Notes

Experimental Evidence of a Ferromagnetic Ground State ($S = {}^9/_2$) for a Dinuclear Gd(III)−Ni(II) Complex

J.-P. Costes,* F. Dahan, A. Dupuis, and J.-P. Laurent

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

Received June 12, 1997

Since 1985,[1] the magnetic behavior of complexes containing both f (noted Ln(III) in the following) and d ions has attracted increasing interest. This interest has been mainly focused on the Gd(III)−Cu(II) couple which displays magnetic properties amenable to a rather simple analysis. Indeed Gd(III), with an $^8S_{7/2}$ single-ion ground state, does not possess a first-order orbital moment. Several polynuclear complexes[1−6] involving Gd(III) and Cu(II) ions have been shown to display an overall ferromagnetic behavior. Recent studies[7,8] devoted to perfectly insulated dinuclear species have demonstrated that ferromagnetism is an intrinsic property of the Gd(III)−Cu(II) pair and have expressed interest in studying other (d, f) complexes in which the exchange interaction would be restricted to one d ion with one f ion. Partly relevant to the present work, we note that the structure of a heterodinuclear La(III)−Ni(II) complex was recently reported.[9] Obviously, this complex cannot display magnetic cooperativity.

Experimental Section

[2,2′-[2,2-Dimethyl-1,3-propanediylbis(nitrilomethylidyne)]bis(6-methoxyphenolato)(2−)]nickel(II)] (LNi). This complex was obtained as previously described.[10] Anal. Calc for $C_{21}H_{24}N_2NiO_4 \cdot H_2O$: C, 56.7; H, 5.8; N, 6.3. Found: C, 56.7; H, 5.6; N, 6.2.

[LNi(H$_2$O)$_2$Gd(NO$_3$)$_3$]. Addition of $Gd(NO_3)_3 \cdot 5H_2O$ (0.25 g, 5.5 × 10^{-4} mol) to LNi (0.25 g, 5.5 × 10^{-4} mol) in acetone induced the formation of a precipitate, which was filtered off and washed with cold acetone and diethyl ether. Yield: 0.38 g, 85%. Anal. Calc for $C_{21}H_{24}GdN_5NiO_{13} \cdot 2H_2O$: C, 31.3; H, 3.5; N, 8.7. Found: C, 31.2; H, 3.4; N, 8.6. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): m/z = 708 (100%), $[C_{21}H_{24}GdN_4NiO_{10}]^+$.

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, France (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[11] (−333 × 10^{-6} emu mol^{-1}). Positive FAB mass spectra were recorded in DMF as a solvent and with a 3-nitrobenzyl alcohol matrix by using a Nermag R10-10 spectrometer. Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Crystal data and atomic coordinates are gathered respectively in Tables 1 and 2.

Table 1. Crystallographic Data for $[(C_{21}H_{24}N_2O_4)Ni(H_2O)_2Gd(NO_3)_3]$

empirical formula	$C_{21}H_{28}GdN_5NiO_{15}$	fw	806.44
		space group	$P2_1$ (No. 4)
a	10.1351(6) Å	T	293(2) K
b	16.079(2) Å	λ	0.710 73 Å
c	8.8948(9) Å	D_{calc}	1.848 g cm^{-3}
β	91.138(7)°	μcalc	29.97 cm^{-1}
V	1449.2(3) Å^3	R^a [all, obsd]	0.0177, 0.0163
Z	2	$R_w{}^b$ [all, obsd]	0.0427, 0.0416

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

Results and Discussion

In previous papers,[7,12] we have exemplified the synthetic possibilities offered by Schiff base ligands derived from 2-hydroxy-3-methoxybenzaldehyde to obtain strictly dinuclear Ln(III)−Cu(II) complexes. Apparently, there is no major difficulty in extending this strategy to the Gd(III)−Ni(II) couple. Indeed, reacting the nickel complex of 2,2′-[2,2-dimethyl-1,3-propanediylbis(nitrilomethylidyne)]bis(6-methoxyphenol) (abbreviated as LH_2 in the following) with $Gd(NO_3)_3 \cdot 5H_2O$ yields a compound which, from elemental analysis, infrared and mass spectrometries, and thermogravimetric analysis data, has the formula $LNi(H_2O)_2Gd(NO_3)_3$.

Description of the Structure. That the complex is a strictly dinuclear Gd(III)−Ni(II) entity is definitively supported by a structural determination. Indeed, the central region of the unit represented in Figure 1 is occupied by the Gd(III) and Ni(II) ions, which are doubly bridged by the phenoxo oxygen atoms of the dideprotonated ligand L. The four atoms of the GdO_2Ni network are almost coplanar, the dihedral angle between the GdO(1)Ni and GdO(2)Ni planes being equal to 4.2(5)° and the Gd···Ni separation to 3.5213(3) Å. The two Gd−O(j) (j = 1, 2) distances differ by less than 0.04 Å, while the two Ni−O(j) distances are identical to one another. The Gd−O(j)−Ni angles are equal to 106.49(7)° (j = 1) and 107.90(7)° (j = 2).

