

An original heterodinuclear VO²⁺,Gd³⁺ complex with a nonet ground state

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Reaction of the vanadyl complex of *N,N'*-bis(3-methoxy-salicylidene)-1,2-diamino-2-methylpropane (H₂L) with Gd(NO₃)₃·5H₂O yielded a dinuclear complex LV^{IV}OGd^{III}(NO₃)₃·(CH₃)₂CO which presents a ferromagnetic interaction between the paramagnetic (*S* = ½) vanadyl and the gadolinium (*S* = 7/2) ions, with a *J* value of 1.3 cm⁻¹.

Since 1985,¹ increasing interest has been given to the magnetic properties of complexes containing both d and f ions. This interest has been focused on the Cu²⁺,Gd³⁺ couple which has magnetic properties amenable to a rather simple analysis based on a spin-only Hamiltonian. Indeed Gd³⁺, with a ⁸S_{7/2} single-ion ground state, does not possess a first-order orbital moment. Several polynuclear Cu²⁺,Gd³⁺ complexes¹⁻¹² have been shown to display an overall ferromagnetic behaviour irrespective of the details of their molecular structure and nuclearity. The same situation holds when a Cu²⁺ ion is replaced by a radical.^{13,14} Recent works¹⁵⁻¹⁹ devoted to perfectly insulated dinuclear species have confirmed that ferromagnetism is an intrinsic property of the Cu²⁺,Gd³⁺ and Ni²⁺,Gd³⁺ pairs. From the whole body of experimental observations, it has been suggested^{1-3,5,11} that a rather general mechanism based on the ideas of Goodenough²⁰ would apply. In order to test the validity of this assumption, we have considered the VO²⁺,Gd³⁺ couple.

Reaping advantage from the synthetic possibilities offered by a Schiff-base ligand deriving from 2-hydroxy-3-methoxybenzaldehyde, we have prepared and isolated the mononuclear precursor LVO·H₂O **1** [where H₂L = *N,N'*-bis(3-methoxysalicylidene)-1,2-diamino-2-methylpropane], which in a subsequent step, was reacted with gadolinium nitrate to yield the expected heterodinuclear complex LVOGd(NO₃)₃·(CH₃)₂CO **2**. These compounds have been obtained in a similar manner described previously for analogous copper complexes.¹⁵ A schematic representation of complex **2** is given in Fig. 1.

Although we did not succeed in obtaining crystals suitable for an X-ray diffraction study, the identity of the complex is not questionable.‡ In addition to the analytical data, the most important information is afforded by positive-ion FAB mass spectroscopy. The main signal (*I* = 100%) occurs at *m/z* = 703. This value together with the isotropic pattern are attributable to the [LVOGd(NO₃)₃]⁺ ion. A second signal with lower intensity (*I* = 48%) and a simpler isotropic feature is observed at *m/z* = 422. It corresponds to the [LVOH]⁺ species. The frag-

mentation pattern is identical to that of the related Cu,Gd and Ni,Gd complexes.^{15,18,19} There is also a great similitude between the IR spectra of the three heterodinuclear complexes. They are practically superimposable with the exception of the presence of a ν_{VO} absorption at 1012 cm⁻¹ in the spectrum of **2**. This absorption appears at 975 cm⁻¹ in the case of compound **1**.

The magnetic properties of **1** and **2** have been investigated.§ For the sake of brevity, only the temperature dependence of the product χ_m*T* of **2** is represented in Fig. 2. As expected, **1** is strictly paramagnetic since χ_m*T* is constant from 4 to 300 K. The Curie constant *C* is equal to 0.371 cm³ K mol⁻² leading to *g* = 1.99. In the case of **2** the profile of the χ_m*T* versus *T* curve indicates that a ferromagnetic interaction is operative. In this instance, the spectrum of the low-spin states comprises a nonet ground state and a septet state, separated by an energy gap of 4 *J* where *J* is the exchange parameter occurring in the spin-

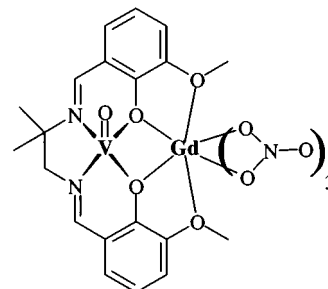


Fig. 1 Schematic representation of LVOGd(NO₃)₃ **2**

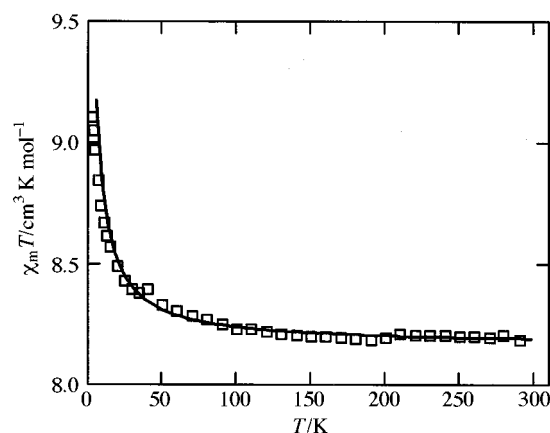


Fig. 2 Thermal dependence of χ_m*T* for LVOGd(NO₃)₃ **2** at 0.1 T. The full line corresponds to the best data fit

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‡ Compounds **1** and **2** gave satisfactory elemental analyses (Found: C, 54.3; H, 5.4; N, 6.2. C₂₀H₂₄N₂O₆V **1** requires C, 54.7; H, 5.5; N, 6.4. Found: C, 33.4; H, 3.4; N, 8.6. C₂₃H₂₈GdN₅O₁₅V **2** requires C, 33.6; H, 3.4; N, 8.5%). They were also identified by mass spectrometry (positive-ion FAB using DMSO as solvent and 3-nitrobenzyl alcohol matrix) and UV/VIS spectroscopy (λ_{max} 600 nm for **1** and 592 for **2**).

