Inorg. Chem. **2000,** *39,* 169−173 **169**

Is Ferromagnetism an Intrinsic Property of the Cu^{II}/Gd^{III} Couple? 1. Structures and Magnetic Properties of Two Novel Dinuclear Complexes with a μ-Phenolato−μ-Oximato (Cu,Gd) Core

Jean-Pierre Costes,*,† Françoise Dahan, Arnaud Dupuis, and Jean-Pierre Laurent

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, liée par conventions à l'Université
Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 route de Narbonne,
31077 Toulouse Cedex, France

Received July 21, 1999

Two original dinuclear (Cu^{II},Gd^{III}) complexes (**1** and **2**) deriving from polydentate nonsymmetrical Schiff base ligands L^iH_2 have been prepared. Formally they differ by the length of the diamino chain. They crystallize in the orthorhombic *Pbca* (No. 61) (**1**) and in the monoclinic $P2_1/n$ (No. 14) (**2**) space groups. The cell parameters are $a = 12.6295(7)$ Å, $b = 20.7894(9)$ Å, $c = 18.3301(13)$ Å, and $Z = 8$ for **1** and $a = 12.7246(16)$ Å, $b = 13.5691(17)$ Å, $c = 14.5310(19)$ Å, $\beta = 94.629(16)°$, and $Z = 4$ for **2**. These structural studies show that in both complexes the Cu^{II} and Gd^{III} ions are doubly bridged by a phenolato oxygen atom and an oximato (N−O) pair. The bridging network is not planar. The more important distortions are observed for the complex having the larger diamino chain. Unexpectedly the latter complex presents an antiferromagnetic interaction, but the related J value is small ($J \cong -0.49$ cm^{-1}). In the former complex the interaction is ferromagnetic ($J \cong 3.5$ cm^{-1}) as it is for complexes containing (CuO_2Gd) bridging cores which yield J values varying from 1.4 to 10.1 cm^{-1}.

Introduction

Ferromagnetic coupling between Cu^{2+} and Gd^{3+} ions was first observed in 1985 in a trinuclear (Cu_2, Gd) complex.[1] Since that time several polynuclear and, recently, strictly dinuclear (Cu, Gd) complexes have been reported.[2−13] Their study has led to the more or less implied conclusion that ferromagnetism is an intrinsic property of the Cu−Gd pair. Reexamination of the available data suggests that such a generalization is questionable since all the yet investigated complexes have very similar bridging networks of the (CuO_2Gd) type, the two oxygen donors being identical and afforded by either phenolato, acetonato, or acetato groups. It may be noted that ferromagnetism is also observed for a polynuclear complex with oxamato groups bridging Cu^{II} and Gd^{III} ions.[5] In search of new bridging cores, we succeeded in obtaining two original dinuclear (Cu, Gd) complexes in which the metallic ions are unsymmetrically bridged by a phenolato oxygen and an oximato (N−O) group (Figure 1). The two complexes essentially differ by the nature of the diamino chain. Preliminary results show that they are representative of two new families of (Cu−Gd) complexes. The present paper is devoted to the preparation, characterization

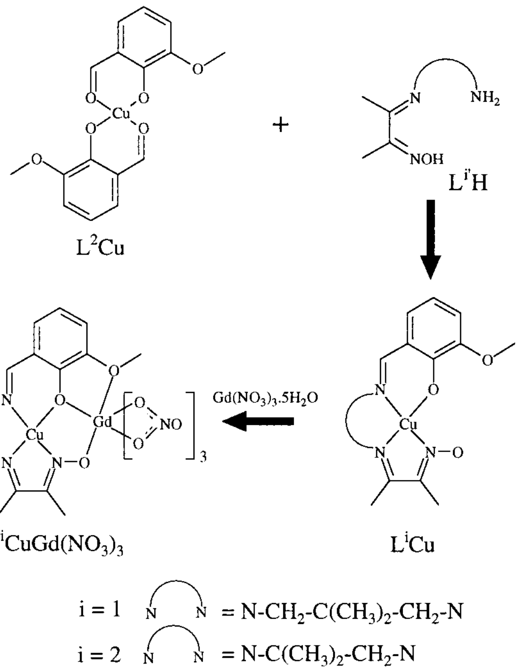

Figure 1. Schematic representation of the synthetic pathway.

---

† Tel: 33 (0)5 61 33 31 52. Fax: 33 (0)5 61 33 30 03. E-mail: costes@lcc-toulouse.fr.

(1) Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 8128.

(2) Bencini, A.; Benelli, C.; Caneschi, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 5, 572.

(3) Matsumoto, N.; Sakamoto, M.; Tamaki, H.; Okawa, H.; Kida, S. *Chem Lett.* **1990**, 853.

