A Very-High-Spin Molecule: Preparation, Characterization and Magnetic Properties of an Fe^{III}–Gd^{III} Complex with an $S = 12/2$ Ground State

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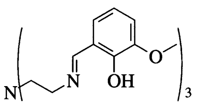
The tripodal ligand tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]amine (H_3vantren) offers two coordination sites, an inner N_4O_3 one and an outer O_6 one. Therefore, it can successively encapsulate two different metal ions, a 3d(III) ion in the N_4O_3 site, and a 4f(III) ion in the O_6 site. This general route to homo- and heterodinuclear complexes has been exploited for the preparation of the vantrenFeGd$(NO_3)_3 \cdot 2\ H_2O$ complex (**2**), featuring a high-spin iron centre. This compound has been characterized by chemical analysis and mass spectrometry (FAB$^+$). Its magnetic properties have been investigated and show that the (Fe,Gd) pair (**2**) exhibits a ferromagnetic interaction of low intensity [$J = 0.50(5)\ cm^{-1}$]. The resulting $S = 12/2$ ground state is, most probably, the highest spin ground state that can be expected for a dinuclear complex.

Introduction

In recent years, there has been increasing interest in the magnetic properties of dinuclear complexes composed of either 4f and 3d ions or of identical 4f ions.[1][2][3][4][5][6][7] This interest has been largely focused on the Cu−Gd couple, but one of our aims is to extend this work to other M−Gd couples (M being a 3d cation such as Ni^{2+},[8] Co^{2+},[9] or VO^{2+}[10]). As for the strategies used to prepare these polynuclear complexes, tripodal ligands derived from tris(2-aminoethyl)amine have so far been employed as hosts for 3d or 4f ions, leading to mononuclear (3d or 4f) and homodinuclear (4f, 4f) complexes.[11][12][13][14][15][16][17][18][19][20][21][22][23][24][25][26][27] Very recently, it has been shown that a mononuclear (4f) complex prepared from a novel tripodal ligand can be deprotonated to incorporate an Ni^{2+} ion.[28] Also relevant to the present paper is the use of 3d-block tripods in obtaining self-assembled triple-stranded heterodinuclear (3d, 4f) complexes.[29][30] The structural determination of an Fe^{II}−La^{III} complex has been carried out.[30]

We have also demonstrated the effectiveness of the potentially decadentate tripodal Schiff base H_3vantren[31] {tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]amine} in generating hetero- (4f, 4f′) as well as homo-dimetallic (4f, 4f) species. A schematic representation of the ligand H_3vantren is given in Figure 1. The aim of the present contribution is to demonstrate the ability of this tripodal ligand to successively incorporate 3d and 4f ions, thereby affording vantrenFe (**1**) and vantrenFeGd$(NO_3)_3 \cdot 2\ H_2O$ (**2**), and to report the magnetic properties of these complexes. At this point we should mention an Fe^{III}−La complex prepared with a compartmental Schiff base ligand, for which neither a structural determination nor magnetic properties were reported.[24]

Figure 1. Schematic representation of the H_3vantren ligand



Results and Discussion

The tripodal H_3saltren ligand, obtained by reaction of salicylaldehyde with tris(2-aminoethyl)amine (tren), and its 5-chloro- ($H_3$5-Clsaltren) and 3-methoxy-substituted (H_3vantren) analogues, react with 3d(III) ions and particularly with Fe^{III} to yield neutral complexes formulated as saltrenFe.[18][19][20][24] The iron centre in 5-ClsaltrenFe[19] resides in an N_3O_3 environment, with the bridgehead nitrogen atom not being involved in coordination. A similar situation is found in vantrenMn.[20][24]

H_3vantren is a potentially decadentate tripodal ligand with two different complexation sites: an inner N_4O_3 site and an outer O_6 site. These differ in their size and nature, thus making easier the stepwise complexation of different metal ions. The marked preference of iron(III) for the inner site has been clearly demonstrated,[18][19] but we have recently shown that 4f metal ions can also be complexed in this deprotonated coordination site.[31] The bridgehead nitrogen atom that caps the structure is "tucked in", with its lone pair of electrons directed towards the Yb^{3+} ion.[31] The same disposition has been observed in mononuclear (Gd, Dy, or Yb) complexes of tripodal ligands.[12][32][33] However, in our case, the bonding interaction is expected to be

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weak, as indicated by the N(2)−Yb separation of 2.626(4) Å, which is significantly larger than the related distances involving the imino nitrogen atoms [2.448(5) to 2.494(4) Å].[31] Furthermore, the difference in ionic radii between 3d(III) and 4f(III) centres induces a large difference in bond lengths between the Fe−N(imine), Fe−O(phenolato) and the Ln−N(imine), Ln−O(phenolato) bonds, respectively, [Fe−N: 2.185(7) Å; Yb−N: 2.448(5)−2.494(4) Å and Fe−O: 1.953(6) Å; Yb−O: 2.259(3)−2.329(3) Å]. This large difference is not expected to be a stabilizing factor for the desired 3d(III)−4f(III) pairs.