The nickel occupies the inner coordination site and has a distorted octahedral environment. The equatorial plane consists of two oxygen and two nitrogen atoms from the ligand L. The four N_2O_2 atoms are almost coplanar, since they are alternately displaced from the mean plane by less than 0.02 Å. The apical positions are occupied by the oxygen atoms of two water molecules; the related Ni−O distances (2.163(2) and 2.138(2) Å) are larger than the basal Ni−O distances (2.035(2) and 2.032(2) Å). The gadolinium ion is decacoordinated, four oxygen donors being afforded by L and six by three bidentate nitrato

---

* Corresponding author. Tel: (33) 561-33-31-52. E-mail: costes@lcc-toulouse.fr. Fax: (33) 561 55 30 03.

(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*, 572.

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

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

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

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

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

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

(9) Archibald, S. J.; Blake, A. J.; Parsons, S.; Schröder, M.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1997**, *173*.

(10) Pfeiffer, P.; Breith, E.; Lülle, E.; Tsumaki, T. *Justus Liebigs Ann. Chem.* **1933**, *503*, 84.

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

(12) Costes, J. P.; Dahan, F.; Dupuis, A.; Laurent, J. P. *Inorg. Chem.*, in press.

S0020-1669(97)00720-9 CCC: $14.00

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

atom	x/a	y/b	z/c	U_{eq}[a]
Gd	0.19176(1)	0.50000	0.74907(1)	3.106(3)
Ni	0.40237(3)	0.43716(2)	0.46014(3)	2.699(6)
O(1)	0.3085(2)	0.3893(1)	0.6408(2)	3.01(4)
O(2)	0.3008(2)	0.5379(1)	0.5329(2)	3.16(4)
O(3)	0.1312(2)	0.3539(1)	0.8352(2)	4.55(5)
O(4)	0.1077(2)	0.6312(1)	0.6202(2)	4.20(5)
O(5)	0.2026(2)	0.4907(2)	1.0327(2)	4.18(5)
O(6)	0.0566(3)	0.5758(2)	0.9463(3)	7.12(9)
O(7)	0.0686(3)	0.5502(2)	1.1852(3)	6.70(8)
O(8)	0.4256(2)	0.5114(2)	0.8389(2)	4.17(5)
O(9)	0.3167(3)	0.6259(1)	0.8394(3)	5.49(6)
O(10)	0.5266(3)	0.6272(2)	0.8895(4)	7.76(9)
O(11)	0.0495(2)	0.4440(2)	0.5410(3)	5.36(6)
O(12)	−0.0647(2)	0.4865(2)	0.7223(3)	6.44(8)
O(13)	−0.1618(2)	0.4452(2)	0.5139(4)	6.72(7)
O(14)	0.2314(2)	0.4056(1)	0.3224(2)	3.83(4)
O(15)	0.5694(2)	0.4723(2)	0.5963(3)	5.19(6)
N(1)	0.4844(2)	0.3271(1)	0.4114(2)	3.11(4)
N(2)	0.4827(2)	0.5014(2)	0.2887(2)	3.29(4)
N(3)	0.1084(2)	0.5398(2)	1.0594(3)	4.40(6)
N(4)	0.4259(3)	0.5900(2)	0.8566(3)	4.46(6)
N(5)	−0.0629(3)	0.4583(2)	0.5906(3)	4.50(6)
C(1)	0.2758(2)	0.3100(2)	0.6499(3)	2.95(5)
C(2)	0.1805(3)	0.2867(2)	0.7556(3)	3.57(6)
C(3)	0.1395(3)	0.2060(2)	0.7731(4)	4.88(7)
C(4)	0.1925(3)	0.1441(2)	0.6832(5)	5.21(8)
C(5)	0.2877(3)	0.1633(2)	0.5819(4)	4.58(7)
C(6)	0.3309(3)	0.2460(2)	0.5630(3)	3.35(5)
C(7)	0.4378(3)	0.2583(2)	0.4579(3)	3.48(6)
C(8)	0.6013(3)	0.3225(2)	0.3174(3)	3.71(6)
C(9)	0.5929(3)	0.3741(2)	0.1724(3)	3.79(6)
C(10)	0.5957(3)	0.4674(2)	0.2064(4)	4.12(6)
C(11)	0.2793(3)	0.6061(2)	0.4524(3)	2.98(5)
C(12)	0.1789(3)	0.6608(2)	0.4988(3)	3.51(5)
C(13)	0.1568(3)	0.7353(2)	0.4284(4)	4.52(7)
C(14)	0.2325(4)	0.7582(2)	0.3066(4)	5.37(8)
C(15)	0.3260(3)	0.7050(2)	0.2546(4)	4.68(7)
C(16)	0.3503(3)	0.6272(2)	0.3244(3)	3.36(5)
C(17)	0.4506(3)	0.5761(2)	0.2563(3)	3.53(5)
C(18)	0.0475(4)	0.3336(3)	0.9582(4)	6.4(1)
C(19)	0.4740(3)	0.3493(2)	0.0763(4)	4.69(7)
C(20)	0.7202(4)	0.3558(2)	0.0886(4)	5.60(9)
C(21)	0.0067(4)	0.6853(2)	0.6755(4)	5.83(9)