(4) Sakamoto, M.; Hashimura, M.; Matsuki, K.; Matsumoto, N.; Inoue, K.; Okawa, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3639.

(5) Guillou, O.; Bergerat, P.; Kahn, O.; Bakalbassis, E.; Boubekeur, K.; Batail, P.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 110.

(6) Andruh, M.; Ramade, I.; Codjovi, E.; Guillou, O.; Kahn, O.; Trombe, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 1822.

(7) Blake, A. J.; Milne, P. E. Y.; Thornton, P.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1139.

(8) Bouayad, A.; Brouca-Cabarrecq, C.; Trombe, J. C.; Gleizes, A. *Inorg. Chim. Acta* **1992**, *195*, 193.

(9) Benelli, C., Blake, A. J.; Milne, P. E. Y.; Rawson, J. M.; Winpenny, R. E. P. *Chem. Eur. J.* **1995**, *1*, 614.

(10) Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *Inorg. Chem.* **1996**, *35*, 2400.

(11) Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *Inorg. Chem.* **1997**, *36*, 3429.

(12) Ramade, I.; Kahn, O.; Jeannin, Y.; Robert, F. *Inorg. Chem.* **1997**, *36*, 930.

(13) Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *New J. Chem.* **1998**, 1525.

10.1021/ic990864p CCC: $19.00 © 2000 American Chemical Society
Published on Web 12/28/1999

including structural determination, and magnetic properties of both species.

Experimental Section

Cu(SalOMe)$_2$[11] complexes and L$^{1'}$H and L$^{2'}$H ligands[14] were obtained as previously described. As the experimental procedures are quite similar, we will only describe the preparation of the L^{1}Cu·H$_2$O mononuclear precursor and of a 3d−4f complex while analytical results and yields will be reported in each case.

L^{1}Cu·H$_2$O. A mixture of Cu(SalOMe)$_2$ (0.73 g, 2 × 10^{-3} mol) and L$^{1'}$H ligand (0.37 g, 2 × 10^{-3} mol) in acetone (20 mL) was heated for 10 min and then left to cool with stirring. The black precipitate which appeared was filtered off and washed with acetone and diethyl ether. Yield: 0.65 g (60%). Anal. Calcd for $C_{17}H_{25}CuN_3O_4$: C, 51.2; H, 6.3; N, 10.5. Found: C, 51.1; H, 6.4; N, 10.5. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m*/*z* = 381, [L^{1}Cu + 1]$^+$.

L^{1}CuGd(NO$_3$)$_3$ (1). A mixture of L^{1}Cu·H$_2$O (0.19 g, 5 × 10^{-4} mol) and Gd(NO$_3$)$_3$·5H$_2$O (0.22 g, 5 × 10^{-4} mol) in acetone (20 mL) was heated for 10 min and then left to cool with stirring. The reddish precipitate which appeared was filtered off and washed with acetone and diethyl ether. Yield: 0.35 g (78%). Anal. Calcd for $C_{17}H_{23}CuGdN_6O_{12}$: C, 28.2; H, 3.2; N, 11.6. Found: C, 28.4; H, 3.2; N, 11.3. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m*/*z* = 662, [L^{1}CuGd(NO$_3$)$_2$]$^+$.

L^{2}Cu·H$_2$O. Yield: 78%. Anal. Calcd for $C_{16}H_{23}CuN_3O_4$: C, 49.9; H, 6.0; N, 10.9. Found: C, 49.9; H, 6.0; N, 10.9. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m*/*z* = 367, [L^{2}Cu + 1]$^+$.

L^{2}CuGd(NO$_3$)$_3$·2H$_2$O (2). Yield: 80%. Anal. Calcd for $C_{16}H_{25}CuGdN_6O_{14}$: C, 25.8; H, 3.4; N, 11.3. Found: C, 25.6; H, 3.4; N, 11.2. Mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m*/*z* = 648, [L^{2}CuGd(NO$_3$)$_2$]$^+$.

A few milligrams each of L^{1}Cu·H$_2$O or L^{2}Cu·H$_2$O and of Gd(NO$_3$)$_3$·6H$_2$O were deposited in a tube with acetone as solvant. The solutions kept at room temperature provided crystals suitable for a X-ray structure determination study. They were collected by filtration and air-dried.

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 Microanalyze du Laboratoire de Chimie de Coordination, Toulouse, France (C, H, N). 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. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.[15] Positive FAB mass spectra were recorded in dmf as a solvent and 3-nitrobenzyl alcohol matrix with a Nermag R10-10 spectrometer.