Infrared spectra of vantrenFe (**1**) and vantrenFeGd$(NO_3)_3 \cdot 2\ H_2O$ (**2**) mainly serve to reveal the presence of water and nitrate ions in **2**. Bands attributable to bidentate nitrates are observed at 1462 and 1335 cm^{-1}. A splitting of the 1620 cm^{-1} band for **1** into two bands at 1615 and 1641 cm^{-1} for **2** is also observed.

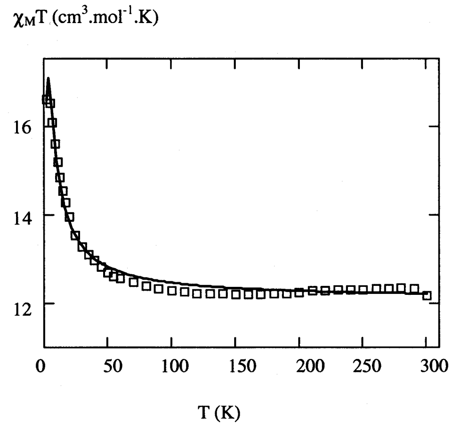
In addition to the analytical results, important information is provided by positive-ion FAB mass spectrometry. The main peak appears at *m/z* = 602 (100%) for the vantrenFe compound. This value together with the isotopic feature is attributable to the [vantrenFe + 1]$^+$ ion. In the case of vantrenFeGd$(NO_3)_3 \cdot 2\ H_2O$, the signal corresponding to [vantrenFeGd$(NO_3)_2]^+$ is not observed. However, a signal appears at *m/z* = 821. This corresponds to the [vantrenFeGd$(NO_3)]^+$ ion, suggesting a change in the oxidation state of a metal centre (Fe or Gd). A similar observation has been made in previous reports.[1][3][8][9][10] The existence of a species such as [vantrenFeGd$(NO_3)_2]_2 \cdot Gd(NO_3)_5$ is ruled out by the analytical results and the absence of a signal attributable to the $[Gd(NO_3)_5]^-$ anion in the FAB$^-$ spectrum.[31]

The temperature dependence of the magnetic susceptibility over the range 5−300 K for vantrenFeGd$(NO_3)_3 \cdot 2\ H_2O$ is shown in Figure 2 in the $\chi_M T$ vs.T form, the applied magnetic field being equal to 0.05 T. At 300 K, $\chi_M T$ is equal to 12.17 cm^3 K mol^{-1}, which roughly corresponds to the value expected for two uncoupled metal ions (12.25 cm^3 K mol^{-1}). On lowering the temperature, $\chi_M T$ remains practically constant until 80 K and then increases, reaching a maximum of 16.55 cm^3 K mol^{-1} at 5 K. The behaviour observed in the 300−5 K range is indicative of a ferromagnetic interaction between the Gd^{III} and Fe^{III} ions. The maximum value of 16.55 is lower than the value of 21 cm^3 K mol^{-1} that would be expected for the spin state $S = 6$ resulting from ferromagnetic coupling between Gd^{III} ($S = 7/2$) and Fe^{III} ($S = 5/2$), both ions having g values of 2.0. The decrease of $\chi_M T$ observed below 5 K is most likely attributable to saturation effects or to zero-field splitting. In this instance, the experimental results obtained between 5 and 300 K can be analysed on the basis of a spin-only Hamiltonian for isotropic exchange $H = -JS_{Fe} \cdot S_{Gd}$. The six low-lying spin levels, $E(6) = 0$, $E(5) = 6J$, $E(4) = 11J$, $E(3) = 15J$, $E(2) = 18J$ and $E(1) = 20J$ are characterized by different g values[34], $g_6 = (7g_{Gd} + 5g_{Fe})/12$, $g_5 = (37g_{Gd} + 23g_{Fe})/60$, $g_4 = (27g_{Gd} + 13g_{Fe})/40$, $g_3 = (19g_{Gd} + 5g_{Fe})/24$, $g_2 = (13g_{Gd} - g_{Fe})/12$, $g_1 = (9g_{Gd} - 5g_{Fe})/4$. Finally, the experimental data may be fitted to the following expression:

$$\chi_M T = \frac{N\beta^2}{k} \frac{91g_6^2 + 55g_5^2 e(\frac{-6J}{kT}) + 30g_4^2 e(\frac{-11J}{kT}) + 14g_3^2 e(\frac{-15J}{kT}) + 5g_2^2 e(\frac{-18J}{kT}) + g_1^2 e(\frac{-20J}{kT})}{13 + 11e(\frac{-6J}{kT}) + 9e(\frac{-11J}{kT}) + 7e(\frac{-15J}{kT}) + 5e(\frac{-18J}{kT}) + 3e(\frac{-20J}{kT})}$$

In the 5−300 K temperature range, a satisfactory fit [$R = \Sigma(\chi_{obs.}T - \chi_{calcd.}T)^2/\Sigma(\chi_{obs.}T)^2 = 2.4 \cdot 10^{-4}$] is obtained for the following set of parameters: $g_{Fe} = 1.96$, $g_{Gd} = 2.00$, $J = 0.50(5)\ cm^{-1}$. In order to account for the decrease of the product below 5 K, a θ parameter has been introduced to gauge second-order effects. Then, the best fit over the 2−300 K temperature range yields $g_{Fe} = 1.96$, $g_{Gd} = 2.00$, $J = 0.66(5)\ cm^{-1}$ and $\theta = -0.46$ K, with $R = 1.0 \cdot 10^{-4}$.

Figure 2. Thermal dependence of $\chi_M T$ for LFeGd$(NO_3)_3 \cdot 2\ H_2O$ **2** at 0.05 T; the solid line corresponds to the best data fit



The sign of the magnetic interaction between the Fe^{3+} and Gd^{3+} ions is definitively supported by the field dependence of the magnetization M at 5 K. In Figure 3, the experimental values of M have been fitted to the Brillouin function, yielding $g = 1.94$ and $S = 5.6$ with $R = \Sigma[M_{calcd.} - M_{obsd.}]^2/\Sigma[M_{obsd.}]^2 = 2.5 \cdot 10^{-3}$. The S value differs little from the value ($S = 12/2$) expected for a ferromagnetic ground state. Although the agreement cannot be considered as perfect, we can state that the experimental magnetization is larger than that for isolated Gd^{III} and Fe^{III} metal ions. In spite of the lack of a structural determination, the ferromagnetic behaviour confirms the existence of a genuine strictly dinuclear Fe−Gd complex.

Based on the structural determination of [vantrenYbLa$(NO_3)_2]^+$,[31] a possible structure for **2** has been obtained using CAChe molecular modelling software. It is shown in Figure 4. This view indicates that the bridgehead nitrogen atom is not involved in coordination to the iron centre, in full agreement with structural determinations of complexes of 3d^{III} elements with H_3vantren[24] or similar ligands.[19][20][22]

Finally, the main purpose of this paper is to report the first example of a discrete heterodinuclear Fe^{III}−Gd^{III} complex that displays ferromagnetic behaviour. In this respect, the Fe^{3+}−Gd^{3+} pair resembles the Cu^{2+}−Gd^{3+},[1][3] Ni^{2+}−Gd^{3+},[8] Co^{2+}−Gd^{3+},[9] and VO^{2+}−Gd^{3+}[10] pairs

Figure 3. Field dependence of the magnetization; the solid line corresponds to the best data fit (cf. text)

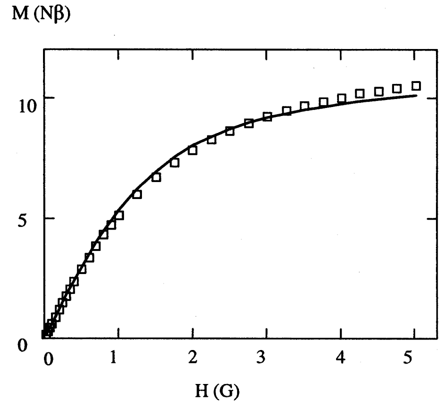
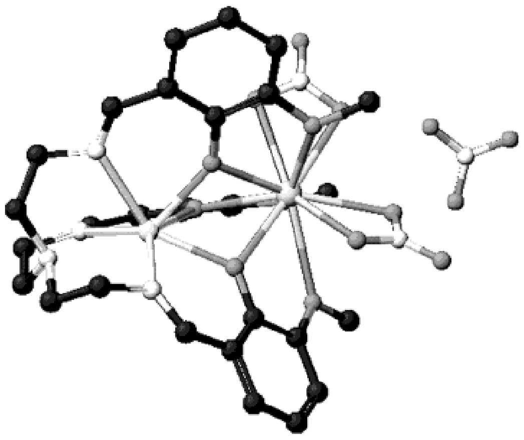


