Unprecedented Ferromagnetic Interaction in Homobinuclear Erbium and Gadolinium Complexes: Structural and Magnetic Studies

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Recent papers have shown that the interaction between a gadolinium ion and a second spin carrier (M) is not compulsorily ferromagnetic as suggested earlier for the complexes in which M is an organic radical[1, 2] or a metal ion (Cu^{2+},[3, 4] VO^{2+}[5]). Moreover, little attention has been paid to the fact that the Gd⋯Gd interaction, which is a particular case of Gd⋯M interactions, was found to be antiferromagnetic in all the complexes reported by now.[6–11] It should be noted that the number of di- and polynuclear gadolinium compounds for which structural and magnetic data are available is restricted[12] and that the factors governing the nature and magnitude of the Gd⋯Gd interaction have not been clarified. Here we report two lanthanide(III) dimers—namely $[LnL_3(H_2O)_n]_2 \cdot x H_2O$ with Ln = Er (**1**; $n=2$, $x=4$) and Gd (**2**; $n=1$, $x=0$), and HL = salicylic acid—that display an unprecedented ferromagnetic behavior. Well-shaped crystals of **1** have been obtained, which allows a structural study to be performed.[14]

The molecular structure of **1** is shown in Figure 1. Obviously the molecular entity is binuclear and possesses an inversion center while the previously published lanthanide salicylate complexes are polynuclear.[15–17] Of the six salicylato anions, four are acting as bridging ligands through their carboxylato groups; two function in the usual η^1:η^1:μ_2 mode whereas the two other bridge in the less common η^2:η^1:μ_2 fashion.[18] In the latter case one oxygen atom (O2, O2′) is terminally bound to the related erbium ions (Er, Er′) and the second oxygen (O1, O1′) is involved in a monoatomic bridge between the two lanthanide ions. Each of the two remaining anions chelates a metal ion (Er and Er′). As a result of the inversion center the Er(O1, O1′)Er′ double bridging network is perfectly planar. The second bridge through the atoms O4, Er, O5′, O4′, Er′, and O5 is not planar. The dihedral angle between the two planes Er(O1, O1′)Er′ and Er(O4, O4′)Er′ is equal to 81.58(4)° whereas the erbium ions are separated by 4.0093(2) Å. The coordination of each lanthanide ion is completed to nine by two water molecules and one bidentate chelating carboxylato group. It should be noted that the phenolic OH function of the ligand is not involved in any coordination sphere. The bridging network present in **1** is original for salicylate bridges but not unprecedented if we consider the acetate bridges. An almost identical core has yet been observed in the structure of $[Ce_2(CH_3COO)_6(bipy)_2]$[6] (bipy = 2,2′-bipyridine) and extended to the related gadolinium complex (these complexes are numbered **3** and **4**, respectively, in the following text). The dinuclear units are well isolated from each other, with intermolecular distances greater than 6 Å.

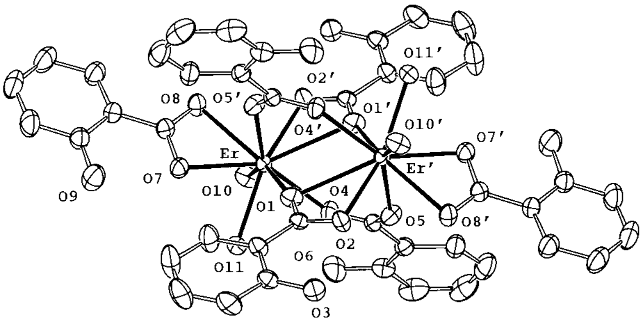

Figure 1. Zortep plot of **1** (thermal ellipsoids for 50% probability). Hydrogen atoms are omitted. Selected bond lengths [Å]: Er-O1 2.282(2), Er-O2′ 2.353(2), Er-O5′ 2.329(2), Er-O8 2.492(2), Er-O11 2.377(2), Er-O4 2.349(2), Er-O1′ 2.724(2), Er-O7 2.354(2), Er-O10 2.360(2), Er′-O1 2.724(2), Er′-O2 2.353(2), Er′-O5 2.329(2).

