Inorg. Chem. **2002**, *41*, 605–609

Inorganic Chemistry
Note

A Study on the Novel d–f Heterodinuclear Gd(III)–Ni(II) Cryptate: Synthesis, Crystal Structure, and Magnetic Behavior

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Received March 9, 2001

Introduction

The unique properties of heterodinuclear complexes have attracted increasing interest.[1] Recently, new research has been focused on d−f heterodinuclear complexes containing both transition metal and lanthanide(III) ions.[2,3] Studies on these complexes have promising applications on the designs of bimetallic catalysts,[4] precursors of magnetic materials,[5] and novel molecule devices.[6] Since the first Gd(III)−Cu(II) intramolecular ferromagnetic interaction in the complex was reported, great interest has been aroused in the design and synthesis of d−f heteronuclear compexes.[1b,7] In most d−f nickel(II) complexes, Ni(II) forming a square-planar structure is diamagnetic.[8] Therefore, studies on magnetic properties of Ln(III)−Ni(II) complexes are reported seldom.[9] Macrocyclic ligands with polyamines have a flexible cavity and are able to tune their diameter to allow selective coordination of metal ions of different size and coordination geometry.[10] To date, only a few d−f heteronuclear macrocyclic complexes have been reported.[8a] The synthesis of d−f heterodinuclear cryptates is even more difficult and challenging. We reported the first d−f heteronuclear (Dy(III)−Cu(II)) cryptate in 2000.[11] Here a d−f heteronuclear Robson-type cryptate $[GdNiL(DMF)](ClO_4)_2$ was synthesized in two steps: 1, the mononuclear Gd(III) cryptate precursor was obtained by the condensation of tris(2-aminoethyl)amine (tren) with 2,6-diformyl-4-chlorophenol (dcp) in the presence of Gd^{3+} ion; 2, the Gd(III) complex was reacted with nickel(II) perchlorate. The crystal structure and ES-MS spectrum of the cryptate demonstrated a strict Gd(III)−Ni(II) entity. A quantitative analysis shows that the Gd(III) and Ni(II) interact ferromagnetically.

Experimental Section

Synthesis of $[Gd(H_3L^1)(NO_3)(H_2O)](ClO_4)_2$, 1. The cryptate **1** was synthesized by our method.[12] Yield: 0.28 g, 60%. Anal. Calcd for $C_{36}H_{41}Cl_5N_9O_{15}Gd$: C, 36.78; H, 3.49; N, 10.72. Found: C, 37.08; H, 3.55 N, 10.68. IR (cm^{-1}): 3300 s [ν(OH)]; 1650 s [ν(C=N)]; 1640 s [ν(C=N)]; 1540 s [ν(C−O)]; 1478 s [ν(N=O)]; 1296 s [$\nu_{asym}(NO_2)$ and 1051 s [$\nu_{sym}(NO_2)$]; 1078 s [$\nu(ClO_4$-)]; 625 m [$\nu(ClO_4^-)$]. UV−vis [(λ_{max} (nm), CH_3CN)]: 407 (14800 mol^{-1} dm^3 cm^{-1}), 271 (23800 mol^{-1} dm^3 cm^{-1}), 240 (41200 mol^{-1} dm^3 cm^{-1}). 226 (55800 mol^{-1} dm^3 cm^{-1}). Λ_m (DMF, 298 K): 125 $S\cdot cm^2\cdot mol^{-1}$.

Synthesis of $[GdNiL(DMF)](ClO_4)_2\cdot MeCN$, 2. The mononuclear gadolinium(III) cryptate (**1**) (0.117 g, 0.1 mmol) was

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10.1021/ic010270y CCC: $22.00