Single-Crystal X-ray Analysis. Suitable crystals were obtained from acetone for **1** and **2**. 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 Kα radiation (λ = 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.[16] Numerical absorption corrections[17] for **1** and absorption corrections[18] from ψ scans for **2** were applied. The structures of **1** and **2** were solved by the Patterson method[19] and refined by the full-matrix least-squares technique,[20] using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were introduced in calculations using a riding model, except those of the water molecules in **2** (H bonded to O(4) and O(5) atoms), which were refined isotropically. Atomic scattering factors were taken from a standard source.[21] The fractional coordinates are given in Tables 2 for **1** and 3 for **2**.

Table 1. Crystallographic Data for L^{1}CuGd(NO$_3$)$_3$ (**1**) and L^{2}Cu(H$_2$O)Gd(H$_2$O)(NO$_3$)$_3$ (**2**)

	1	**2**
chem formula	$C_{17}H_{23}CuGdN_6O_{12}$	$C_{16}H_{25}CuGdN_6O_{14}$
fw	724.20	746.21
space group	*Pbca* (No. 61)	*P*2$_1$/*n* (No. 14)
a, Å	12.6295(7)	12.7246(16)
b, Å	20.7874(9)	13.5691(17)
c, Å	18.3301(13)	14.5310(19)
β, deg		94.629(16)
V, Å^3	4812.3(5)	2500.8(6)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.999	1.982
λ, Å	0.710 73	0.710 73
T, K	293 ± 2	293 ± 2
μ(Mo Kα), cm^{-1}	35.76	35.59
R^a obs, all	0.0264, 0.0573	0.0279, 0.0364
w*R*^{b} obs, all	0.0535, 0.0678	0.0578, 0.0608

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

Results and Discussion

The synthetic route to complexes **1** and **2** is schematized in Figure 1. The cornerstones of the process are the complexes L^{i}Cu.[22] They are readily obtained by reacting the mononuclear complex L$_2$Cu (LH = 3-methoxysalicylaldehyde) with the polyfunctional ligands L$^{i'}$H (1-(2,5,5,-trimethylhexahydro-2-pyrimidinyl)-1-ethanone oxime for L$^{1'}$H and 1-(2,4,4,-trimethylhexahydro-2-imidazolidinyl)-1-ethanone oxime for L$^{2'}$H), which have been previously described.[14] They are isolated in their deprotonated form. The affinity of Cu^{II} for nitrogen donors forces L^i to adopt such a configuration that Cu^{II} is surrounded by a (N$_3$O) chromophore while an outer coordination site (O$_3$) becomes available for a lanthanide ion. The formulation of the complexes resulting from reaction with gadolinium salts, [L^{i}CuGd(NO$_3$)$_3$·*x*H$_2$O], is deduced from analytical data and further supported by mass spectroscopy [FAB$^+$]. Indeed the spectrum of compound **1** displays two signals at *m*/*z* = 381 (100%) and 662 (68%). They are respectively attributable to [L^{1}Cu + 1]$^+$ and [L^{1}CuGd(NO$_3$)$_2$]$^+$, with isotopic patterns perfectly consistent with the attributions. In the case of **2**, the [L^{2}CuGd(NO$_3$)$_2$]$^+$ cation at *m*/*z* = 648 (100%) is present, thus confirming the expected formulation with a 1/1 Cu/Gd ratio.

Structural Study of L^{1}CuGd(NO$_3$)$_3$ (1) and L^{2}Cu(H$_2$O)Gd(H$_2$O)(NO$_3$)$_3$ (2). ORTEP views of both structures are reported in Figures 2 and 3, respectively. Relevant bond distances and angles are quoted in Table 4.

In both complexes, the central part of the structure is occupied by the Cu^{II} and Gd ^{III} ions connected by a double bridge involving, on one hand, a phenolato oxygen and, on the other hand, nitrogen and oxygen atoms of a deprotonated oxime function. The bridging networks Cu(O, N−O)Gd are not planar, and the deviations from planarity are different in **1** and **2**. The

---

(14) Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *New J. Chem.* **1997**, *21*, 1211.

(15) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5.

(16) Fair, C. K. *MolEN. Structure Solution Procedures*; Enraf-Nonius: Delft, Holland, 1990.

(17) Coppens, P.; Leiserowitz, L.; Rabinovitch, D. *Acta Crystallogr*. **1965**, *18*, 1035.

(18) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

(19) Sheldrick, G. M. *SHELXS-97. Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1990.

(20) Sheldrick, G. M. *SHELXL-97. Program for the refinement of crystal structures from diffraction data*; University of Göttingen: Göttingen, Germany, 1997.