As we have not succeeded in obtaining crystals of **2**, a wide-angle X-ray scattering study (WAXS) has been performed to check the similarity of the structures **1** and **2**. Indeed a comparison of the experimental RDF for **2** and the calculated one for **1**, extracted from the WAXS data (Figure S3, Supplementary Material) clearly shows that a very good agreement is obtained for distances lower than 8 Å. As an example, the Ln⋯Ln distance, equal to 4.00 Å in **1**, is now equal to 4.25 Å in **2**, as a result of the lanthanide contraction on going from the lighter to the heavier Ln ions. The difference appearing beyond 8 Å suggests that the two complexes are not isostructural. This is not really surprising if we remember that the number of water molecules linked to the Ln center is different for **1** and **2** (two for **1** and one for **2**). Nevertheless, this study confirms the dimeric structure of the gadolinium complex **2**.

The thermal variation of the $\chi_M T$ product (χ_M = molar magnetic susceptibility) for **1** is shown in Figure 2. At 300 K, $\chi_M T$ is equal to 22.2 $cm^3 mol^{-1} K$ which is the value expected for two magnetically insulated Er^{3+} ions in the $^4I_{15/2}$ ground state. As the temperature is lowered, $\chi_M T$ decreases down to 4 K. At that temperature, it reaches a minimum of 12.0 $cm^3 mol^{-1} K$ and then increases as T is further lowered.

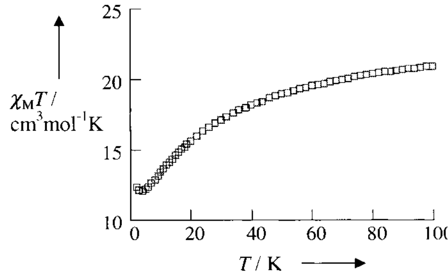

Figure 2. Temperature dependence of $\chi_M T$ for **1** at 0.1 T.

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The decrease in $\chi_M T$ undoubtedly originates in the thermal depopulation of the highest Stark components resulting from the splitting of the free ion ground state $^4I_{15/2}$ by the crystal field. The profile of the $\chi_M T$ vs. T curve at low temperature indicates that the effects of the depopulation of the Stark levels conflict with an antagonist process. In keeping with the structural data, this additional process must be an intramolecular ferromagnetic interaction between the lanthanide ions, both of which are most probably in a local ground Kramers doublet state. As noticed above, intermolecular interactions have to be excluded because the dinuclear units are well isolated from each other. Furthermore, there is no pathway to transmit a magnetic interaction between these dinuclear units.

This situation is simpler in the case of **2** since Gd^{3+} has an $^8S_{7/2}$ ground state without first-order orbital momentum. At 300 K, $\chi_M T$ (Figure 3) is equal to 15.7 $cm^3 mol^{-1} K$ which is the value attributable to two noninteracting spin carriers, each being characterized by $S = 7/2$ and $g = 2.0$. Lowering the temperature causes $\chi_M T$ to increase. A value of 18.9 $cm^3 mol^{-1} K$ is reached at 2 K. Fitting the experimental data to the equation[6] deduced from the isotropic spin Hamiltonian $\mathcal{H} = -J S_{Gd1} S_{Gd2}$ yields $J = 0.05\ cm^{-1}$ and $g = 1.98$, with an agreement factor R equal to 2.0 10^{-3} ($R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2 / \Sigma[(\chi_M T)_{obs}]^2$). The unexpected ferromagnetic nature of the Gd⋯Gd interaction is further supported by magnetization measurements in the 0–5 T range at 2 K (Figure 4). The experimental values of M are fairly well reproduced by the Brillouin function that corresponds to the parameters extracted from the static susceptibility data (Figure 4, full line). In addition, this line is comprised in between the two dashed lines that correspond to (A) two uncoupled Gd centers and (B) to a $S = 7$ state, which confirms the weak ferromagnetic correlation between the two gadolinium ions. This conclusion contrasts with previous findings which unanimously document the occurrence of an antiferromagnetic ground state in homopolynuclear gadolinium complexes,[6–12] in which the coupling constants vary from -0.05 to $-0.21\ cm^{-1}$. The most impressive comparison concerns complexes **2** and **4**. Although both complexes are bridged by carboxylato groups, the two gadolinium ions do present opposite magnetic interactions. At that stage, that is, without structural determinations, we cannot indicate which structural differences are responsible for the sign reversal of the interaction. A similar situation has been reported for (Cu, Gd)[3, 4] and (VO, Gd)[5] complexes, which suggests that in all these species the observed coupling results from a delicate balance between two contributions of opposite signs and slightly different magnitudes. Work is in progress to design and characterize new examples of ferromagnetic Gd⋯Gd interactions for a better understanding of the interaction mechanism.