§ Magnetic susceptibility data were collected on powdered samples of compounds **1** and **2** using a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants (−205 × 10⁻⁶ for **1** and −316 × 10⁻⁶ cm³ mol⁻¹ for **2**).

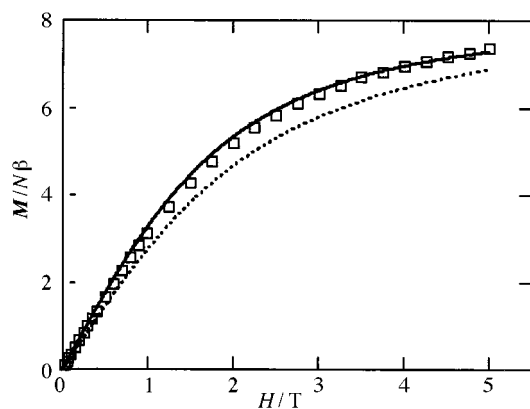


Fig. 3 Field dependence of the magnetization: experimental data (□); theoretical curve for isolated $V^{IV}O$ and Gd^{III} ions (—); theoretical curve for an $S = 4$ spin state (---). They are respectively labelled **a**, **b** and **c** in the text. $N\beta = 5.585 \text{ J T}^{-1} \text{ mol}^{-1}$

Hamiltonian for isotropic exchange $\mathcal{H} = -J(S_{VO}S_{Gd})$. The experimental data may be analyzed by a simple expression derived from the Hamiltonian, *i.e.* equation (1). Least-squares

$$\chi_m = \frac{4N\beta^2 g^2}{k(T - \theta)} \frac{7 + 15 \exp(-4J/kT)}{7 + 9 \exp(-4J/kT)} \quad (1)$$

fitting of the experimental data leads to $J = 1.3 \text{ cm}^{-1}$, $\theta = 0$ and $g = 1.99$. The agreement factor $\Sigma(\chi T_{\text{calc}} - \chi T_{\text{obs}})^2 / \Sigma(\chi T_{\text{obs}})^2$ is then equal to 2.5×10^{-4} . The zero value of θ suggests that second-order effects (such as intermolecular interactions, zero-field splitting, *etc.*) are, at best, very weak.

To confirm the ferromagnetic nature of the ground state, the field dependence of the magnetization M at 5 K was considered. In Fig. 3, the experimental values of M (curve **a**) are compared to the sum of the Brillouin functions for isolated Gd^{3+} ($S = \frac{7}{2}$) and VO^{2+} ($S = \frac{1}{2}$) ions (curve **b**) and the Brillouin function for an $S = 4$ state (curve **c**). For any value of the field, the experimental magnetization is larger than that for isolated ions and close to the value expected for an $S = 4$ spin state. The slight difference observed between curves **a** and **c** is due to an incomplete population of the $S = 4$ state at 5 K. Indeed the experimental values of M can be exactly fitted with the Brillouin function to yield $g = 1.99$ and $S = 3.97$, the agreement factor $\Sigma(M_{\text{calc}} - M_{\text{obs}})^2 / \Sigma(M_{\text{obs}})^2$ being equal to 2.5×10^{-4} .

In our opinion, the main result of the present work is that the magnetic behaviour of the VO^{2+}, Gd^{3+} pair is very similar to that of the Cu^{2+}, Gd^{3+} and Ni^{2+}, Gd^{3+} pairs. In the three cases, the $M^{2+}-Gd^{3+}$ couples, which are surrounded by the same ligand, have a ferromagnetic ground state.

In the case of the Cu^{2+}, Gd^{3+} couple, it has been proposed^{5,11} that the stabilization of the parallel spin state arises from the coupling between the $Cu^{II}-Gd^{II}$ ground configuration and the $Cu^{III}-Gd^{III}$ charge-transfer excited configuration in which an electron is transferred from the singly-occupied 3d-type copper orbital towards an empty 5d-type gadolinium orbital. There is no obvious reason why this mechanism could not be operative in the case of the VO^{2+}, Gd^{3+} couple. The difference in the

nature of the singly-occupied orbital in the ground state ($d_{x^2-y^2}$ for Cu^{2+} versus d_{xy} for VO^{2+}) does not militate against an extension of the mechanism. Among the set of vacant 5d gadolinium orbitals, at least one has the correct symmetry to favour the transfer. However, this difference in ground-state orbitals may alter the value of the factors (transfer integral β_{5d-3d} , energy cost of the transfer, *etc.*) determining the value of the interaction parameter J and be responsible for its variation from 7 (Cu, Gd) to 1.3 cm^{-1} (VO, Gd). Another reason for the lowering of J could also originate from the fact that vanadyl is most probably pulled out of the mean co-ordination plane while Cu^{II} remains in its co-ordination plane.

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