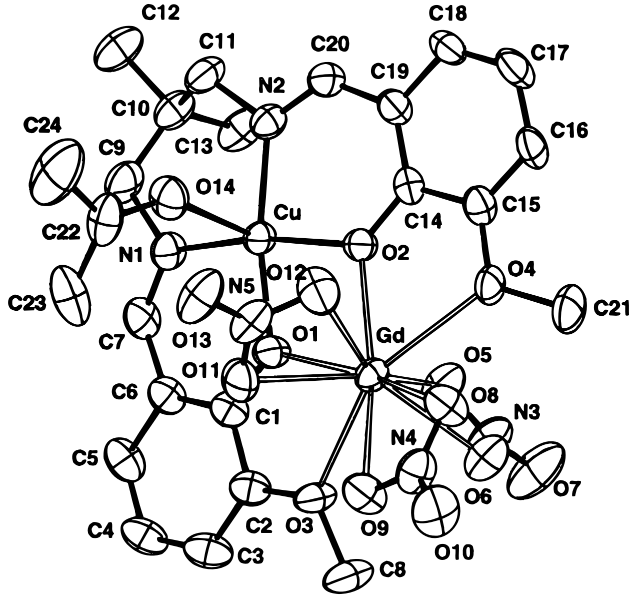

**Figure 3.** ORTEP plot for [$L^4Cu(C_3H_6O)Gd(NO_3)_3$] (**7**) with ellipsoids drawn at the 50% probability level.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for [$L^2{}_2Cu(MeOH)Gd(NO_3)_3$] (**2**) and [$L^4Cu(OCMe_2)Gd(NO_3)_3$] (**7**), Compared with Those for [$L^3CuGd(NO_3)_3$] (**6**)[1]

| | **2** | **7** | **6**[a] |
|---|---|---|---|
| Cu–O(1) | 1.943(2) | 1.953(2) | 1.879(5) |
| Cu–O(2) | 1.940(2) | 1.952(2) | 1.904(5) |
| Cu–N(1) | 1.944(3) | 1.980(3) | 1.942(6) |
| Cu–N(2) | 1.938(3) | 1.987(3) | 1.918(7) |
| Gd–O(1) | 2.327(2) | 2.387(2) | 2.398(5) |
| Gd–O(2) | 2.395(2) | 2.390(2) | 2.337(5) |
| Gd–O(3)Me | 2.581(2) | 2.528(2) | 2.626(5) |
| Gd–O(4)Me | 2.586(2) | 2.541(2) | 2.614(5) |
| Gd–O(nitrato)[b] | 2.483(2)–2.525(2) | 2.448(3)–2.550(3) | 2.452(5)–2.529(5) |
| Gd–O(1)–Cu | 109.05(9) | 108.15(9) | 105.9(2) |
| Gd–O(2)–Cu | 106.48(9) | 108.05(9) | 107.4(2) |
| O(1)–Cu–O(2) | 79.31(8) | 78.29(9) | 81.8(2) |
| O(1)–Gd–O(2) | 63.29(7) | 62.14(7) | 63.0(2) |
| *a*[c] | 12.5(2) | 16.6(2) | 12.9(2) |

[a] Cf. ref 1. [b] Minimum and maximum values. [c] Dihedral angle between CuO(1)O(2) and GdO(1)O(2) planes.

delocalization occurring in these complexes, any absorption cannot be considered in isolation and attributed with certainty. Two bands at 1464(±2) and 1308(±1) $cm^{-1}$ are attributable to bidentate $NO_3$ ions. Finally, the complexes **3**, **4**, and **5**, like their counterpart **2**, may be considered as genuine dinuclear (Cu/Ln) entities.

**Description of the Structures of 2 and 7.** In both cases, the unit cell contains four discrete entities, [$L^2{}_2Cu(MeOH)Gd(NO_3)_3$] and [$L^4Cu(OCMe_2)Gd(NO_3)_3$], respectively. Views of these dinuclear units are represented in Figures 2 and 3 with significant bond distances and angles in Table 4.

At first sight, the two structures offer great similitudes. Indeed, in each unit, the following four features are noted:

(i) The central region is occupied by Cu(II) and Gd(III) ions which are bridged one to the other by two phenolato oxygen atoms from the ligand $L^2$ (or $L^4$) and with copper gadolinium separations of 3.4842(3) and 3.5231(4) Å, respectively.

(ii) The copper ion adopts a square-based 4 + 1 coordination mode; the equatorial $N_2O_2$ donors being afforded by $L^2$ (or $L^4$) while the axial position is occupied by an oxygen atom from a solvent molecule.

(iii) The gadolinium ion is decacoordinated. In addition to the two phenolate oxygens, the rare earth ion completes its environment with two oxygens from the OMe side arms and six oxygens coming from the three bidentate nitrato ions.