Table 1. The Assignments for ES-MS Peaks of Cryptates **1** and **2** in MeOH Solution

cryptate	peak (*m*/*z*)	ES-MS (*m*/*z*)[a]
$[Gd(H_3L)(NO_3)(H_2O)](ClO_4)_2$	974.2	$[Gd(H_2L)(NO_3)(H_2O)]^+$ (18)
	894.2	$[Gd(H_2L)]^+$ (84)
	832.8	$[Gd(H_2L - 2Cl) + H_2O]^+$ (14)
	446.6	$[Gd(HL)]^{2+}$ (100)
$[GdNiL(DMF)](ClO_4)_2$	1663.9	$\{[GdNi(L - 3Cl)] + [Gd(L - 3Cl)] + Cl^-\}^+$ (14)
	1205.2	$\{[GdNiL(DMF)]_2 + 2(ClO_4^-) + 4H_2O + 3MeOH\}^{2+}$ (15)
	1064.1	$[GdNi(L - 3Cl)(DMF) + (ClO_4^-) + MeOH + H_2O]^+$ (62)
	1010.0	$[GdNi(L - 2Cl) + (ClO_4^-) + MeOH]^+$ (100)
	968.3	$[GdNi(L - 3Cl)(DMF) + Cl^- + H_2O]^+$ (24)
	857.4	$[Gd(L - Cl) + H^+]^+$ (8)
	648.1	$\{[(L - 3Cl) + 4H^+]_2 + MeOH\}^{2+}$ (14)
	474.7	$[GdNiL]^{2+}$ (44)

[a] Relative abundance is given in the parentheses.

dissolved in a mixture of methanol (15 cm^3) and DMF (1.0 cm^3). The pH of the solution was adjusted to 7−8 with excess CaH_2. Hydrated nickel perchlorate (0.1 mmol) was added to the filtered solution before refluxing for ca. 4 h. The solution was concentrated until the green precipitate was formed. $[GdNiL(DMF)](ClO_4)_2 \cdot MeCN$, yield: 0.66 g, 52%. Anal. Calcd for $C_{41}H_{46}Cl_5N_{10}O_{12}$-GdNi: C, 38.96; H, 3.67; N, 11.08. Found: C, 38.87; H, 3.58; N, 11.28. IR (cm^{-1}): 1640 s [ν(C=N)]; 1540 s [ν(C−O)]; 1078 s [$\nu(ClO_4^-)$]; 625 m [$\nu(ClO_4^-)$]. UV−vis [(λ_{max} (nm), CH_3CN)]: 650 (50 $mol^{-1}\ dm^3\ cm^{-1}$) 377 (18300 $mol^{-1}\ dm^3\ cm^{-1}$), 249 (64900 $mol^{-1}\ dm^3\ cm^{-1}$), 225 (85300 $mol^{-1}\ dm^3\ cm^{-1}$). Λ_m (DMF, 298 K): 135 S $cm^2\ mol^{-1}$.

CAUTION! *Perchlorate salts are potentially explosive and should be treated with care and used only in small quantities.*

Physical Measurements. The electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrograph (1.0 μmol dm^{-3}). The diluted solution was electrosprayed at a flow rate of $5 \times 10^{-6}\ dm^{-3}\ min^{-1}$ with a needle voltage of +4.5 kV. The mobile phase was an aqueous solution of methanol (v/v, 1:1). Samples were run in the positive-ion mode.

The variable-temperature magnetic susceptibility was measured on a SQUID-based sample magnetometer for powder sample (2−300K, 0.5 T). Diamagnetic corrections were made on the base of Pascal's constants (-311×10^{-6} emu mol^{-1}).[13]

Crystal Structure Determination. Single crystals of $[GdNi(DMF)](ClO_4)_2 \cdot MeCN$ were obtained as green prisms by a slow diffusion of diethyl ether vapor to an acentonitrile solution of the cryptate for a week. A summary of the parameters is given in Table 2. Diffraction data were collected on a SIEMENS SMART/CCDC area-detector[14] with monochromatic Mo Kα ($\lambda = 0.71073$) radiation using Φ and ω scans. The collected data was reduced using the SADABS program, and empirical absorption correction was made by using the SADABS program.[15] The structure was solved by direct methods. All non-hydrogen atoms were refined anistropically by full-matrix least squares. Hydrogen atoms of the ligands were placed in their calculated positions with C−H = 0.93 Å. All of the hydrogen atoms were assigned fixed isotropic thermal parameters (1.2 times those of the atoms to which they are attached) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. All computations were carried out using the SHELXTL-PC program package.[16]