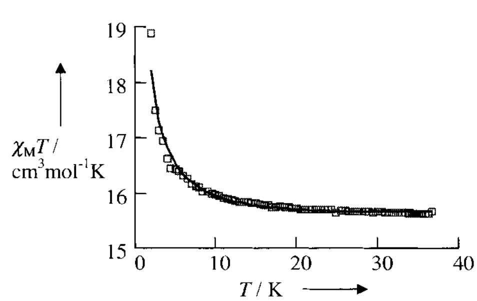

Figure 3. Temperature dependence of $\chi_M T$ for **2** at 0.1 T. The solid line represents the best fit (see text).

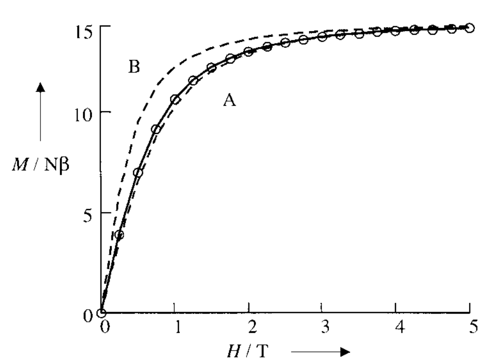

Figure 4. Field-dependent magnetization of **2** at 2 K (circles). The solid line corresponds to the Brillouin function for the parameters extracted from the static susceptibility data (see text) and the dashed lines represent the Brillouin function for (A) two uncoupled Gd centers and (B) an $S = 7$ state.

Experimental Section

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C,H,N) were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse. Magnetic susceptibility data were collected on powdered samples of the different compounds with 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.[19] Amorphous powder of **2** was sealed in a Lindemann capillary. The scattering diffusion spectrum of the samples irradiated with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) was obtained using a LASIP diffractometer.[20]

$[L_6Gd_2] \cdot 2H_2O$: After stirring a mixture of salicylic acid (1.38 g, 10 mmol) and lithium hydroxide hydrate (0.42 g, 10 mmol) in methanol (40 mL) for ten minutes a solution of gadolinium nitrate $Gd(NO_3)_3 \cdot 5H_2O$ (1.50 g, 3.4 mmol) dissolved in water (30 mL) was added. The resulting solution was heated and concentrated for 30 minutes to yield a white precipitate. After cooling, the precipitate was filtered off and washed with water/methanol (1:1), acetone, and diethyl ether. Yield: 1.5 g (77 %). Anal. calcd for $C_{42}H_{34}Gd_2O_{20}$: C 43.0, H 2.9, Gd 26.8; found: C 42.6, H 2.7, Gd 26.7.

$[L_6Er_2] \cdot 8H_2O$: This compound was prepared following the experimental procedure described above. Yield: 1.0 g (48 %). Anal. calcd for $C_{42}H_{46}Er_2O_{26}$: C 38.8, H 3.6, Er 25.7; found: C 38.6, H 3.4. In another experiment, the mother solution was set aside. Three days later, crystals suitable for X-ray analysis could be isolated.

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[1] C. Lescop, D. Luneau, E. Belorisky, P. Fries, M. Guillot, P. Rey, *Inorg. Chem.* **1999**, *38*, 5472.

[2] A. Caneschi, A. Dei, D. Gatteschi, L. Sorace, K. Vostrikova, *Angew. Chem.* **2000**, *112*, 252; *Angew. Chem. Int. Ed.* **2000**, *39*, 246.

[3] J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **2000**, *39*, 169.

[4] J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **2000**, *39*, 5994.