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

ions. This environment is similar to those of the related Gd−Cu complexes and the same comments are applicable.[7,12]

The separations between metal ions belonging to neighboring molecules are large (Gd···Ni = 6.7115(3) Å, Gd···Gd = 8.8948(1) Å, and Ni···Ni = 8.3065(1) Å) and preclude any significant intermolecular interaction of magnetic nature. This conclusion is not weakened by the presence of two intermolecular hydrogen bonds. Indeed, they link the oxygens of the water molecules with the oxygen atoms of two nitrato ions belonging to symmetry-related units. They are unable to support any interaction between the two metal ions.

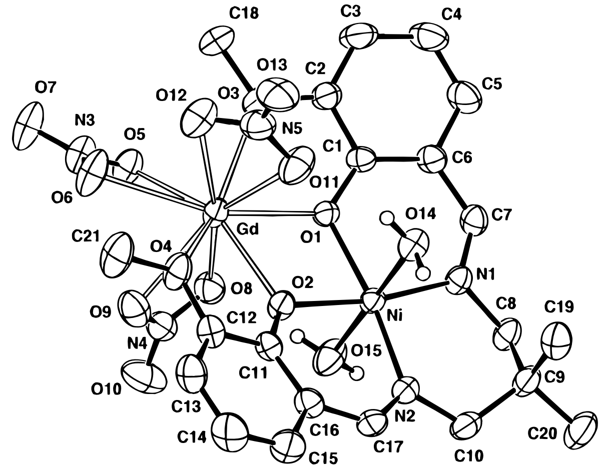

Figure 1. Molecular plot for $LNi(H_2O)_2Gd(NO_3)_3$ with ellipsoids drawn at the 50% probability level. Selected bond lengths (Å): Gd···Ni = 3.5213(3), Gd−O(1) = 2.354(2), Gd−O(2) = 2.319(2), Gd−O(3)= 2.550(2), Gd−O(4) = 2.541(2), Gd−O(5) = 2.528(2), Gd−O(6) = 2.556(2), Gd−O(8) = 2.492(2), Gd−O(9) = 2.512(2), Gd−O(11) = 2.492(2), Gd−O(12) = 2.614(2), Ni−O(1) = 2.035(2), Ni−O(2) = 2.032(2), Ni−O(14) = 2.163(2), Ni−O(15) = 2.138(2), Ni−N(1) = 2.006(2), Ni−N(2) = 2.027(2). Selected angles (deg): Gd−O(1)−Ni = 106.49(7), Gd−O(2)−Ni = 107.90(7).

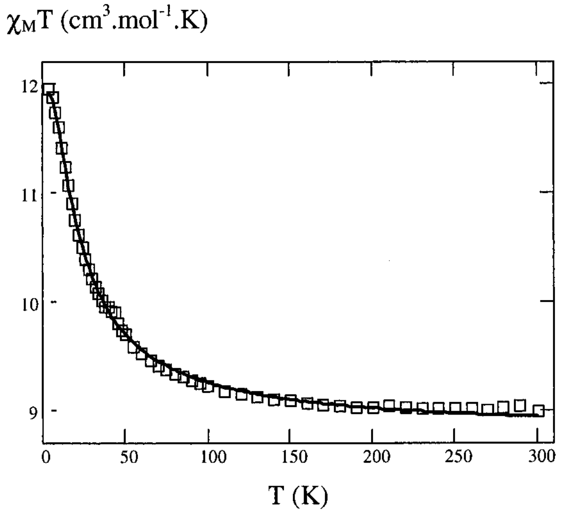

Figure 2. Thermal dependence of $\chi_M T$ for $LNi(H_2O)_2Gd(NO_3)_3$ at 0.1 T. The full line corresponds to the best data fit.