Table 2. Crystallographic Data for $[GdNi(DMF)](ClO_4)_2 \cdot MeCN$

formula	$C_{41}H_{46}Cl_5N_{10}O_{12}GdNi$
MW	1264.09
cryst syst	monoclinic
space group	*P*2(1)/*c*
a/Å	19.6609(12)
b/Å	11.8710(6)
c/Å	21.4993(12)
β/deg	97.8130(10)
index range	$-16 \le h \le 23, -11 \le k \le 14, -25 \le l \le 24$
V/Å^3	4971.2(5)
Z	4
μ/mm^{-1}	2.039
T/K	293(2)
θ range for data collection (deg)	1.05−24.99
no. of data measd	18863
no. of data with $I > 2\sigma(I)$	8723
R(int)	0.0385
GOF	1.174
$R\ [I > 2\sigma(I)]$	0.0562
$R_w\ [I > 2\sigma(I)]$	0.1115

[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

Syntheses and Characterization. The heterodinuclear cryptate $[GdNiL(DMF)](ClO_4)_2$ was synthesized in two steps. It is different from the usual method for the phenol-based two-dimensional macrocyclic complexes.[17] In the synthesis of Gd(III)−Ni(II) cryptate, one water molecule encapsulated in a mononuclear precursor complex $[Gd(H_3L)(NO_3)(H_2O)](ClO_4)_2$ was replaced by Ni^{2+} ion at controlled pH conditions. In general, the two-dimensional macrocyclic heterodinuclear complexes are synthesized by (2 + 1) condensation of aldehyde with amine in the presence of metal ions and then by the cyclization condensations using a second metal ion as a template.[17,18] The general method is not applicable to the syntheses of our three-dimensional cryptates.

In the IR spectrum of Gd(III)−Ni(II) cryptate, disappearance of the absorption at ca. 3300 cm^{-1} (ν(OH)) implies nonexistence of a water molecule in the cryptate. The UV spectrum is dominated by intense ligand absorption at 225, 249, and 377 nm. The band at 377 nm is assigned to the C=N chromophores, which blue-shifted about 30 nm due to the coordination of the Ni^{2+} ion, and the bands at 225

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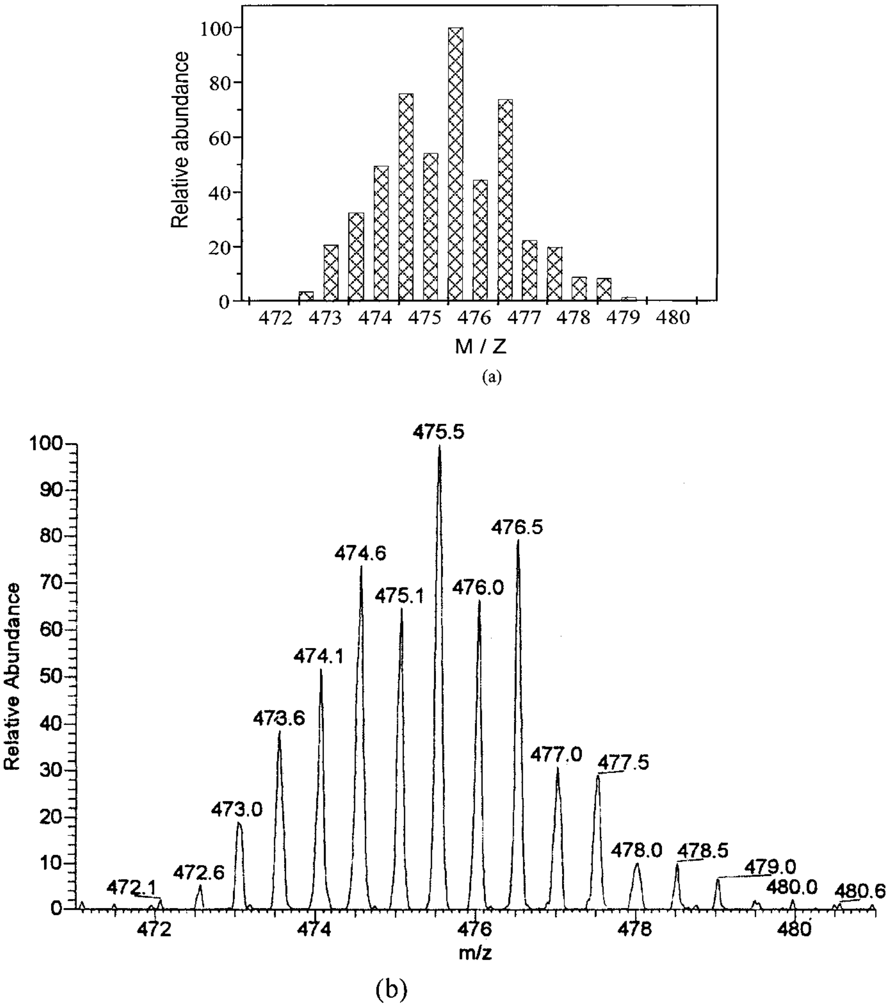