Figure 4. Possible structure of **2** based on CAChe molecular modelling software; the H atoms are not shown



described previously. In the case of the $Cu^{2+}-Gd^{3+}$ couple, it has been proposed[35][36] that the stabilization of the parallel spin state arises from coupling between the $Cu^{II}-Gd^{III}$ ground configuration and the $Cu^{III}-Gd^{II}$ charge-transfer excited configuration, in which an electron is transferred from the singly occupied 3d-type copper orbital to an empty 5d-type gadolinium orbital. There is no obvious reason why this mechanism could not be operative in the case of the $Fe^{3+}-Gd^{3+}$ couple as well. Indeed, although the ligands involved in these different complexes are not identical, they all give rise to phenolato bridges, two with 3d(II) and three with 3d(III) metal ions. We emphasize that the value $S = 12/2$ is most probably the highest spin ground state that can be expected for a dinuclear complex. Theoretically, a higher value ($S = 14/2$) could result from a ferromagnetic coupling between two Gd^{3+} ions, but the available data[5][7] show that such a magnetic state is unlikely.

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Experimental Section

Materials and Methods: All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). Magnetic susceptibility data were collected from a powdered sample of the compound using a SQUID-based sample magnetometer with a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand, as estimated from Pascal's constants[38] ($-381 \cdot 10^{-6}$ emu mol^{-1} for **2**). Positive-ion FAB mass spectra were recorded in DMF as solvent with 3-nitrobenzyl alcohol as the matrix with a Nermag R10-10 spectrometer.

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]amine: This ligand was obtained as described previously.[37]

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]aminato-(3−)iron(III) (**1**): To a mixture of H_3vantren (0.55 g, 1 mmol) and anhydrous $FeCl_3$ (0.16 g, 1 mmol) in methanol (25 ml) was added triethylamine (0.3 g, 3 mmol). The mixture was heated under stirring for 20 min and, after cooling, the black precipitate produced was filtered off and washed with methanol and diethyl ether. Yield: 0.5 g (85%). − $C_{30}H_{33}FeN_4O_6$ (601.4): calcd. C 59.9, H 5.5, N 9.3; found C 59.6, H 5.3, N 9.1. − MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 602$ [LFe + 1]$^+$.

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]aminato-(3−)iron(III)gadolinium(III)·2 H_2O (**2**): A mixture of vantrenFe (0.5 g, $8.3 \cdot 10^{-4}$ mol) and $Gd(NO_3)_3 \cdot 6\ H_2O$ (0.37 g, $8.3 \cdot 10^{-4}$ mol) in acetone (20 ml) was heated under stirring for 15 min. After cooling, the resulting precipitate was filtered off and washed with acetone and diethyl ether. Yield: 0.8 g (97%). − $C_{30}H_{37}FeGdN_7O_{17}$ (980.7): calcd. C 36.7, H 3.8, Fe 5.7, Gd 16.0, N 10.0; found C 36.4, H 3.6, Fe 5.6, Gd 15.2, N 9.7. − MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): $m/z = 821$ [LFeGd(NO$_3$)]$^+$.