(21) *(21)International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

(22) Similar ligands[23] have been recently used to prepare dinuclear 3d complexes with a (O, N−O) bridging core.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 100) for [$L^1CuGd(NO_3)_3$] (**1**)

	x	*y*	*z*	U_{eq}[a]
Gd	0.30300(2)	0.29615(1)	0.48740(1)	2.77(1)
Cu	0.48472(4)	0.34973(2)	0.62967(3)	2.95(1)
O(1)	0.3762(2)	0.3801(1)	0.5612(1)	2.90(6)
O(2)	0.1887(2)	0.4047(1)	0.5126(2)	3.93(7)
O(3)	0.3223(2)	0.2535(2)	0.6016(2)	4.35(8)
O(4)	0.1198(3)	0.2751(2)	0.5410(2)	4.94(8)
O(5)	0.1553(3)	0.2120(2)	0.4537(2)	6.0(1)
O(6)	0.0082(2)	0.2001(2)	0.5117(2)	5.8(1)
O(7)	0.1911(3)	0.3310(2)	0.3824(2)	4.81(8)
O(8)	0.3422(3)	0.3788(2)	0.3956(2)	4.63(8)
O(9)	0.2314(4)	0.4122(2)	0.3133(2)	7.7(1)
O(10)	0.3774(3)	0.1868(2)	0.4748(2)	5.29(9)
O(11)	0.3637(3)	0.2403(2)	0.3755(2)	5.78(9)
O(12)	0.4333(4)	0.1451(2)	0.3739(3)	9.1(2)
N(1)	0.5635(3)	0.4290(2)	0.6244(2)	3.06(7)
N(2)	0.5702(3)	0.3106(2)	0.7098(2)	3.51(8)
N(3)	0.4077(3)	0.2691(2)	0.6408(2)	3.35(8)
N(4)	0.0925(3)	0.2288(2)	0.5023(2)	3.57(8)
N(5)	0.2544(4)	0.3751(2)	0.3622(2)	4.6(1)
N(6)	0.3928(3)	0.1895(2)	0.4068(3)	5.4(1)
C(1)	0.3501(3)	0.4424(2)	0.5563(2)	2.57(8)
C(2)	0.2486(3)	0.4583(2)	0.5305(2)	3.00(8)
C(3)	0.2161(4)	0.5212(2)	0.5264(3)	4.3(1)
C(4)	0.2834(4)	0.5705(2)	0.5469(3)	4.6(1)
C(5)	0.3826(4)	0.5564(2)	0.5708(3)	4.2(1)
C(6)	0.4179(3)	0.4925(2)	0.5766(2)	3.00(8)
C(7)	0.5240(3)	0.4819(2)	0.6037(2)	3.31(9)
C(8)	0.0814(4)	0.4178(2)	0.4905(3)	5.5(1)
C(9)	0.6731(3)	0.4292(2)	0.6519(2)	3.6(1)
C(10)	0.6788(3)	0.4108(2)	0.7330(2)	3.8(1)
C(11)	0.6664(4)	0.3376(2)	0.7431(3)	4.7(1)
C(12)	0.5992(4)	0.4480(2)	0.7776(3)	5.0(1)
C(13)	0.7908(4)	0.4267(2)	0.7581(3)	5.3(1)
C(14)	0.5391(3)	0.2536(2)	0.7268(2)	3.9(1)
C(15)	0.4460(4)	0.2285(2)	0.6876(2)	3.8(1)
C(16)	0.5903(4)	0.2116(2)	0.7831(2)	5.1(1)
C(17)	0.4035(5)	0.1634(2)	0.6978(3)	6.5(2)

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

dihedral angles between the planes (O(1)CuN(3)) and (O(1)-GdO(3)) are greater in **1** (39.1(1)°) than in **2** (6.1(3)°). Significant differences between **1** and **2** are also afforded by the torsion angles within the Cu(O, N−O)Gd network. From the data reported in Table 5, it appears that the larger distortions affect **1**. Otherwise, these distortions are centered around N(3) and O(1) in **1** and **2**, respectively. It may be noted that the (CuO(1)Gd) angles display similar values, 113.4(1) and 114.2(1)°, while larger differences (10.3 and 7.5°) are observed for the (O(1)GdO(3)) and (N(3)CuO(1) angles in **1** and **2**, respectively. Outside the bridging entity, the large variation (12.5°) of the N(1)CuN(2) angles reflects the change of the diamino chain length. In order from **1** to **2**, the bond distances are little altered. The largest variation affects Gd−O(3) with a value of 0.073 Å, and the smallest one is for O(3)−N(3), which decreases by 0.005 Å. The Cu···Gd separation varies from 3.6481(6) Å in **1** to 3.6210(4) Å in **2**.

In **1**, the Cu^{II} center and its four neighbors (O(1), N(1), N(2) and N(3)) are nearly coplanar. The deviations from the mean coordination plane are at the best 0.05 Å for the donors and equal to 0.0740(5) Å for the metal ion. In **2**, Cu^{II} has a square-pyramidal environment with an axial water molecule. The four basal donors deviate from the mean coordination plane by less than 0.06 Å while the copper ion and the water molecule are displaced in the same direction by 0.1921(4) and 2.554(3) Å, respectively.