Magnetic Properties. The temperature dependence of the magnetic susceptibility in the range 4−300 K is shown in Figure 2 in the $\chi_M T$ *vs* T form, the applied field being equal to 0.1 T. The profile of the curve indicates that the Gd(III)−Ni(II) interaction is ferromagnetic, leading to an $S = {}^9/_2$ ground state. This is definitively supported by the field dependence of the magnetization M at 5 K. In Figure 3, the experimental values of M are compared to the sum of the Brillouin functions for isolated Gd(III) ($S = {}^7/_2$) and Ni(II) ($S = 1$) ions and the Brillouin function for an $S = {}^9/_2$ pair state. For any value of the field, the experimental magnetization is larger than that for isolated metal ions and close to the value expected for an $S = {}^9/_2$ pair state. The slight difference observed between (a) and (c) is due to an incomplete population of the $S = {}^9/_2$ state at 5 K. Indeed, the experimental values of M can be exactly fitted with the Brillouin function to yield $g = 2.0$ and $S = 4.4$, which differ little from the expected $S = {}^9/_2$ values, the agreement factor $\sum[M_{calc} - M_{obs}]^2/\sum[M_{obs}]^2$ being equal to 2.5×10^{-6}.

Unexpectedly, the experimental values of the susceptibility $\chi_M T$ may be represented by a simple expression deriving from a spin-only Hamiltonian for isotropic exchange:

$$H = -J\mathbf{S}_{Gd}\cdot\mathbf{S}_{Ni}$$

In this instance, the spectrum of the low-lying spin states would comprise three states [$E({}^9/_2) = 0$, $E({}^7/_2) = 9J$ and $E({}^5/_2) = 16J$] and the expression for $\chi_M T$ would be

$$\chi_M T = \frac{N\beta^2 g^2}{3k}\,\frac{\dfrac{495}{2} + 126\exp\left(\dfrac{-9J}{kT}\right) + \dfrac{105}{2}\exp\left(\dfrac{-16J}{kT}\right)}{10 + 8\exp\left(\dfrac{-9J}{kT}\right) + 6\exp\left(\dfrac{-16J}{kT}\right)}$$

Using a fixed g value of 2.0 (obtained in the magnetization study), least-squares fitting of the experimental data leads to J

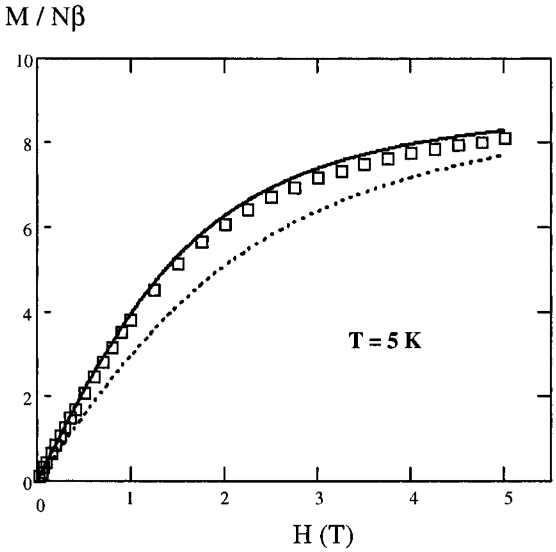

Figure 3. Field dependence of the magnetization: experimental data (□); theoretical curve for isolated Ni(II) and Gd(III) ions (dashed line); theoretical curve for an $S = {}^{9}/_{2}$ spin state (full line). These plots are referred to respectively as (a), (b), and (c) in the text.

$= 3.6$ cm^{-1}. The agreement factor $R = \sum[\chi_M T_{calc} - \chi_M T_{obs}]^2/\sum[\chi_M T_{obs}]^2$ is then equal to 1.25×10^{-5}. Obviously, the accuracy of the J value is limited by the crude nature of the model. However, it may be noted that the refinements that could be introduced into the analysis would likely lead to antiferromagnetic contributions. Furthermore, no manisfestation of such effects (zero-field splitting, intermolecular interaction, ...) are detectable in our experiments.

Finally, the main result of the present work a structurally characterized example of a discrete dinuclear Gd(III)−Ni(II) complex that displays ferromagnetic behavior. In this respect, the Gd−Ni pair resembles the Gd−Cu pair. The stabilization of the $S = 4$ state in GdO_2Cu systems has been related[3] to the coupling between the Gd(III)−Cu(II) ground configuration and the Gd(II)−Cu(III) charge transfer excited configuration. We could speculate that a similar process is operative in stabilizing the $S = {}^{9}/_{2}$ spin state for the Gd(III)−Ni(II) complex.

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 acquisition of mass spectral data.

Supporting Information Available: Listings of X-ray structural data for $LNi(H_2O)_2Gd(NO_3)_3$ including a summary of crystallographic experimental details, hydrogen coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, and least-squares planes equations and atom deviations from the planes (10 pages). See any current masthead page for ordering instructions.

IC970720F