[5] J. P. Costes, F. Dahan, B. Donnadieu, J. Garcia-Tojal, J. P. Laurent, *Eur. J. Inorg. Chem.* **2001**, 363.
[6] A. Panagiotopoulos, T. F. Zafiropoulos, S. P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis, C. P. Raptopoulou, *Inorg. Chem.* **1995**, *34*, 4918, and references therein.
[7] R. Hedinger, M. Ghisletta, K. Hegetschweiler, E. Toth, A. E. Merbach, R. Sessoli, D. Gatteschi, V. Gramlich, *Inorg. Chem.* **1998**, *37*, 6698.
[8] J. P. Costes, F. Dahan, F. Nicodème, *Inorg. Chem.* **2001**, *40*, 5285.
[9] S. Liu, L. Gelmini, S. J. Rettig, R. C. Thompson, C. Orvig, *J. Am. Chem. Soc.* **1992**, *114*, 6081.
[10] P. Guerriero, S. Tamburini, P. A. Vigato, C. Benelli, *Inorg. Chim. Acta* **1991**, *189*, 19.
[11] J. P. Costes, A. Dupuis, J. P. Laurent, *Inorg. Chim. Acta* **1998**, *268*, 125.
[12] To our knowledge, the two sets of data have been reported for a binuclear species,[9] for $[Gd_2(thd)_6]$ (thd = 2,2,6,6-tetramethylheptanedionato)[11] (see ref. [13] for the structural determination) and for two trinuclear complexes.[7,8] In all compounds, the ground state is antiferromagnetic with J values between -0.045 and $-0.21\ cm^{-1}$.
[13] I. Baxter, S. R. Drake, H. B. Hursthouse, K. M. Abdul Malik, J. McAleese, D. J. Otway, J. Plakatouras, *Inorg. Chem.* **1995**, *34*, 1384.
[14] Crystal structure analysis: The data were collected on an Enraf-Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation. The structure was solved using Patterson techniques (SHELXS97) and refined on F^2 (SHELXL-97). **1**: $C_{42}H_{46}Er_2O_{26}$, $M_r = 1301.31$, triclinic, space group $P\bar{1}$, $a = 9.9231(11)$, $b = 14.313(2)$, $c = 9.4312(13)$ Å, $\alpha = 91.663(16)$, $\beta = 115.677(14)$, $\gamma = 99.054(13)^\circ$, $V = 1185.0(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.823\ Mg\,m^{-3}$, $F(000) = 642$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 3.608\ mm^{-1}$, $T = 293$ K, crystal size $0.45 \times 0.35 \times 0.20$ Å^3. 5153 collected reflections are unique; max./min. residual electron density $0.837/-0.682$ eÅ^3, $R1 = 0.0158$ ($F_o^2 > 2\sigma(F_o^2)$, wR2 = 0.0434 (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163647. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[15] J. H. Burns, W. H. Baldwin, *Inorg. Chem.* **1977**, *16*, 289.
[16] M. Jian-Fang, J. Zhong-Sheng, N. Jia-Zuan, *Chin. J. Struct. Chem.* **1991**, *10*, 125.
[17] M. A. Nabar, S. D. Barve, *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 341.
[18] See, for example: A. Ouchi, Y. Suzuki, Y. Ohki, Y. Koizumi, *Coord. Chem. Rev.* **1988**, *92*, 29.
[19] P. Pascal, *Ann. Chim. Phys.* **1910**, *19*, 5.
[20] The LASIP diffractometer has a geometry specially set up for scattering measurements. It minimizes every external parasite scattering phenomenon. Experimental details are given in the Supplementary Material.

Foldamers as Dynamic Receptors: Probing the Mechanism of Molecular Association between Helical Oligomers and Rodlike Ligands[**]

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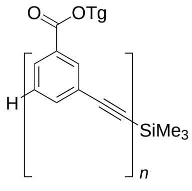
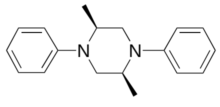
The helix is one of the most significant structural motifs observed in biological[1] and synthetic[2] polymers. We have previously shown that *m*-phenylene ethynylene oligomers **1** exhibit unique helical structures in polar solvents[3] and possess a cavity which can bind hydrophobic molecules.[4] The rodlike ligand **2** exhibited affinities to **1** that were dependent on either the length of the oligomer or the height of the helical cavity. The association constants rose steadily as the length of the oligomer increased from the decamer to the octadecamer but then reached a plateau, with a weak maximum at the icosamer. Only nonspecific, nondirectional solvophobic interactions stabilize these complexes.



1 (*n* = 16, 18, 20, 22, 24)



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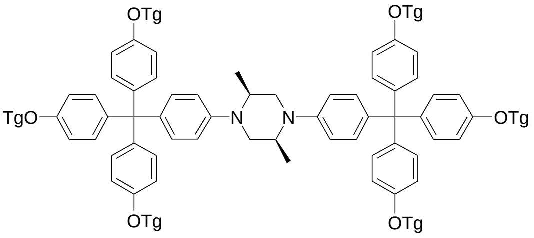

3: Tg = $(CH_2CH_2O)_3CH_3$

Intuitively, a capped rod, namely, a dumbbell-shaped ligand, may exhibit greater specificity by blocking the strong binding of oligomers which are too long to fit between the caps. However, the ability of capped rods to function as ligands depends on the presence of a kinetically accessible complexation pathway. Two possible limiting mechanisms can be imagined in a polar solvent that favors the folded state of **1**:

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