The gadolinium ion is decacoordinated in both complexes. It is surrounded by three oxygens (O(1), O(2), and O(3)) from L^i and seven oxygens from auxiliary ligands (NO_3 and/or H_2O). In **1**, of three (NO_3) ions, two chelate Gd^{III} while the third one chelates Gd^{III} through O(4) and O(5) and, via O(6), acts as a monodentate ligand toward another symmetry-related ($i = -{}^1/_2 + x, {}^1/_2 - y, 1 - z$) gadolinium ion. The net result is the formation of a chain of dinuclear units $=Gd(Cu)-ONO_2=Gd(Cu)-ONO_2=$. Due to the respective orientations of neighboring dinuclear units, the shortest contact is not a Gd···Gd

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 100) for [$L^2Cu(H_2O)Gd(H_2O)(NO_3)_3$]

	x	*y*	*z*	$\mathbf{U}_{eq}$[a]
Gd	0.53284(1)	0.14177(1)	0.33347(1)	2.82(1)
Cu	0.27019(3)	0.20116(3)	0.39531(3)	3.35(1)
O(1)	0.4022(2)	0.2586(2)	0.3663(2)	3.14(5)
O(2)	0.5976(2)	0.3117(2)	0.3706(2)	3.66(6)
O(3)	0.4085(2)	0.0247(2)	0.3761(2)	3.74(6)
O(4)	0.3352(2)	0.2219(2)	0.5531(2)	4.85(7)
O(5)	0.5365(2)	0.1506(2)	0.5041(2)	4.15(6)
O(6)	0.6158(2)	−0.0179(2)	0.3836(2)	4.70(7)
O(7)	0.7226(2)	0.1050(2)	0.3933(2)	5.03(7)
O(8)	0.7849(2)	−0.0445(3)	0.4023(3)	7.3(1)
O(9)	0.4839(2)	0.2408(2)	0.1837(2)	4.57(7)
O(10)	0.3941(2)	0.1106(2)	0.2087(2)	4.34(6)
O(11)	0.3623(3)	0.1908(3)	0.0802(2)	6.7(1)
O(12)	0.6833(3)	0.2018(2)	0.2212(2)	6.36(9)
O(13)	0.6151(2)	0.0589(2)	0.2051(2)	4.98(7)
O(14)	0.7206(2)	0.1089(3)	0.1069(2)	5.77(8)
N(1)	0.1885(2)	0.3218(2)	0.3824(2)	3.48(7)
N(2)	0.1350(2)	0.1410(2)	0.4046(2)	3.69(7)
N(3)	0.3106(2)	0.0603(2)	0.3801(2)	3.14(6)
N(4)	0.7092(3)	0.0131(3)	0.3933(2)	4.63(8)
N(5)	0.4116(3)	0.1807(3)	0.1544(2)	4.42(8)
N(6)	0.6797(3)	0.1214(3)	0.1808(2)	4.33(8)
C(1)	0.4192(3)	0.3562(2)	0.3727(2)	2.78(7)
C(2)	0.5247(3)	0.3876(3)	0.3740(2)	2.98(7)
C(3)	0.5526(3)	0.4863(3)	0.3775(3)	4.20(9)
C(4)	0.4739(3)	0.5578(3)	0.3808(3)	4.46(9)
C(5)	0.3702(3)	0.5292(3)	0.3789(3)	3.84(8)
C(6)	0.3417(3)	0.4283(2)	0.3766(2)	3.52(8)
C(7)	0.2299(3)	0.4088(3)	0.3762(2)	3.39(7)
C(8)	0.7083(3)	0.3396(3)	0.3825(4)	6.6(2)
C(9)	0.0707(3)	0.3083(3)	0.3774(3)	4.43(9)
C(10)	0.0508(3)	0.2100(2)	0.4260(3)	4.15(9)
C(11)	0.0329(4)	0.3026(4)	0.2755(3)	6.2(1)
C(12)	0.0162(3)	0.3902(3)	0.4249(3)	5.4(1)
C(13)	0.1283(3)	0.0486(3)	0.3875(2)	3.17(7)
C(14)	0.2323(3)	0.0012(2)	0.3752(2)	3.14(7)
C(15)	0.0299(3)	−0.0107(3)	0.3803(3)	4.9(1)
C(16)	0.2396(3)	−0.1080(3)	0.3625(3)	4.05(9)