Figure 1. The isotopic distribution of the peak cluster at *m/z* 474.7: (a) calculated; (b) experimental.

and 249 nm are designated to $\pi-\pi^*$ transitions of the K band of the benzene ring. The d−d transition of Ni(II) is at 650 nm and shows that Ni(II) is located in a distorted octahedral environment. The solution molar conductivity value indicates that the Gd(III)−Ni(II) complex is a 1:2 electrolyte, being consistent with both the elemental analysis results and the predicated chemical formula.

Electrospray Mass Spectrum. The positive-ion ES-MS results are listed in Table 1. The simplicity of the spectrum for mononuclear cryptate **1** is attributed to the thermodynamic stability and kinetic inertness of cryptates as well as the relatively low energy process of ES-MS. The dominant peaks of $[Gd(HL)]^+$ and $[Gd(H_2L)]^{2+}$ are due to the loss of water and coordinated nitrate anion in **1**. Most peaks in $[GdNiL(DMF)](ClO_4)_2$ correspond to the fragments containing Ni^{2+} ions, confirming the presence of a Gd(III)−Ni(II) core. The dominant peak at *m/z* =1010.0 corresponds to $[GdNi(L - 2Cl) + ClO_4^- + MeOH]^+$, which is formed from the loss of two chlorine atoms from the benzene rings and the binding of a perchlorate anion and a methanol. The loss of coordinated DMF led to the formation of a new species $[GdNiL]^{2+}$, *m/z* = 474.7. A revised program[19] was used to calculate the isotopic distribution at *m/z* = 474.7. The calculated pattern (Figure 1a) is similar to the experimental one (Figure 1b), which further confirms the heterodinuclear structure.

Crystal Structure. Structure analysis of cryptate **2** confirms that the complex is a dinuclear Gd(III)−Ni(II) entity. The structure of complex cation $[GdNiL(DMF)]^{2+}$ is shown in Figure 2. Gd(III) and Ni(II) ions are encapsulated in the cavity of the macrocycle with a Gd(III)···Ni(II) distance of 3.210 Å, bridged by the oxygen atoms O(1), O(2), O(3) of three deprotonated phenyl groups. Gd(III) is located at one end of the cavity and is eight-coordinated with the bridgehead nitrogen atom N(1), three imino-nitrogen atoms (N(2), N(3), N(4)), the oxygen atom O(4) of DMF, and three phenoxy atoms (O(1), O(2), O(3)). The coordination configuration is best described as distorted dodecahedral. The Gd(III)−N(imino) distances are in the range 2.486−2.499 Å (Table 3), which are shorter than that of Dy(III)−Cu(II) heteronuclear (2.443−2.509 Å)[11] with the same ligand. The Gd(III)−(phenolate) distances are in the range 2.304−2.331 Å, which are slightly shorter than that of Dy(III)−Cu(II) heteronuclear complexes (2.253−2.331 Å).

