Versatility of the Nature of the Magnetic Gadolinium(III)−Vanadium(IV) Interaction − Structure and Magnetic Properties of Two Heterobinuclear [Gd, V(O)] Complexes

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It has been known for a long time that the magnetic exchange interaction between copper and gadolinium ions is always ferromagnetic. Very recently, three exceptions to this general trend were revealed. They involve complexes associating a gadolinium(III) ion with a copper(II) ion or with radicals of the nitroxide or semiquinone types. We want to show that this trend is more general than expected, for such a behavior can also be observed in heterobinuclear vanadyl-gadolinium complexes.

Introduction

The interest given to magnetic interactions between rare earth ions and other types of spin carriers has been focused mainly on gadolinium(III) derivatives containing free radicals[1−4] or copper(II)[5−11] complexes. Very few examples involving nickel(II), cobalt(II), iron(III) and vanadium(IV)[12] ions have been reported. In all these species the interaction between gadolinium(III) and the other paramagnetic center was found to be ferromagnetic. Recently three exceptions to this general trend were revealed; they involve radicals of the nitroxide and semiquinone types[13,14] and a copper(II) complex.[15] Preliminary studies show that an antiferromagnetic behavior is also observed in new trinuclear(Gd, Cu_2) complexes. In search of original examples of antiferromagnetic coupling we have considered the systems consisting of the gadolinium(III) and vanadium(IV) ions and several ligands H_2L^i derived from 2-hydroxy-3-methoxybenzaldehyde.

Results and Discussion

In two instances we succeeded in obtaining well-defined, crystalline complexes by very slow and careful addition of the suitable mononuclear precursors $L^iV(O)$ to $Gd(NO_3)_3 \cdot 6H_2O$, in acetone.[16] Chemical analysis data lead to the following formulae: $[L^1V(O)Gd(H_2O)(NO_3)_3] \cdot H_2O$ (**1**) and $[L^2V(O)\{(CH_3)_2CO\}Gd(NO_3)_3]$ (**2**) [H_2L^1 and H_2L^2 stand for *N,N′*bis(3-methoxysalicylidene)-1,2-diamino-2-methylpropane and *N,N′*-bis(3-methoxysalicylidene)-1,3-diamino-2,2′-dimethyl-propane, respectively].

The heterobinuclear nature of **1** and **2** is supported by the molecular structures[17] shown in Figure 1 and 2. In each compound the metallic ions are doubly bridged by two phenolato oxygen atoms [O(1) and O(2)] of the ligand L^i. The most pertinent difference between the two complexes concerns the GdO_2V bridging core, which is almost planar in **1** with a dihedral angle α between the [O(1)−Gd−O(2)] and [O(1)−V−O(2)] planes of 3.5(7)°, while in compound **2** the value is 20.7(l)°. The related Gd···V separations are equal to 3.5191(5) and 3.5043(4) Å in **1** and **2**, respectively. In both compounds, gadolinium(III) is decacoordinated, although in **2** the coordination sphere comprises four oxygens from L^2 and six from three chelating NO_3, while in **1** one chelating NO_3 is replaced by one monodentate (NO_3) and a water molecule. This water molecule is involved in a hydrogen bonding network through an uncoordinated H_2O and a bound NO_3. Nevertheless, the intermolecular Gd···Gd distance is large [7.7512(2) Å] and slightly shorter than in **2** [8.3816(4) Å], where hydrogen bonds are absent. The vanadium(IV) ion is pentacoordinated in **1** and hexacoordinated in **2** due to the presence of an additional acetone molecule which is loosely bound in an axial position. The vanadium-oxo bond has the same length in both complexes, while the basal bonds are slightly shorter in **1** than in **2**. The metal ions are displaced from the mean basal planes by 0.6183(5) and 0.3418(4) Å in **1** and **2**, respectively. All the intermolecular metal contacts are large (≥7.47 Å) with the exception of a V···V separation of 5.7665(7) Å in **2**. The analogous value in **1** is 7.475(l) Å. However, the lack of bridging pathway between the two V^{IV} ions militates against the possibility of a discernible interaction. Finally, the magnetic data for both complexes may be analyzed on the basis of isolated binuclear species.