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[1] J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **1996**, *35*, 2400−2402 and refs. therein.
[2] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, *Inorg. Chem.* **1997**, *36*, 930−936 and refs. therein.
[3] J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **1997**, *36*, 3429−3433 and refs. therein.
[4] S. Wang, Z. Pang, K. D. L. Smith, Y. Hua, C. Delippe, M. J. Wagner, *Inorg. Chem.* **1995**, *34*, 908−917 and refs. therein.
[5] A. Panagiotopoulos, T. F. Zafiropoulos, S. P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis, C. P. Raptopoulou, *Inorg. Chem.* **1995**, *34*, 4918−4920 and refs. therein.
[6] I. A. Kahwa, S. Folkes, D. J. Williams, S. V. Ley, C. A. O'Mahoney, G. L. McPherson, *J. Chem. Soc., Chem. Comm.* **1989**, 1531−1533 and refs. therein.
[7] J. P. Costes, A. Dupuis, J. P. Laurent, *Inorg. Chim. Acta* **1998**, *268*, 125−130 and refs. therein.
[8] J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **1997**, *36*, 4284−4286.
[9] J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *C. R. Acad. Sci.*, in press.
[10] J. P. Costes, A. Dupuis, J. P. Laurent, *J. Chem. Soc., Dalton Trans.* **1998**, 735−736.
[11] A. Smith, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1988**, *27*, 3929−3934.
[12] D. J. Berg, S. J. Rettig, C. Orvig,. *J. Am. Chem. Soc.* **1991**, *113*, 2528−2532.
[13] L. Yang, S. Liu, E. Wong, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1995**, *34*, 2164−2178.
[14] U. Casellato, S. Tamburini, P. Tomasin, P. A. Vigato, M. Botta, *Inorg. Chim. Acta* **1996**, 247, 143−145.
[15] P. Blech, C. Floriani, A. Chiesti-Villa, C. Guastini, *J. Chem. Soc., Dalton Trans.* **1990**, 3557−3561.
[16] P. L. Jones, A. J. Amoroso, J. C. Jeffery, J. A. McCleverty, E. Psillakis, L. H. Rees, M. D. Ward, *Inorg. Chem.* **1997**, *36*, 10−18.
[17] O. Kocian, K. W. Chiu, R. Demeure, B. Gallez, C. J. Jones, J. R. Thornback, *J. Chem. Soc., Perkin Trans. 1* **1994**, 527−535.
[18] J. A. Broomhead, D. J. Robinson, *Aust. J. Chem.* **1968**, *21*, 1365−1367.

[19] D. F. Cook, D. Cummins, E. D. McKenzie, *J. Chem. Soc., Dalton Trans.* **1976**, 1369−1375.

[20] N. W. Alcock, D. F. Cook, E. D. McKenzie, J. M. Worthington, *Inorg. Chim. Acta* **1980**, *38*, 107−112.

[21] P. G. Sim, E. Sinn, *J. Am. Chem. Soc.* **1981**, *103*, 241−243.

[22] Y. Elerman, M. Kabak, I. Svoboda, M. Geselle, *Acta Crystallogr.* **1994**, *C50*, 1694−1696.

[23] G. A. McLachlan, G. D. Fallon, L. Spiccia, *Acta Crystallogr.* **1996**, *C52*, 309−312.

[24] A. Aguiari, E. Bullita, U. Casselato, P. Guerriero, S. Tamburini, P. A. Vigato, *Inorg. Chim. Acta* **1997**, *219*, 135−146.

[25] S. Liu, L. Gelmini, S. J. Rettig, R. C. Thompson, C. Orvig, *J. Am. Chem. Soc.* **1992**, *114*, 6081−6087.

[26] L. Yang, S. Liu, S. J. Rettig, C. Orvig, *Inorg. Chem.* **1995**, *34*, 4921−4925.

[27] H. C. Aspinall, M. R. Tillotson, *Inorg. Chem.* **1996**, *34*, 2163−2164.

[28] S. J. Archibald, A. J. Blake, S. Parsons, M. Schröder, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.* **1997**, 173−179.

[29] C. Piguet, G. Bernardinelli, J. C. G. Bünzli, S. Petoud, G. Hopfgartner, *J. Chem. Soc., Chem. Comm.* **1995**, 2575−2577.

[30] C. Piguet, E. Rivara-Minten, G. Bernardinelli, J. C. G. Bunzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **1997**, 421−433.

[31] J. P. Costes, F. Dahan, A. Dupuis, S. Lagrave, J. P. Laurent, *Inorg. Chem.* **1998**, *37*, 153−155.

[32] M. G. B. Drew, O. W. Howarth, C. J. Harding, N. Martin, J. Nelson, *J. Chem. Soc., Chem. Comm.* **1995**, 903−905.

[33] F. Avecilla, R. Bastida, A. de Blas, D. E. Fenton, A. Macias, A. Rodriguez, T. Rodriguez-Blas, S. Garcia-Granda, R. Corzo-Suarez, *J. Chem. Soc., Dalton Trans.* **1997**, 409−413.

[34] A. Bencini, D. Gatteschi, *EPR of Exchange Couples Systems*, Springer-Verlag, Berlin, **1990**.

[35] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J. C. Trombe, *J. Am. Chem. Soc.* **1993**, *115*, 1822−1829.

[36] O. Guillou, R. L. Oushoorn, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batail, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 626−628.

[37] S. Liu, L. W. Yang, S. J. Rettig, R. C. Thompson, C. Orvig, *Inorg. Chem.* **1993**, *32*, 2773−2778.

[38] P. Pascal, *Ann. Chim. Phys.* **1910**, *19*, 5−70.

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