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Antiferromagnetic Coupling in a Gadolinium(III) Semiquinonato Complex**

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Rare earth ions have long been exploited to influence the properties of magnets by introducing anisotropic contributions and by changing the compensation temperature.^[1] In general little is known about the nature of the exchange interactions of rare earth ions among themselves and with other magnetic groups, because until recently few simple compounds containing magnetically coupled f-block ions were available. Recently, complexes of lanthanide ions with various paramagnetic ligands, ranging from metal complexes to organic radicals, were reported.^[2–6] In particular gadolinium(III) complexes exhibited ferromagnetic couplings ranging from 0.5 to 10 cm^{−1}. The rather unexpected sign of the coupling was explained by a mechanism in which the magnetic orbitals of the paramagnetic ligands have negligible overlap with the 4f orbitals, but overlap with the empty d and s orbitals of gadolinium polarizes the f electrons with their spins parallel to that of the paramagnetic ligand.^[7,8]

Some exceptions to ferromagnetic coupling were recently reported for copper(II) complexes and nitronyl nitroxide radicals.^[9,10] An antiferromagnetic coupling of 6 cm^{−1} was

observed in a chelating nitronyl nitroxide triazole derivative. This suggests that the observed coupling is actually the sum of two contributions, one from the direct overlap of the magnetic orbitals of the ligands with the f orbitals, which presumably results in antiferromagnetism, and the other from the overlap with the s and d orbitals, which leads to ferromagnetism. The former may become dominant when the radical ligands are stronger donors. Therefore we investigated the coupling of gadolinium(III) with semiquinonates, which are much better ligands than nitroxide-type radicals.

The complex [Gd(Hbpz₃)₂(dtbsq)] · 2CHCl₃ (**1**; Hbpz₃ = hydrotris(pyrazolyl)borate; dtbsq = 3,5-di-*tert*-butylsemiquinonato) was obtained by metathetical reaction between the parent metal benzoato derivative^[11] and 3,5-di-*tert*-butylcatechol in alkaline methanol. Recrystallization from chloroform/hexane yielded blue crystals of **1**.

Cyclic voltammetry experiments in acetonitrile showed that **1** undergoes a reversible one-electron redox process at −0.65 V and an irreversible process at +0.02 V versus ferrocene/ferrocenyl cation (Fc/Fc⁺). Both processes involve the coordinated dioxolene ligand, and the reversible one is assigned to the semiquinonato/catecholato couple, and the irreversible one to the quinone/semiquinonato couple. Given the electrochemical properties of other metal *o*-dioxolene complexes,^[12,13] this behavior is as expected when the different charge density of the metal acceptor is taken into account. The electronic spectrum shows a band at 12600 cm^{−1} and a pattern of bands in the region 26400–28400 cm^{−1}, which were suggested^[12] to be internal transitions of the semiquinonato ligand.

Figure 1 shows the X-ray crystal structure of **1**.^[14] The coordination sphere around gadolinium comprises six nitro-

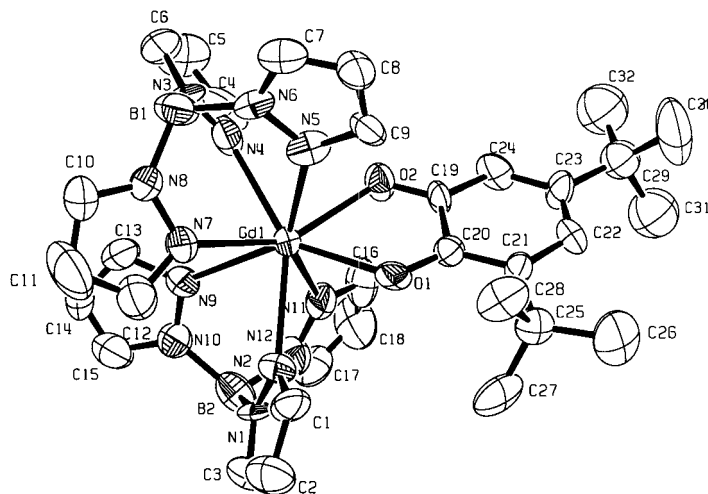
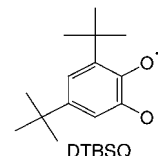


Figure 1. ORTEP view of complex **1** (50% probability thermal ellipsoids); hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Gd1–O1 2.343(9), Gd1–O2 2.354(12), Gd1–N4 2.48(2), Gd1–N2 2.503(14), Gd1–N11 2.53(2), Gd1–N7 2.53(2), Gd1–N5 2.571(11), Gd1–N9 2.585(14), C19–C20 1.49(2), O1–C20 1.27(2), O2–C19 1.25(2); O1–Gd1–O2 67.7(6), O2–Gd1–N4 81.5(5), O1–Gd1–N2 73.1(5), O1–Gd1–N11 88.8(5), O2–Gd1–N11 73.8(5), N2–Gd1–N11 72.9(6), N4–Gd1–N7 79.5(6), N2–Gd1–N7 78.5(5), O1–Gd1–N5 75.6(4), O2–Gd1–N5 78.7(6), N4–Gd1–N5 72.3(5), N7–Gd1–N5 71.3(6), N4–Gd1–N9 75.4(5), N2–Gd1–N9 74.4(5), N11–Gd1–N9 69.3(5), N7–Gd1–N9 72.1(5).