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

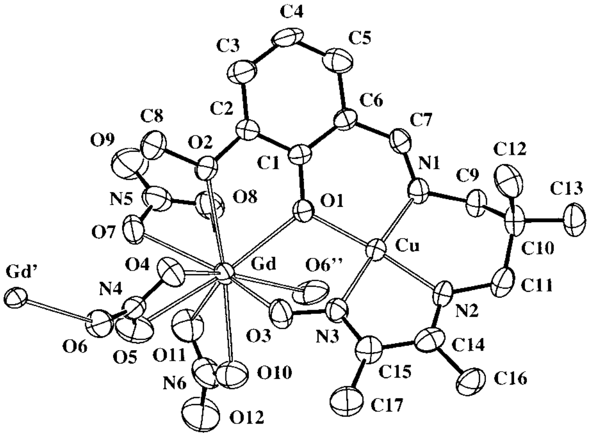

Figure 2. Molecular plot for **1** with ellipsoids drawn at the 50% probability level.

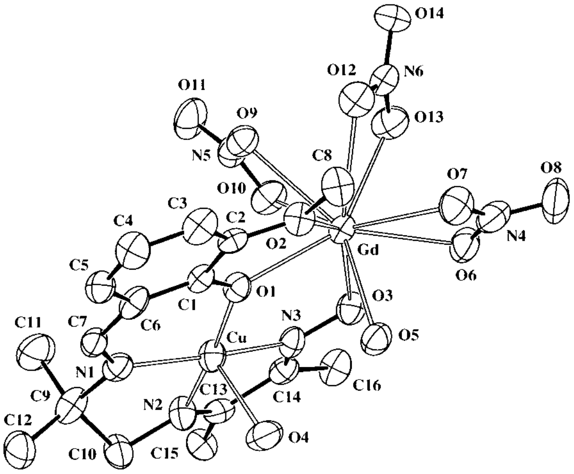

Figure 3. Molecular plot for **2** with ellipsoids drawn at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1		2
Cu−O(1)	1.963(3)	Cu−O(1)	1.929(2)
Cu−N(1)	1.927(3)	Cu−N(1)	1.941(3)
Cu−N(2)	1.997(3)	Cu−N(2)	1.919(3)
Cu−N(3)	1.949(3)	Cu−N(3)	1.996(3)
		Cu−O(4)	2.391(3)
Gd−O(1)	2.393(3)	Gd−O(1)	2.373(2)
Gd−O(2)	2.718(3)	Gd−O(2)	2.493(2)
Gd−O(3)	2.287(3)	Gd−O(3)	2.360(2)
Gd−O(4)	2.551(3)	Gd−O(5)	2.479(3)
Gd−O(5)	2.631(4)	Gd−O(6)	2.493(3)
Gd−O(6″)	2.593(3)	Gd−O(7)	2.549(3)
Gd−O(7)	2.496(3)	Gd−O(9)	2.590(3)
Gd−O(8)	2.455(3)	Gd−O(10)	2.464(3)
Gd−O(10)	2.471(3)	Gd−O(12)	2.738(4)
Gd−O(11)	2.479(3)	Gd−O(13)	2.481(3)
Gd−O(1)−Cu	113.40(11)	Gd−O(1)−Cu	114.23(10)
O(1)−Cu−N(3)	89.70(13)	O(1)−Cu−N(3)	97.25(11)
Cu−N(3)−O(3)	123.7(3)	Cu−N(3)−O(3)	126.7(2)
N(1)−Cu−N(2)	96.11(14)	N(1)−Cu−N(2)	83.66(13)
Gd−O(3)−N(3)	118.9(2)	Gd−O(3)−N(3)	114.45(18)
O(1)−Gd−O(3)	73.99(10)	O(1)−Gd−O(3)	84.35(8)
c[a]	39.1(1)	*c*[a]	6.1(3)

[a] Dihedral angle between the CuO(1)N(3) and GdO(1)O(3) planes.

Table 5. Torsion Angles (deg) within the Cu(O,N−O)Gd Core for **1** and **2**

	1	2
Gd−O(1)−Cu−N(3)	−34.2(1)	−1.0(1)
O(1)−Cu−N(3)−O(3)	5.9(3)	15.2(3)
Cu−N(3)−O(3)−Gd	27.6(4)	−21.6(3)
N(3)−O(3)−Gd−O(1)	−38.5(2)	14.7(2)
O(3)−Gd−O(1)−Cu	40.1(1)	5.6(1)

one (6.6159(1) Å) but a Gd⋯Cu one (5.4735(5) Å). The related Cu⋯Cu separation is equal to 7.5803(6) Å.

In complex **2** the Gd^{III} coordination sphere is completed by seven oxygens from three chelating (NO_3) anions and a water molecule. Several hydrogen bonds are operative. One of them, O(4)⋯H−O(5), participates in a third bridging mode between Cu^{II} and Gd^{III} ions of the same dinuclear units. The other ones are associated with oximato or nitrato groups to connect metal ions of different units. The shortest interunit metal contacts are Cu⋯Gd = 6.4709(4) Å, Gd⋯Gd = 6.2910(3) Å, and Cu⋯Cu = 7.9861(5) Å.