(iv) The separations between metal ions belonging to neighboring molecules are large: the Cu···Cu separations are equal to 8.3461(1) and 7.9522(1) Å for **2** and **7**, respectively while values of 8.3514(1) and 8.9063(3) Å are observed for Gd···Gd and values of 6.2711(3) and 7.8489(4) Å for Cu···Gd. They preclude any significant intermolecular interaction of a magnetic nature. This conclusion is not questioned by the presence of two intermolecular hydrogen bonds in the structure of **2**. Indeed polyatomic pathways, such as Cu–N(1)–H(1)···O(9′)–Gd and Cu–N(2)–H(2)···O(6′)–Gd are unable to support any noticeable magnetic interaction between the metal ions.

These general features have already been examined for complex **6**.[1] However, a more acute inspection of the structural data points to several significant differences between **2**, **6**, and **7**. These differences primarily concern the $CuO_2Gd$ core. They are quoted in Table 4.

The two Gd–O(i)–Cu angles (*i* = 1, 2), the two Gd–O(*i*) bond lengths, and the two Cu–O(*i*) bond lengths have almost identical values in complex **7** while they differ in **2** and **6**. Otherwise the related Cu–O(*i*), Gd–O(*i*), and Gd–Cu distances are larger in **7** than in **2** and **6**.

In the three complexes, the four atoms of the bridging entity are not exactly coplanar, leading to a roof-shaped $CuO_2Gd$ core. Interestingly, the dihedral angle between the planes CuO(1)O(2) and GdO(1)O(2) is larger in **7**, with a value of 16.6(2)°, than in **6** and **2**, with values of 12.9(2)° and 12.5(2)°, respectively.

In **6** and **7**, the copper environment can be considered as square-planar since the four equatorial donor atoms are displaced from the mean plane by less than 0.03 Å in **6** and 0.05 Å in **7**. Many important displacements from 0.151(3) to 0.182(2) Å are observed for **2**. In that complex, the atoms O(1), N(1), C(1) to C(7) on the one hand and O(2), N(2), C(9) to C(15) on the other hand are almost coplanar but the angle between the two planes is equal to 32.42(8)°, pointing out a strong deformation of the copper environment.

In accordance with the bidentate nature of the $NO_3$ ligands, we note, in every case, that two N–O bond lengths are nearly equal and longer than the third one.

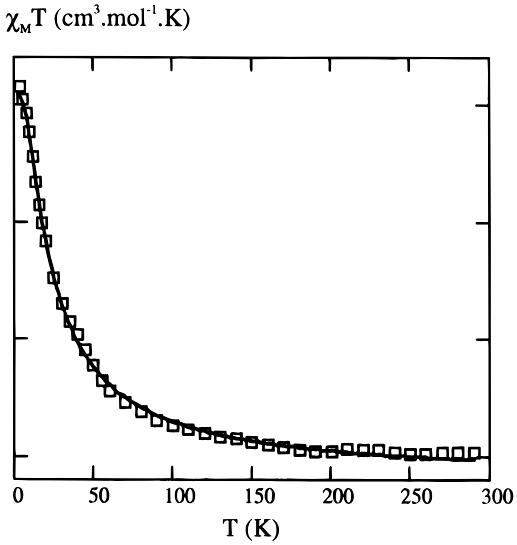

**Figure 4.** Thermal dependence of $\chi_M T$ for $[L^4Cu(C_3H_6O)Gd(NO_3)_3]$ (**7**) at 0.1 T. The full line corresponds to the best data fit (cf. text).

**Table 5.** Magnetic Data for Cu/Gd Complexes **1**, **2**, **6**, and **7**

| | $J$ (cm$^{-1}$) | $g_{Cu}$ | $g_{Gd}$ | $R^a$ |
|---|---|---|---|---|
| **1** | 5.0 | 1.98 | 2.0 | $1.2 \times 10^{-5}$ |
| **2** | 6.8 | 1.99 | 2.0 | $1.3 \times 10^{-5}$ |
| **6**$^b$ | 7.2 | 2.02 | 1.99 | $1.6 \times 10^{-5}$ |
| **7** | 4.8 | 1.96 | 2.0 | $1.9 \times 10^{-5}$ |

[a] $R = \Sigma(\chi_{obs}T - \chi_{calc}T)^2/\Sigma(\chi_{obs}T)^2$. [b] Data taken from ref 1.

**Magnetic Properties of 1, 2, and 7.** The temperature dependence of the magnetic susceptibility of complex **7** in the range 2−300 K is shown in Figure 4 in the $\chi_M T$ vs $T$ form. At 300 K, $\chi_M T$ is equal to 8.5 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 and then at 8 K to reach a plateau of 10.1 cm$^3$ K mol$^{-1}$. That value 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) ($S = {}^1/_2$) and assuming that $g_{Gd} = g_{Cu} = 2.0$. Very similar data have been obtained for **1** and **2**.