From our previous work,[12a] compound **1** has a ferromagnetic ($S_T = 4$) ground state with a coupling constant J of 1.5 cm^{-1}. As for **2**, the profile of the $\chi_M T$ vs. T curve (Figure 3) differs significantly from that of **1** and suggests an antiferromagnetic ($S_T = 3$) ground state. In the 2−300 K

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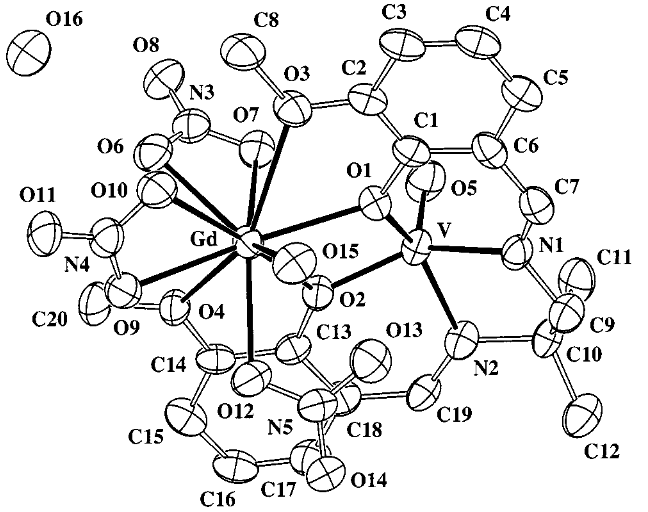

Figure 1. Zortep drawing of **1** with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted; selected bond lengths [Å] and angles [°]: V−O(1) 1.942(2), V−O(2) 1.937(2), V−O(5) 1.588(3), Gd−O(1) 2.376(2), Gd−O(2) 2.424(2), O(1)−V−O(2) 80.82(9), O(1)−Gd−O(2) 63.19(7), Gd−O(1)−V 108.76(9), Gd−O(2)−V 107.08(9), V···Gd 3.5191(5)

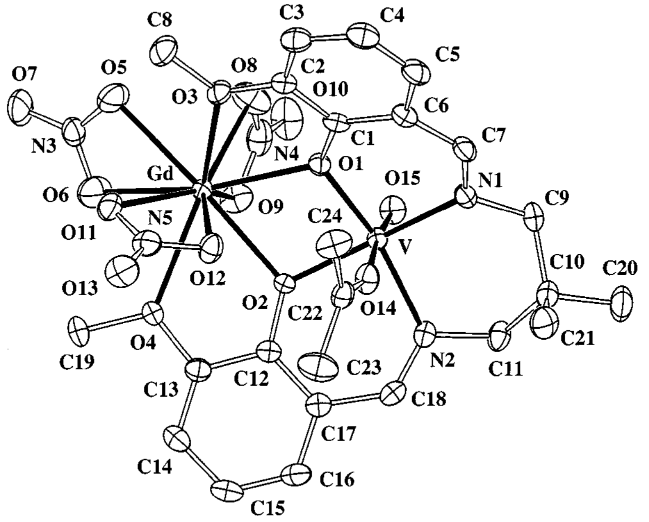

Figure 2. Zortep drawing of **2** with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted; selected bond lengths [Å] and angles [°]: V−O(1) 1.988(2), V−O(2) 1.986(1), V−O(15) 1.588(2), Gd−O(1) 2.405(2), Gd−O(2) 2.414(2), O(1)−V−O(2) 80.25(6), O(1)−Gd−O(2) 64.20(5), Gd−O(1)−V 105.42(6), Gd−O(2)−V 105.14(6), V···Gd 3.5043(4)

range, fitting the experimental data to the expression[18] derived from the Hamiltonian $H = -JS_{\mathrm{Gd}}\cdot S_{\mathrm{V}}$ yields $J = -2.6$ cm^{-1}, $g_{\mathrm{Gd}} = 2.0$ and $g_{\mathrm{V}} = 2.1$, the agreement factor R $[(\chi_{\mathrm{M}}T_{\mathrm{calcd.}} - \chi_{\mathrm{M}}T_{\mathrm{obs}})^2/(\chi_{\mathrm{M}}T_{\mathrm{obs}})^2]$ being equal to 3.8×10^{-5}. There is no sign of secondary effects (intermolecular coupling, zero field splitting, ...). The nature of the ground state is definitely substantiated by field-dependent magnetization measurements. Up to 5×10^4 G, the data comply with the values calculated from the Brillouin function for an $S_{\mathrm{T}} = 3$, $g = 2.1$ spin system.