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gen atoms of pyrazolylborate ligands and two oxygen atoms of the semiquinone. The eight-coordinate Gd atom lies in a distorted square-antiprismatic environment, in which O1, N5, N2, N7 lie approximately on one face, and N9, N4, N11, O2 on the other. The asymmetric unit is the whole molecule, and each molecule crystallizes with two molecule of chloroform. The C–O bond lengths are slightly shorter and the C19–C20 distance slightly longer than those usually observed in semiquinonato metal complexes.^[15]

The magnetic susceptibility of **1** was measured in the temperature range 2–245 K with a SQUID susceptometer in applied magnetic fields of 1000 and 10000 Oe (Figure 2). The χT value at high temperature (ca. 7.9 emu K mol^{−1} at 245 K) is

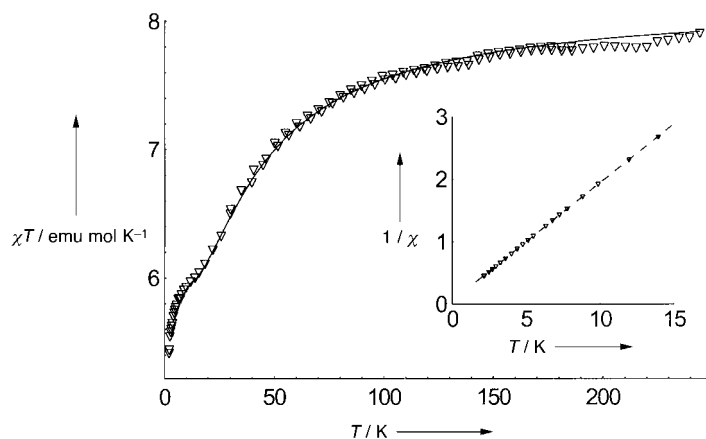


Figure 2. Temperature dependence of χT for **1**. The solid line represents the best-fit curve (see text for parameters). The inset shows the plot of $1/\chi$ versus T at low temperature; the dashed line is the best-fit curve under the assumption of Curie–Weiss behavior.

slightly lower than expected for Curie behavior of uncorrelated spins of 7/2 and 1/2 with $g = 2.00$ (8.25 emu K mol^{−1}); hence, the two centers are still weakly interacting at this temperature. On lowering the temperature, χT decreases, and this suggests antiferromagnetic interactions between the two spin carriers, which give rise to an $S = 3$ ground state and an $S = 4$ excited state. The decrease of χT to a value below that expected for an $S = 3$ state (5.98 emu K mol^{−1}) at $T < 10$ K can be attributed to zero-field splitting (ZFS) effects or to a weak antiferromagnetic interaction between neighboring molecules.

The χT versus T curve in the range 10–245 K was reproduced by assuming antiferromagnetic coupling between the two centers and by using the Hamiltonian $H = -JS_1 \cdot S_2 + g\mu_B \mathbf{H} \cdot \mathbf{S}$. The best fit to the experimental data was obtained with $J = -11.4$ cm^{−1}, $g_{\text{SQ}} = 2.00$, $g_{\text{Gd}} = 1.99$ (Figure 2).

The possibility that the decrease in χT at low temperature is a ZFS effect was ruled out by the field-dependent magnetization curves up to 7 T, measured at 2.15 K and 4.5 K (Figure 3). The experimental data are reproduced well by the Brillouin function for an $S = 3$ system without any ZFS effects. Preliminary X-band EPR spectra also show evidence for only a small ZFS ($D < 0.2$ cm^{−1}).

The decrease of χT to a value below that expected for an $S = 3$ ground state could then be explained by the existence of

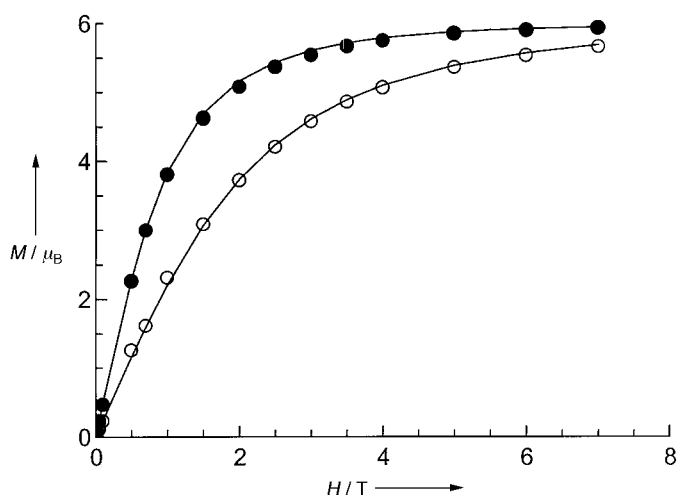


Figure 3. Field-dependent magnetization of **1** at 2.15 K (filled circle) and 4.5 K (empty circle). The lines represent the Brillouin function for an $S = 3$ state at the two temperatures.