A quantitative analysis can be performed on the basis of a spin only expression derived from a spin Hamiltonian $H = -JS_{Cu}\cdot S_{Gd}$. Keeping under consideration that the two low-lying levels $E_{(4)} = 0$ and $E_{(3)} = 4J$ may have different $g$-values,[21] $g_4 = (7g_{Gd} + g_{Cu})/8$ and $g_3 = (9g_{Gd} - g_{Cu})/8$, the experimental data are fitted using the expression[21]

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

The resulting values of the parameters $J$, $g_{Cu}$, and $g_{Gd}$ and those of the agreement factor $R = \Sigma(\chi_{obs}T - \chi_{cal}T)^2/\Sigma(\chi_{obs}T)^2$ are quoted in Table 5.

For the three structurally characterized complexes (**2**, **6**, and **7**) there is no doubt that the observed ferromagnetic behavior is an intrinsic property of the (Cu/Gd) couple. The stabilization of the $S = 4$ state in $GdO_2Cu$ systems has been attributed[6] to the coupling between the Gd(III)−Cu(II) ground configuration and the Gd(II)−Cu(III) excited configuration in which an electron has been transferred from the singly occupied 3d copper orbital to an empty 5d gadolinium orbital. The corresponding $J$ value has been estimated at 4.8 cm$^{-1}$ while the experimental values related to polynuclear complexes[3,4,6] extend from 1.2 to 7.4 cm$^{-1}$. We note that complexes **2** and **6** display the same $J$ value (≈7.0 cm$^{-1}$), which is slightly but significantly larger than the value (4.8 cm$^{-1}$) observed for **7**. Interestingly the variation of $J$ parallels that of the dihedral angle $a$ between the two halves (OCuO and OGdO) of the bridging core (cf. Table 4). A more pertinent example of the influence of $a$ has been recently afforded.[11] For that complex an important bending of the $GdO_2$-Cu core ($a \approx 40°$) results in a depressed magnetic interaction ($J = 1.42$ cm$^{-1}$).

As for complexes **3** and **5**, the ground state of the related Ln(III) has a first-order angular momentum so that the magnetic properties of the (Cu/Ln) couples are not amenable to a simple analysis based on a spin Hamiltonian comprising only isotropic exchange. In the case of complex **4**, the first-order magnetic moment of Eu(III) is 0 due to the nonmagnetic ground term ($^7F_0$). However, the excited terms $^7F_1$ and $^7F_2$ are very close to $^7F_0$ and contribute appreciably to the magnetic behavior yielding a moment of 3.5 $\mu_B$ at room temperature. Additional difficulties may arise from the crystal field effects and the connected magnetic anisotropy.[22] For the three complexes, $(\chi_M T)_{exp}$ decreases on lowering the temperature. Indeed, we observe at 300, 100, and 2 K, respectively, $(\chi_M T)_{exp}$ values of 2.71, 2.19, and 0.76 cm$^3$ K mol$^{-1}$ for **3**, 1.80, 1.07, and 0.48 cm$^3$ K mol$^{-1}$ for **4**, and 2.03, 1.58, and 0.37 cm$^3$ K mol$^{-1}$ for **5**. In the simplest approximation, these experimental values may be compared to the sum of the susceptibilities attributable to Cu(II) and Ln(III), the susceptibility of Ln(III) being that of the free-ion ground term (**3** and **5**) or deduced from the two low-lying excited terms (**4**).[22] The resulting values are 2.90, 1.91, and 1.81 cm$^3$ K mol$^{-1}$ for **3**, **4**, and **5**, respectively. Large discrepancies exist between the two sets of values. They are attributable to crystal field effects and/or the occurrence of an interaction between the Cu(II) and the Ln(III) ions so that, in their present state of analysis, the experimental data do not provide any firm information on the coupling between the two metal ions of these (Cu/Ln) pairs.

In our opinion the main interest of this paper is the description of simple synthetic pathways to strictly dinuclear (Cu/Ln) complexes in which the nature of the lanthanide ion may be largely varied, including ions with a first-order angular momentum in the ground state. One process is particularly attractive since it involves one precursor which is itself a genuine dinuclear (Cu/Ln) complex. A quantitative analysis of the magnetic properties of the (Cu/Gd) complexes shows that, in the four available cases, the interaction is of the ferromagnetic type with a $J$ constant varying from 4.8 to 7.0 cm$^{-1}$.

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**Supporting Information Available:** Tables of full experimental details (Tables S0.2 and S0.7), atomic coordinates (Tables S1.2 and S1.7), hydrogen parameters (Tables S2.2 and S2.7), anisotropic thermal parameters (Tables S3.2 and S3.7), bond distances and angles (Tables S4.2 and S4.7), and least-squares plane equations (Tables S5.2 and S5.7) (22 pages). Ordering information is given on nay current masthead page.

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