The another end of the cavity is occupied by the Ni(II) ion. Three μ-phenolate oxygen atoms and three imino nitrogen atoms are coordinated to Ni(II), forming a distorted

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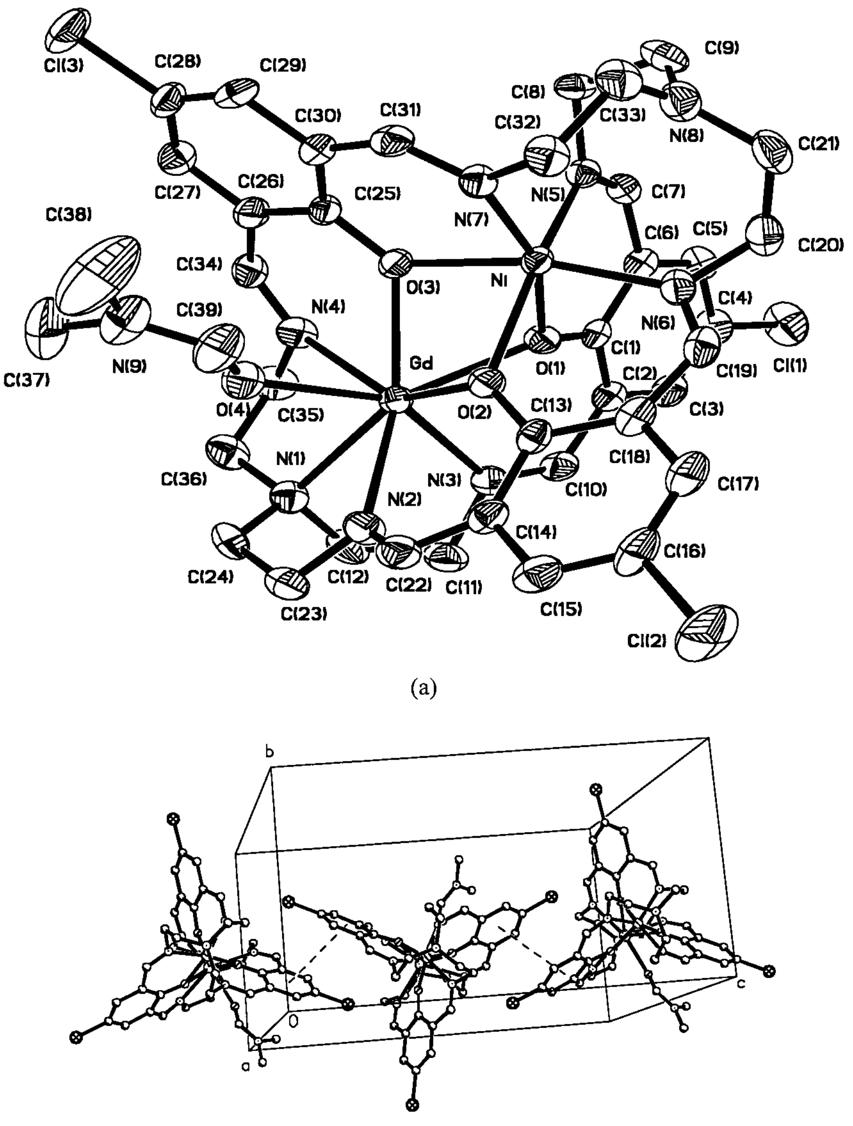

(a)

(b)

Figure 2. (a) The crystal structure of $[GdNiL(DMF)]^{2+}$. (b) A packing diagram.

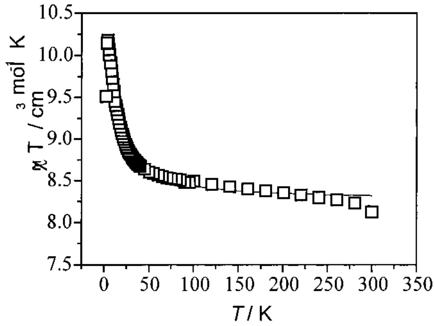

Figure 3. Plot of $\chi_m T$ vs T for $[GdNiL(DMF)](ClO_4)_2$ at 1.9−300 K. Squares: experimental values. Curve: the fitting curve.