As usual, the Gd−O bond lengths depend on the nature of the oxygen atoms. The shortest bond is from the oximato O(3) (2.287(3) Å in **1** and 2.360(2) Å in **2**). Larger values (2.393(3) Å in **1** and 2.373(3) Å in **2**) characterize the bond from the phenolato oxygen O(1). The bond from the methoxy oxygen atom O(2) has an abnormally large value (2.718(3) Å) in **1**, while a smaller value (2.493(3) Å) consistent with those previously reported[10−13] is observed in complex **2**. The length of the Gd−O(nitrato) bonds vary from 2.551(3) to 2.631(4) Å in **1** and from 2.464(3) to 2.738(4) Å in **2**.

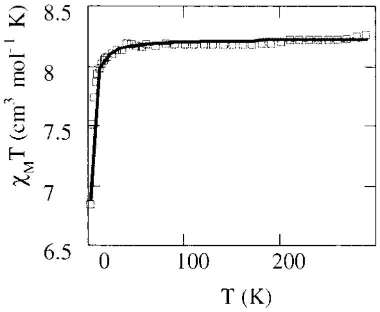

Figure 4. Thermal dependence of $\chi_M T$ for **1** at 0.1 T. The full line corresponds to the best data fit.

Magnetic Properties of Complexes 1 and 2. In Figure 4 we report the magnetic behavior of complex **1** in the form of the thermal variation of the product $\chi_M T$ (χ_M is the molar magnetic susceptibility corrected for the diamagnetism of the ligands).[15] The profile of the plot is different from those previously observed[10−13] for complexes with a (CuO_2Gd) bridging network which have a ferromagnetic ground state. In the present case $\chi_M T$ is practically constant in the 300−50 K range. The mean value of $\chi_M T$, 8.20 ± 0.02 cm^3 K mol^{-1}, corresponds to that expected for two isolated Cu and Gd ions. On lowering further the temperature, $\chi_M T$ decreases more and more rapidly to become equal to 6.84 cm^3 K mol^{-1} at 2 K. Finally the experimental data indicate the occurrence of an overall antiferromagnetic interaction in complex **1**. At this stage of the discussion one may wonder whether the antiferromagnetism is wholly attributable to the Cu−Gd interaction occurring within each dinuclear unit. Structural data point to possible long-range Gd−Gd interactions mediated by NO_3 anions. Such interactions are expected to be very weak since NO_3 is not known as being able to support any significant magnetic coupling.[24] Furthermore previous works[25−28] have shown that, even through efficient monatomic bridges, coupling between gadolinium ions is at the best equal to ca. −0.15 cm^{-1}. Otherwise no interaction can be detected in the homologous Ni^{II} (low-spin) complex.[29] An interunit Cu−Gd interaction has not been considered due to the extended character of the bridging pathway. Finally we tried to fit the experimental data to a simple model derived from the spin-only Hamiltonian for dinuclear (Cu−Gd) complexes $H = -J_{Cu,Gd}S_{Cu}{\cdot}S_{Gd}$. The best fit is obtained with $g_{Cu} = 2.11(2)$, $g_{Gd} = 1.992(1)$ and $J_{Cu,Gd} = -0.49(1)$ cm^{-1}. The excellent quality of the fit and the reliability

---

(23) Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *J. Chem. Soc., Dalton Trans.* **1998**, 1307.

(24) Hendricks, H. M. J.; Birker, P. J. M. W. L.; van Rijn, J.; Verschoor, G. C.; Reedijk, J. *J. Am. Chem. Soc.* **1982**, *104*, 3607.

(25) Liu, S.; Gelmini, L.; Rettig, S. J.; Thompson, R. C.; Orvig, C. *J. Am. Chem. Soc.* **1992**, *114*, 6081.

(26) Panagiotopoulos, A.; Zafiropoulos, T. F.; Perlepes, S. P.; Bakalbassis, E.; Masson-Ramade, I.; Kahn, O.; Terzis, A.; Raptopoulou, C. P. *Inorg. Chem.* **1995**, *34*, 4918.

(27) Costes, J. P.; Dahan, F.; Dupuis, A.; Lagrave, S.; Laurent, J. P. *Inorg. Chem.* **1998**, *37*, 153.

(28) Costes, J. P.; Dupuis, A.; Laurent, J. P. *Inorg. Chim. Acta* **1998**, *268*, 125.

(29) Costes, J. P. Unpublished results.

