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Unprecedented Antiferromagnetic Metal−Ligand Interactions in Gadolinium−Nitroxide Derivatives

Christophe Lescop,[†] Dominique Luneau,[†] Elie Belorizky,[‡] Pascal Fries,[†] Maurice Guillot,[§] and Paul Rey*,[†]

CEA-Département de Recherche Fondamentale sur la Matière Condensée, Service de Chimie Inorganique et Biologique, Laboratoire de Chimie de Coordination (URA CNRS No. 1194), 38054 Grenoble cedex 09, France, Laboratoire de Spectrométrie Physique (CNRS-UMR 5588), Université Joseph Fourier Grenoble 1, BP 87, 38402 Saint Martin d'Hères cedex, France, and Laboratoire des Champs Magnétiques Intenses, CNRS-Max Planck Institut für Festköperforschung, 25 avenue des Martyrs, 38042 Grenoble cedex 09, France

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Studies aimed at understanding the coupling mechanism in paramagnetic rare earth complexes involving other spin carriers are mainly restricted to gadolinium(III) derivatives including $S = {}^1/_2$ species such as copper(II)[1−5] or vanadyl(II)[6] metal centers or nitroxide free radicals.[7−11] Consistently, in all species studied so far, the intramolecular interaction between the gadolinium ion and the other spins has been found weak and ferromagnetic. To justify the preferred parallel alignment of the spins in nitroxide-containing complexes, it has been proposed that a fraction of the organic spin is transferred into empty (5d or 6s) metal orbitals which are orthogonal to the 4f singly occupied orbitals.[2,4]

In contrast to these previous findings, we have characterized eight-coordinate complexes involving four nitroxide ligands which unambiguously document an unexpected antiferromagnetic metal−radical interaction as shown by magnetic susceptibility and magnetization measurements.

The chelating nitroxide ligands **1**, 2-(2-benzimidazolyl)-4,4,5,5-tetramethylimidazolidinyl-1-oxy-3-oxide, (NITBzImH),[12] and **2**, its 2-(4-methylbenzimidazolyl)-substituted analogue (NITMe-BzImH), react with $Gd(ClO_4)_3 \cdot 6H_2O$ in tetrahydrofuran (THF) containing 2% of water leading to the eight-coordinate complexes $Gd(NITBzImH)_4 \cdot (ClO4)_3 \cdot 2THF \cdot 2H_2O$ (**3**) and $Gd(NITMeBzImH)_4 \cdot (ClO_4)_3 \cdot 2THF \cdot 2H_2O$ (**4**).[13]

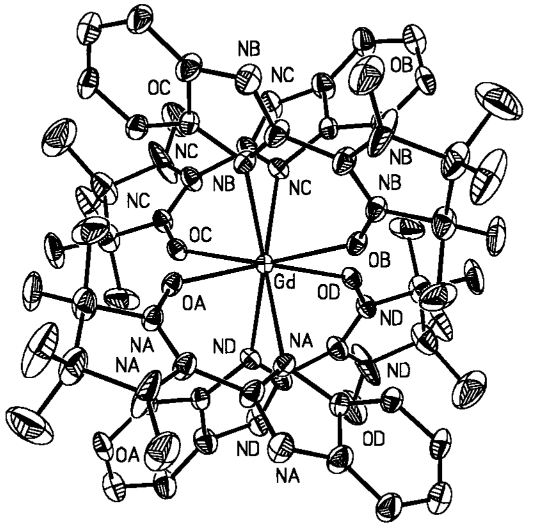

Figure 1. Molecular structure of $[Gd(NITBzImH)_4]^{3+}$((A) *x, y, z*; (B) $-x, 1-y, z$; (C) $-x, y, {}^1/_2-z$; (D) $x, 1-y, {}^1/_2-z$). Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Gd−Oi = 2.352(6), Gd−Ni = 2.582(6), N−O = 1.274(10), OA−OB = OC−OD = 3.867(11), OA−OC = OB−OD = 2.808(10); OA−Gd−OB = 110.0(3), OA−Gd−OC = 162.9(3),-OB−Gd−OD = 72.7(3).

As shown in Figure 1, the cationic fragment of **3** shows the expected eight-coordinate metal environment which can be approximated as distorted rhombohedral.[14] The highly symmetrical metal coordination sphere exhibits bond distances and angles within the range generally observed in related compounds[10,11] and needs no further comment. Particularly interesting is the presence of numerous molecules of THF and water in the crystal lattice which, with the help of the perchlorate anions, well shield the metal−nitroxide cation fragments from significant intermolecular magnetic interactions. Indeed, the uncoordinated NO groups are not engaged in hydrogen bonding and are separated by distances larger than 9.8 Å. All attempts to grow single crystals of **4** were unsuccessful, and X-ray diffraction patterns showed that **4** is not isomorphous with **3**. Nevertheless, owing to the same composition involving solvent molecules in the crystal lattice, a similar eight-coordinate coordination sphere and the same situation of well-isolated cationic fragments was assumed in **4**. Accordingly, for both compounds the magnetic data were analyzed considering isolated $[Gd(nitroxide)_4]^{3+}$ species.