small antiferromagnetic interactions between neighboring molecules. The plot of $1/\chi$ versus T in the low temperature range (inset of Figure 2) is in agreement with this hypothesis: it obeys a Curie–Weiss law with a small negative constant θ (−0.28 K) and a C value that compares quite well with what expected for an $S = 3$ state. The small value of θ is in agreement with the large distances between magnetic centers of neighboring molecules (Gd ⋯ Gd 9.64, Gd ⋯ O 7.53, O ⋯ O 7.33 Å).

The observed coupling confirms the prediction that stronger ligands may give rise to effective antiferromagnetic couplings with gadolinium. It is the strongest so far reported, in agreement with the fact that semiquinonato is the strongest paramagnetic ligand so far investigated with gadolinium(III). Comparing this value with those of other ions, such as iron(III), reveals the weakness of the metal–radical interaction for the rare earth element. Values of J for iron(III) semiquinonato complexes are at least about 600 cm^{−1},^[16] that is, more than an order of magnitude larger. However the present results show that moderate couplings can be obtained between rare earth atoms and semiquinonato ligands. We are now investigating the properties of mono-, bis-, and tris-semiquinonato complexes of rare earth elements.

Experimental Section

1: Solid KOH (0.112 g, 2 mmol) was added to a suspension of [Gd(Hbpz₃)₂(PhCOO)] (1.410 g, 2 mmol) and 3,4-di-*tert*-butylcatechol (0.444 g, 2 mmol) in anhydrous methanol (15 mL). The mixture was stirred in air for 20 min, the deep blue-green solution was filtered, and methanol was evaporated under reduced pressure. The precipitate was dissolved in CHCl₃/hexane (1/10; 30 mL), and the solution was filtered and stored for two weeks at about −5 °C. The precipitate was washed with cold hexane and well-shaped blue-green crystals of **1** were obtained. Elemental analysis calcd (%) for [Gd(Hbpz₃)₂(dtbsq)] · 2CHCl₃: C 39.18, H 4.06, N 16.12; found: C 39.40, H 4.15, N 15.98.

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Improved Electrochemistry in Low-Polarity Media Using Tetrakis(pentafluorophenyl)-borate Salts as Supporting Electrolytes**

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The widespread nature of electron-transfer reactions provides an impetus to extend electrochemical experiments to new matrix conditions (solvents, temperatures, electrolytes).^[1] The choice of supporting electrolyte is crucial in that the "indifferent salt" affects not only mass transport and solution resistance, but possibly determines the chemical fate of the electrolysis products.^[2, 3] Mann and co-workers have shown, for example, that the oxidation of ruthenocene is a reversible one-electron process when the electrolyte anion is $[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$, whereas an irreversible two-electron process is found when the more traditional anions $[\text{ClO}_4]^-$, $[\text{BF}_4]^-$, or $[\text{PF}_6]^-$ are used.^[3] We now bring attention to several electrochemical advancements that are possible when tetraalkylammonium salts of the weakly coordinating^[4] anion tetrakis(pentafluorophenyl)borate, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, are employed in solvents of low dielectric strength. Our results establish that these electrolytes are greatly advantageous for the investigation of electrode processes in such solvents. Voltammetry can now be more accurately performed at conventionally sized electrodes under demanding conditions (e.g., at low temperatures and/or high scan rates) in solvents of very low polarity. The improvements arise from the increased solubilities and dissociation tendencies of cations having a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counterion, phenomena that have received attention in the area of homogeneous catalysis.^[4, 5]

We show here that 1) the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion is extremely effective in solubilizing positively charged species produced in anodic reactions and 2) voltammetric measurements are now possible in solvents having very low dielectric constants, including aliphatic ethers.

Addressing the first point, we note that, although dichloromethane is a preferred solvent for oxidation reactions, the precipitation of polycationic products at the electrode often complicates voltammetric scans in this solvent. As a result, studies are often performed in a more polar (but usually more reactive) solvent such as CH_3CN . Examples of this strategy may be found in the study of polyferrocenyl compounds, where precipitation of multiply charged species frequently passivates electrode surfaces in low-polarity solvents.^[6] Product precipitation is avoided with a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -containing electrolyte. Figure 1 compares cyclic voltammetry (CV) scans of the triferrocenyl compound **1** in CH_2Cl_2 containing 0.1M $[\text{NBu}_4][\text{PF}_6]$ with those of the same system

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