octahedral configuration with the Ni(II)−O(phenolate) distance in the range 2.067−2.207 Å and Ni(II)−N(imino) distances in the range 2.046−2.048 Å. The dihedral angle between the planes (O(1)Gd(2)O(2)) and (O(1)NiO(2)) is 54.9°. The dihedral angles between the planes (O(1)GdO(3)) and (O(1)NiO(3)) and that between planes (O(2)GdO(3)) and (O(2)NiO(3)) are 52.9° and 46.2°, respectively. The distance of 9.135 Å between the two bridgehead nitrogen atoms N(1) and N(8) is quite a bit longer than that of mononuclear Gd(III) cryptate (6.963 Å) with the same ligand,[12] implying that the macrocycles are able to be enlarged for inclusion of transition metal ions. The separations between metal ions in neighboring molecules are quite large, namely, Gd···Gd 9.888 Å, Ni···Ni 9.274 Å, Ni···Gd 11.647 Å, suggesting the absence of any significant intermolecular magnetic interactions. The packing diagram of the Gd(III)−Ni(II) complex is shown in Figure 2b. An intermolecular $\pi-\pi$ stack exists. The angle between the benzene ring ($C_{13}-C_{18}$) (symmetry: X, Y, Z) of one molecule and that ($C_{25}-C_{30}$) (symmetry: X, $0.5 - Y$, $-0.5 + Z$) of a neighboring molecule is 12°. The distance between the planes of two neighboring benzene rings is 3.45 Å. The distance of C_{16} to C_{27A} (symmetry: X, $0.5 - Y$, $-0.5 + Z$) is 3.46 Å. The cryptate molecules arrange into a one-dimensional chain along the c-axis and by $\pi-\pi$ stacking.

Magnetic Properties. The plot of $\chi_m T$ versus T (χ_m denotes molar magnetic susceptibility) in the range 1.9−300 K is shown in Figure 3. The effective magnetic moment

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[GdNi(DMF)](ClO_4)_2 \cdot MeCN$

Gd−O(1)	2.331(5)	Gd−N(1)	2.634(6)
Gd−O(2)	2.324(5)	Gd−N(2)	2.487(7)
Gd−O(3)	2.304(4)	Gd−N(3)	2.499(6)
Gd−O(4)	2.388(6)	Gd−N(4)	2.486(6)
Ni−O(1)	2.117(5)	Ni−N(5)	2.081(6)
Ni−O(2)	2.207(5)	Ni−N(6)	2.046(6)
Ni−O(3)	2.067(5)	Ni−N(7)	2.075(6)
Ni−O(1)−Gd	92.26(18)	Ni−O(3)−Gd	94.35(17)
Ni−O(2)−Gd	90.17(17)	N(6)−Ni−O(3)	166.5(2)
N(6)−Ni−N(7)	100.3(2)	O(3)−Ni−N(7)	85.1(2)
N(6)−Ni−N(5)	96.9(2)	O(3)−Ni−N(5)	94.5(2)
N(7)−Ni−N(5)	98.8(2)	N(6)−Ni−O(1)	97.9(2)
O(3)−Ni−O(1)	75.64(18)	N(7)−Ni−O(1)	160.5(2)
N(5)−Ni−O(1)	86.0(2)	N(6)−Ni−O(2)	86.6(2)
O(3)−Ni−O(2)	80.38(18)	N(7)−Ni−O(2)	98.2(2)
N(5)−Ni−O(2)	161.8(2)	O(1)−Ni−O(2)	75.84(18)
O(3)−Gd−O(2)	73.24(16)	O(3)−Gd−O(1)	67.23(16)
O(2)−Gd−O(1)	69.67(17)	O(3)−Gd−O(4)	76.22(18)
O(2)−Gd−O(4)	90.14(19)	O(1)−Gd−O(4)	141.87(18)
O(3)−Gd−N(4)	70.93(18)	O(2)−Gd−N(4)	143.85(18)
O(1)−Gd−N(4)	100.18(19)	O(4)−Gd−N(4)	77.0(2)
O(3)−Gd−N(2)	133.6(2)	O(2)−Gd−N(2)	108.13(19)
O(1)−Gd−N(2)	70.18(18)	O(4)−Gd−N(2)	147.9(2)
O(3)−Gd−N(3)	134.9(2)	O(2)−Gd−N(3)	74.68(19)
O(1)−Gd−N(3)	127.51(19)	O(4)−Gd−N(3)	73.0(2)
N(4)−Gd−N(3)	130.5(2)	N(2)−Gd−N(3)	86.4(2)
O(3)−Gd−N(1)	137.04(18)	O(2)−Gd−N(1)	142.94(18)
O(1)−Gd−N(1)	134.33(19)	O(4)−Gd−N(1)	80.8(2)
N(4)−Gd−N(1)	68.8(2)	N(2)−Gd−N(1)	68.7(2)
N(3)−Gd−N(1)	68.3(2)		