The temperature dependence of $1/\chi_M$ and $\chi_M T$ is displayed in Figure 2 for both compounds. The linear dependence of $1/\chi_M$ at high temperature ($C = 9.43$ cm^3 K mol^{-1}) is consistent with independent spins; it extrapolates to negative θ values ($\theta =$

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* Author to whom correspondence should be addressed. E-mail: rey@drfmc.ceng.cea.fr.

[†] Laboratoire de Chimie de Coordination.

[‡] Université Joseph Fourier Grenoble 1.

[§] CNRS-Max Planck Institut für Festköperforschung.

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

(2) Benelli, C.; Caneschi, A.; Guillou, O.; Pardi, L.; Gatteschi, D. *Inorg. Chem.* **1990**, *29*, 1750.

(3) Sanz, J. L.; Ruiz, R.; Gleizes, F.; Lloret, F.; Fans, J.; Julve, M.; Borras-Alvenar, J. J.; Journeaux, Y. *Inorg. Chem.* **1996**, *35*, 7384.

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

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

(6) Costes, J.-P.; Dupuis, A.; Laurent, J.-P. *J. Chem. Soc., Dalton Trans.* **1998**, 735.

(7) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913.

(8) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1989**, *28*, 275.

(9) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1990**, *29*, 4223.

(10) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1992**, *31*, 741.

(11) Sutter, J.-P.; Kahn, M. L.; Golhen, S.; Ouahab, L.; Kahn, O. *Chem.—Eur. J.* **1998**, *4*, 571.

(12) Fegy, K.; Luneau, D.; Ohm, T.; Paulsen, C.; Rey, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1270.

(13) The reaction consisted of 40 mg (7×10^{-5} mol) of $Gd(ClO_4)_3 \cdot 6H_2O$ and 80 mg (29×10^{-5} mol) of ligand **1** (or **2**) in 20 mL of anhydrous THF. Then 40 μL of H_2O was added to the blue solution. The crystalline material which formed in 2 days was filtered off (93 mg, 70%, 240 °C, decomposition). Anal. Found/calcd for **3**, $C_{64}H_{88}N_{16}Cl_3O_{24}Gd$: C44.55/44.46, H5.25/5.13, N12.70/12.96, Cl6.03/6.15, Gd8.91/9.09. Found/calcd for **4**, $C_{68}H_{96}N_{16}Cl_3O_{24}Gd$: C44.85/45.75, H5.36/5.42, N12.23/12.55, Cl6.01/5.96, Gd8.63/8.81.

(14) **3**,_$[Gd(NITImBzH)_4](ClO_4)_3 \cdot 2THF \cdot 2H_2O$, *M* = 1729.1, space group: *P*42*c*, *a* = *b* = 16.0682(4) Å, *c* = 18.7190(6) Å, *V* = 4833.0(2) Å^3, *Z* = 2. Refinement on F^2 converged to *R* = 0.073.

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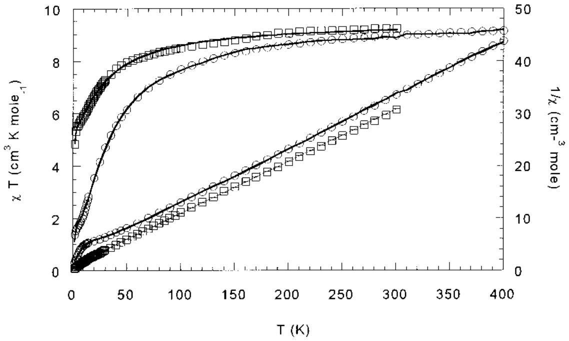

Figure 2. Temperature dependence of $\chi_m T$ and $1/\chi_m$ for **3** (□) and **4** (○). Solid lines are calculated with the parameters reported in the text.