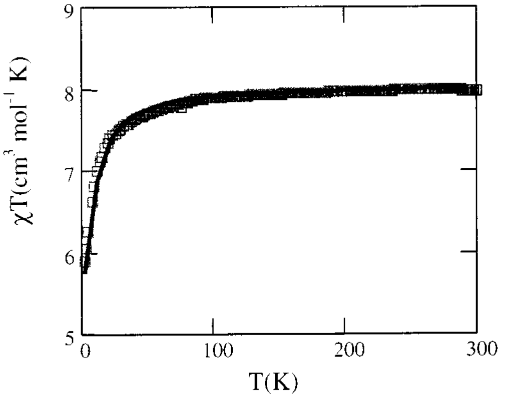

Figure 3. Plot of $\chi_{\mathrm{M}}T$ vs. T for **2** (1000 G); the solid line represents the best data fit

Finally, the present work shows that the magnetic changeability which has so far been observed for (Gd, radical)[13,14] and (Gd, Cu)[15] complexes is also a property of the [Gd, V(O)] compounds. In the two series of bimetallic complexes, a lengthening of the diimino chain of the ligand (from N−C−C−N to N−C−C−C−N) is responsible for a spin-state reversal (from $S = 4$ to $S = 3$). Concurrently there is a significant increase in the bending of the bridging core. The present data reinforce the suggestion[13−15] that the nature and magnitude of the (Gd, M) [M = organic radical, copper(II), vanadium(IV)] interactions result from a sensitive balance between two opposite contributions. The available interaction models[7,18−21] stress the importance of charge transfer (CT) excited states in stabilizing selectively either a low-spin or a high-spin state. The former case corresponds to a CT between two singly occupied orbitals (from $3d_{\mathrm{Cu}}$ or $3d_{\mathrm{VO}}$ to $4f_{\mathrm{Gd}}$) while the second originates from a CT from a singly occupied orbital ($3d_{\mathrm{Cu}}$ or $3d_{\mathrm{VO}}$) to an empty orbital ($6s_{\mathrm{Gd}}$ or more probably $5d_{\mathrm{Gd}}$) . These CT-based mechanisms do not seemingly conflict with the observation that the spin states of the binuclear complexes are little affected by the symmetry change of the magnetic orbitals of the second spin carrier (d_{xy} vs. $d_{x^2-y^2}$ type) but are significantly dependent on the planarity of the bridging network.

Experimental Section

Starting materials were purchased from Acros and Aldrich (*o*-vanillin, 1,3-diamino-2,2′-dimethylpropane, 1,2-diamino-2-methylpropane, vanadyl sulfate and gadolinium nitrate hexahydrate), and used without further purification. The compounds were synthesized as follows.

Vanadyl Complexes: The monomeric vanadyl entities were prepared by addition of an aqueous solution of vanadyl sulfate (10 mmol, 1.63 g) to a mixture of *o*-vanillin (20 mmol, 3.04 g) and the corresponding diamine (10 mmol; 0.88 and 1.02 g, for **1** and **2** respectively) in boiling methanol. The precipitates were filtered off, washed with methanol and diethyl ether, and dried under vacuum.

$L^1VO(H_2O)$: Moss green powder, yield 52%. − $C_{20}H_{24}N_2O_6V$ (439.36): calcd. C 54.7, H 5.5, N 6.4; found C 54.5, H 5.3, N 6.0.

− Selected IR bands: $\tilde{\nu}$ = 3481, 2930, 1617, 1552, 1470, 1443, 1401, 1297, 1248, 1225, 1083, 975, 855, 748, 734 cm^{-1}.

$L^2VO(H_2O)$: Light green powder, yield 58%. − $C_{21}H_{26}N_2O_6V$ (453.39): calcd. C 55.6, H 5.8, N 6.2; found C 55.5, H 5.9, N 6.1. − Selected IR bands: $\tilde{\nu}$ = 3435, 2954, 1652, 1618, 1555, 1471, 1453, 1432, 1412, 1392, 1326, 1297, 1248, 1224, 1086, 1066, 958, 859, 733 cm^{-1}.