μ_{eff} at 299.8 K is 8.06 μ_B, which is close to the spin-only value (8.43 μ_B) calculated by $\mu_{eff}^2 = \mu_{Ni}^2 + \mu_{Gd}^2$ assuming there is no magnetic interaction between Ni(II) ($S_{Ni} = 1$) and Gd(III) ($S_{Gd} = {}^7/_2$). The μ_{eff} increases from 8.17 μ_B at 299.8 K to the maximum value (9.02 μ_B) at 3.99 K with decreasing temperature and then sharply decreases to 8.72 μ_B at 1.99 K. The maximum value 9.02 μ_B is slightly smaller than the spin-only value (9.95 μ_B) for spin state $S = {}^9/_2$ which arises from ferromagnetic spin-coupling of the present spin system ($S_{Ni} = 1$, $S_{Gd} = {}^7/_2$) assuming both ions having g values 2.0. Therefore the observed magnetic properties show an intramolecular ferromagnetic spin-coupling between Ni(II) and Gd(III). The decrease of $\chi_m T$ values below 3.99 K is due to the effects of zero-field splitting[2a] and of partial magnetic saturation resulting from relatively large magnetic fields. The 4−300 K magnetic data were analyzed on the basis of the spin-only equation derived from a spin Hamiltonian $H = -JS_{Ni}S_{Gd}$; χ_m is expressed as follows:

$$\chi_m T = \frac{N\beta^2 g^2}{3k} \frac{\frac{495}{2} + 126 \exp\left(\frac{-9J}{kT}\right) + \frac{105}{2} \exp\left(\frac{-16J}{kT}\right)}{10 + 8 \exp\left(\frac{-9J}{kT}\right) + 6 \exp\left(\frac{-16J}{kT}\right)} \qquad (1)$$

The best fitting is obtained with $g = 1.99$, $J = 0.56$ cm^{-1}, $R = 9.30 \times 10^{-4}$ ($R = \sum(\chi_{obs}T - \chi_{calc}T)^2/\sum(\chi_{obs}T)^2$ where χ_{cal} and χ_{obs} denote the calculated and observed molar magnetic susceptibilities, respectively). The positive J value is coincident with the intramolecular ferromagnetic interaction. In eq 1, we neglected the effect of zero-field splitting. The smaller ferromagnetic coupling interaction may be due to the larger dihedral angle (OGdO, ONiO).[20]

The ferromagnetic behavior of the Gd(III)−Ni(II) pair is similar to that of the Gd(III)−Cu(II) pair in some complexes. The ferromagnetic contribution of the latter has been attributed to the coupling between the Gd(III)−Cu(II) ground configuration and the Gd(III)−Cu(III) charge transfer excited configuration;[21] we could speculate that both have the similar mechanism suggested by Goodenough.[21]

To date, most of the studies with the magnetic properties of 4f−3d complexes have been limited to the Gd(III)−Cu(II) system. The magnetic properties of Gd(III)−Ni(II) complexes have not been studied in detail. A quantitative analysis of ferromagnetic interaction for a Gd(III)−Ni(II) complex with $J = 3.6$ cm^{-1} has been reported by J.-P. Costes et al. The weak ferromagnetic interaction in our cryptate is significant for relating the structure and magnetic functions of 4f−3d complexes. It is predicated that novel magnetic behavior would be obtained via further modification of the cryptand.

Acknowledgment. The project was supported by the National Natural Science Foundation of China and Lanthanide Materials Chemistry State Key Laboratory Fund of Beijing University.

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010270Y

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