$-7.4(4)$ K for **3** and $\theta = -27.6(5)$ K for **4**) indicating that, in both cases, dominant antiferromagnetic interactions are operative. The temperature dependence of $\chi_m T$ for both compounds decreases continuously, tends to a limit ($\approx$5.8 and 2 cm^3 K mol^{-1} for **3** and **4**, respectively), and then decreases again. These features suggest that the gadolinium−nitroxide interaction is antiferromagnetic and that the limit corresponds to the ground spin state of the complex ($S = {}^7/_2$ for **3** and $S = {}^3/_2$ for **4**). These data were analyzed considering an isotropic Hamiltonian, involving Gd−nitroxide and nitroxide−nitroxide interactions. On the basis of the structural study of **3**, only one Gd−nitroxide interaction ($J_{\mathrm{Gd-NO}}$) was considered, but two coupling schemes between the nitroxide ligands were taken into account ($g = 2$, $H = -J\mathbf{S}_i\cdot\mathbf{S}_j$).[15] (i) The coordination sphere was assumed to have T_d symmetry leading to a single nitroxide−nitroxide interaction. The best fit parameters are as follows: **3**, $J_{\mathrm{Gd-NO}} = -1.8(3)$ cm^{-1}, $J_{\mathrm{NO-NO}} = -7.2(5)$ cm^{-1}; **4**, $J_{\mathrm{Gd-NO}} = -3.8(2)$ cm^{-1}, $J_{\mathrm{NO-NO}} = -5.6(2)$ cm^{-1}. (ii) Since short OA−OC and OB−OD distances (2.808 Å) are observed[16] within the coordination sphere, two different nitroxide−nitroxide coupling constants, $J_{\mathrm{AC}} = J_{\mathrm{BD}} = J_{\mathrm{1NO-NO}}$ and $J_{\mathrm{AB}} = J_{\mathrm{CD}} = J_{\mathrm{2NO-NO}}$, were introduced in the calculations. This model affords the following parameters: **3**, $J_{\mathrm{Gd-NO}} = -1.7(2)$ cm^{-1}, $J_{\mathrm{1NO-NO}} = -6.7(3)$ cm^{-1}, $J_{\mathrm{2NO-NO}} = -4.9(6)$ cm^{-1}; **4**, $J_{\mathrm{Gd-NO}} = -3.9(2)$ cm^{-1}, $J_{\mathrm{1NO-NO}} = J_{\mathrm{2NO-NO}} = -4.9(3)$ cm^{-1}. One can note that the value of the antiferromagnetic Gd−nitroxide coupling constant is almost independent of the internitroxide coupling scheme and, importantly, whatever the model, for both compounds no satisfactory agreement could be reached constraining $J_{\mathrm{Gd-NO}}$ to be ferromagnetic.

Confirmation of an antiferromagnetic $J_{\mathrm{Gd-NO}}$ coupling comes from measurements of the magnetization in the 0−5.5 T range at 2, 4.2, 7, and 10 K which are fairly well reproduced with the set of parameters extracted from the susceptibility data; in addition, the data collected at 2 K nicely reached constant values at 5 T of $\approx 7\ \mu_B$ for **3** and $\approx 3\ \mu_B$ for **4**. Finally, for compound **4** data were collected at 4.2 K up to a field of 20 T. One does observe an increase of the magnetization which reaches a value larger than 5 μ_B. It is thus concluded that compounds **3** and **4** are the first genuine gadolinium(III)−nitroxide complexes where the metal−radical interaction is antiferromagnetic.

A theoretical model was recently reported[4] which focuses on the efficiency of excited charge-transfer configurations to stabilize a ground high-spin state in gadolinium−copper(II) species. It also applies to gadolinium−nitroxide complexes since it relies on energetic characteristics such as ionization potentials which are similar for copper(II) ions and nitroxides.[17,18] However, the structures of both types of complexes are dramatically different particularly because nitroxides are directly bound to the metal while copper(II)−gadolinium interactions are mediated by ancillary organic fragments. Therefore, among the different mechanisms which might be operative, the Heitler−London interaction within the ground state may bring a more important contribution in species involving nitroxides. Probably, the nature of the gadolinium−nitroxide interaction is the result of a delicate balance between two opposite contributions and may in some circumstances be antiferromagnetic. Polarized neutron diffraction experiments and DFT calculations which are under way will bring insight into the coupling mechanism in Gd−nitroxide derivatives.

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Supporting Information Available: Tables of crystallographic data including diffractometer and refinement data, atomic coordinates, bond lengths, bond angles and anisotropic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Model i: The Hamiltonian and the expression of the magnetic susceptibility were taken from ref 3. Model ii: The following Hamiltonian $H = -2J\mathbf{S}_{\mathrm{Gd}}\cdot(\mathbf{S}_A + \mathbf{S}_B + \mathbf{S}_C + \mathbf{S}_D) - 2J_1(\mathbf{S}_A\cdot\mathbf{S}_C + \mathbf{S}_B\cdot\mathbf{S}_D) - 2J_2(\mathbf{S}_A\cdot\mathbf{S}_B + \mathbf{S}_C\cdot\mathbf{S}_D)$ was exactly diagonalized providing the energy $E_{\alpha,s}$ of the multiplets. The magnetic susceptibility was derived from the usual Van Vleck expression, and the magnetization was obtained from the relation $M = kT\,\mathrm{d}(\ln Z)/\mathrm{d}H$ where $Z = \Sigma_{\alpha,s,M} \exp(-E_{\alpha,s,M}/kT)$ and $E_{\alpha,s,M} = E_{\alpha,s} + g\mu_B HM$.

(16) Analogous complexes of lanthanum were obtained but not structurally characterized. Although they exhibit the same stoichiometry, they are not isomorphous to **3** or **4**. Their magnetic properties are consistent with model ii.

(17) Roe, S. P. *J. Coord. Chem.* **1973**, *3*, 187.

(18) Morishima, I.; Yoshikawa, K.; Yonezawa, T.; Matsumoto, H. *Chem. Phys. Lett.* **1972**, *16*, 336.