Vanadyl-Gadolinium Complexes. The vanadyl precursors (1 mmol) were dissolved in acetone and equimolar amounts of the corresponding lanthanide nitrates (1 mmol) were added. Stirring for 90 minutes at room temperature [$L^1VO(H_2O)$ precursor] or stirring and boiling for 40 minutes [$L^2VO(H_2O)$ precursor] yielded green precipitates that were filtered off, washed with acetone and diethyl ether, and dried under vacuum. Dark green crystals of the gadolinium derivatives suitable for X-ray studies were obtained by slow diffusion in a cell device. In the case of **2**, solutions of both gadolinium nitrate and the corresponding precursor in acetone were allowed to react for 10 days at room temperature. Compound **1** required a dichloromethane/acetone (5:2) solution in the compartment occupied by the vanadyl monomer, and the diffusion was carried out at 255 K during nine days.

$[L^1VOGd(NO_3)_3(H_2O)](H_2O)$ (1): Green precipitate, yield 69%. − $C_{20}H_{26}GdN_5O_{16}V$ (800.63): calcd. C 30.0, H 3.3, N 8.8; found C 30.1, H 3.0, N 8.8. − Selected IR bands: $\tilde{\nu}$ = 3470, 2977, 1615, 1560, 1521, 1462, 1437, 1400, 1384, 1306, 1281, 1249, 1226, 1078, 1005, 859, 746 cm^{-1}.

$[L^2VO(C_3H_6O)Gd(NO_3)_3]$ **2**. Green precipitate, yield 56%. − $C_{24}H_{30}GdN_5O_{15}V$ (836.71): calcd. C 34.4, H 3.6, N 8.4; found C 34.5, H 3.3, N 8.3. − Selected IR bands: $\tilde{\nu}$ = 3391, 2962, 1703, 1630, 1609, 1567, 1521, 1489, 1473, 1435, 1311, 1283, 1245, 1230, 1064, 995, 857, 741, 735 cm^{-1}.

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[16] Crystals were obtained at 255 K for **1** and 295 K for **2**. In the case of **1**, we were unable to collect the data at a temperature lower than 255 K without destroying the crystal.

[17] Crystal structures analysis: The data were collected on a STOE IPDS diffractometer with Mo-K_α radiation. The structures were solved using direct methods (SHELXS-97) and refined on F^2 (SHELXL-97). A numerical absorption correction was used for **1**.
1: $C_{20}H_{26}GdN_5O_{16}V$, M_r = 800.65, monoclinic, space group $P2_1/n$, a = 16.234(2), b = 10.4958(7), c = 16.467(2) Å, β = 90.99(1)°, V = 2805.4(5) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.896 $Mg{\cdot}m^{-3}$, F(000) = 1584, λ = 0.71073 Å, μ(Mo-K_α) = 2.761 mm^{-1}, T = 255 K, crystal size 0.25 × 0.15 × 0.10 mm^3. Of the 24339 reflections collected (3.3 < 2θ < 52.1°), 5448 were independent; max./min. residual electron density 0.703/−1.159 e/$Å^3$, $R1$ = 0.0294 [$I > 2\sigma(I)$], $wR2$ = 0.0603 (all data).
2: $C_{24}H_{30}GdN_5O_{15}V$, M_r = 836.72, monoclinic, space group $P2_1/c$, a = 9.992(1), b = 17.556(2), c = 18.293(2) Å, β = 105.68(1)°, V = 3089.4(6) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.799 $Mg{\cdot}m^{-3}$, F(000) = 1664, λ = 0.71073 Å, μ(Mo-K_α) = 2.509 mm^{-1}, T = 160 K, crystal size 0.50 × 0.25 × 0.13 mm^3. Of the 18864 reflections collected (2.9 < 2θ < 48.4°), 4523 were independent; max./min. residual electron density 0.832/−0.338 e/ $Å^3$, $R1$ = 0.0198 [$I > 2\sigma(I)$], $wR2$ = 0. 0438 (all data).
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146861 **(1)** and -146862 **(2)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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