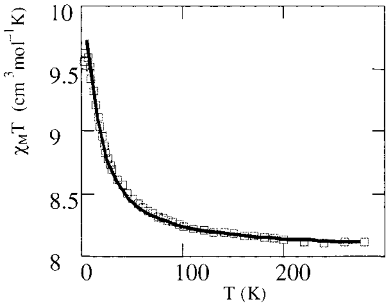

Figure 5. Thermal dependence of $\chi_M T$ for **2** at 0.1 T. The full line corresponds to the best data fit.

of the model are certified by the value (4.8×10^{-5}) of the agreement factor $R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{obs}]^2$.

In complex **2** intermolecular interactions are expected to be vanishingly weak due to the extended character of the possible bridging pathways. The magnetic data offer a great difference from those obtained for **1** but are strongly reminiscent of those previously observed for complexes with a CuO_2Gd core. The temperature dependence of the magnetic susceptibility of complex **2** in the range 2−300 K is shown in Figure 5 in the $\chi_M T$ vs T form. At 300 K, $\chi_M T$ is equal to 8.27 cm^3 K mol^{-1} which nicely corresponds to the value expected for the two uncoupled metal ions (8.25 cm^3 K mol^{-1}). Lowering the temperature causes $\chi_M T$ to increase and reach a maximum of 10.02 cm^3 K mol^{-1} at 4 K and then to decrease to 9.95 cm^3 K mol^{-1}. These values are in good agreement 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 $g_{Gd} = g_{Cu} = 2.0$. They are least-squares fitted to the simple model previously used to yield $g_{Cu} = 2.05(3)$, $g_{Gd} = 1.99(1)$, $J_{Cu,Gd} = 3.5(1)$ cm^{-1}, and $R = 1 \times 10^{-4}$.

Finally the most striking result of the present paper is to afford experimental evidence that ferromagnetism is not an intrinsic property of the Cu^{II}/Gd^{III} pair. Indeed the reported data point out the occurrence of an antiferromagnetic coupling between the two ions in complex **1**. On the contrary complex **2** supports a ferromagnetic interaction. These two behaviors do not basically conflict with each other nor with the data previously reported.[10−13] Indeed the trend observed for complexes with a CuO_2Gd core is that the larger the dihedral angle (OCuO, OGdO), the smaller is the magnitude of the ferromagnetic interaction. In this prospect complex **1** would be a limiting case in which severe distortions of the Cu(O, N−O)Gd network would cause any ferromagnetic contribution to vanish and any underlying antiferromagnetism to become exposed. Conversely the distortions of the bridging core in complex **2** would be small enough to allow an overall ferromagnetic behavior.

The ferromagnetic contribution has been attributed[6] to coupling between the 4f−3d ground configuration and the excited configuration resulting from $3d_{Cu}/5d_{Gd}$ electron transfer according to a mechanism first suggested by Goodenough.[30] As for the antiferromagnetism observed for **1**, two mechanisms may be considered. In the Kahn approach[31] the antiferromagnetic coupling solely arises, in the ground-state configuration, from overlap between localized magnetic orbitals. In the model of Anderson−Hoffmann,[32,33] the antiferromagnetism originates in the interaction between the 3d−4f ground configuration and the metal−metal charge transfer (3d/4f or 4f/3d) configuration. These two mechanisms have been assumed to be inoperative in the (CuO_2Gd) complexes. It has been stated that, due the contraction of the 4f orbitals around the gadolinium nucleus and their shielding by the 5s and 5p orbitals, all the integrals involving a 4f−3d density overlap would be vanishingly small. A different situation may hold in the case of **1**; the observed antiferromagnetism demands that the Kahn mechanism and/or the Anderson one are operative and overcome the eventual effect of the Goodenough process. This would imply that the 4f−3d overlap density takes a weak but finite value.

At the moment we prefer to stay at the experimental evidence and avoid any further speculation on the implication of the covalent effects in the antiferromagnetic behavior of the unsymmetrical bridging core Cu(O,N−O)Gd in complex **1**.

Acknowledgment. We thank Dr. A. Mari for his contribution to the magnetic measurements and Mrs. S. Richelme (Service Commun de Spectroscopie de Masse) for her contribution to the mass spectral data.

Supporting Information Available: X-ray crystallographic files including the structural data for [$L^1CuGd(NO_3)_3$] (**1**) and [$L^2Cu(H_2O)$-$Gd(NO_3)_3 \cdot H_2O$] (**2**), in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990864P

---

(30) Goodenough, J. B. In *Magnetism and the Chemical Bond*; Interscience: New York, 1963.

(31) Kahn, O. In Magneto-Structural Correlations in Exchange Coupled Systems; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel: Dordrecht, The Netherlands, 1985.

(32) Anderson, P. W. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press: NewYork, 1963; Vol. 1, Chapter 2.

(33) Hay, P. J.; Thibeault, J. C.; Hofmann, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 4884.