

# Notes

## A Trinuclear Gadolinium Complex: Structure and Magnetic Properties

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Received April 4, 2001

### Introduction

The mechanisms responsible for the magnetic interactions between 3d ions are reasonably well understood, and efficient models have been proposed to rationalize the various types of magnetic behavior.<sup>1,2</sup> As far as magnetic coupling between lanthanide ions is concerned, the situation is much less advanced. This is due, at least partly, to the scarcity of experimental data.<sup>3,4</sup> In only a few cases, structural and magnetochemical results are simultaneously available.<sup>5–11</sup> Limiting our attention to polynuclear gadolinium(III) complexes which are amenable to a relatively simple analysis of their magnetic behavior, it appears that only a few complexes have been identified through spectroscopic arguments as containing interacting Gd ions.<sup>12–14</sup> In all cases the interaction is of the antiferromagnetic nature with a magnitude varying from 0.045 to 0.211 cm<sup>-1</sup>.<sup>5–7,9,11,13,14</sup>

As a part of our attempt to fill the dearth of experimental data, we have explored the coordinative ability of 3-methoxysalicylaldehyde (or orthovanillin, abbreviated as HL in the following) toward 4f ions. The present paper is devoted to the structural and magnetochemical investigations of a polynuclear

**Table 1.** Crystallographic Data for [L<sub>3</sub>Gd<sub>3</sub>(OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>

chem formula	C <sub>24</sub> H <sub>39</sub> Gd <sub>3</sub> N <sub>4</sub> O <sub>31</sub>	Z	4
fw	1351.34	$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	2.149
space group	P <sub>2</sub> 1 <sub>2</sub> 1 <sub>2</sub> (No. 19)	$\lambda$ , Å	0.71073
a, Å	12.226(1)	T, K	293
b, Å	17.875(1)	$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	48.16
c, Å	19.109(2)	R <sup>a</sup>	0.0265, 0.0407
V, Å <sup>3</sup>	4176.2(6)	R <sub>w</sub> <sup>b</sup>	0.0520, 0.0552

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum w|F_o|^2]^{1/2}.$$

gadolinium complex. They show that this complex is trinuclear (Gd<sub>3</sub>), with an antiferromagnetic behavior which must be attributed to the three (Gd, Gd) pairs.

### Experimental Section

**Materials and Methods.** All starting materials were purchased from Aldrich and were used without further purification. L'Gd was obtained as previously described.<sup>9</sup>

**[Tri-(3-methoxysalicylaldehydato)di- $\mu$ -3-hydroxotetraquo-1kO,2kO,3k<sup>2</sup>O-di-( $\eta^2$ -nitrate)trigadolinium(3+)] Dinitrato Tetrahydrate (1).** 3-Methoxysalicylaldehyde (0.47 g, 3.1 mmol) was dissolved in 20 mL of water. Then cesium hydroxyde (0.89 g, 5.3 mmol) was added and the solution was heated for 10 min while being stirred. Finally gadolinium(III) nitrate pentahydrate (1.34 g, 3.1 mmol) was added. The yellow precipitate which appeared was stirred at room temperature overnight and then filtered off, washed with water, and dried under vacuum, leaving a yellow powder. Yield: 0.26 g (20%). Anal. Calcd for C<sub>24</sub>H<sub>39</sub>Gd<sub>3</sub>N<sub>4</sub>O<sub>31</sub>: C, 21.3; H, 2.9; N, 4.1. Found: C, 21.0; H, 2.7; N, 4.2. MS (FAB<sup>+</sup>, 3-nitrobenzyl alcohol matrix, dmsO):  $m/z$  = 1084 amu (45%), [L<sub>3</sub>Gd<sub>3</sub>(OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> + 1]<sup>+</sup>;  $m/z$  = 982 amu (100%), [L<sub>4</sub>Gd<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. MS (FAB<sup>+</sup>, 3-nitrobenzyl alcohol matrix, dmf):  $m/z$  = 1084 amu (12%), [L<sub>3</sub>Gd<sub>3</sub>(OH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> + 1]<sup>+</sup>;  $m/z$  = 982 amu (42%), [L<sub>4</sub>Gd<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>]<sup>+</sup>;  $m/z$  = 893 amu (100%), [L<sub>3</sub>Gd<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Crystals were obtained by slow evaporation of a solution containing L'Gd (L' being the deprotonated form of tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]amine)<sup>9</sup> dissolved in dichloromethane and an alcohol–water (1/1) solution of Gd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O. Their analytical and spectroscopic data are identical to the results given above for the powdered sample.

**Methods.** 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 on ground crystals with use of a SQUID-based sample magnetometer on a QUANTUM Design model MPMS instrument. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.<sup>15</sup> Positive FAB mass spectra were recorded in dmf or dmsO as a solvent and 3-nitrobenzyl alcohol matrix with a Nermag R10-10 spectrometer.

**X-ray Crystallographic Procedures.** Crystal data for 1 are presented in Table 1. Data were measured on an Enraf-Nonius CAD4 diffractometer with Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation and  $\omega$ -2 $\theta$  scans. The temperature of measurement was 293 K. The reflections were corrected for Lorentz–polarization effects with the MolEN package.<sup>16</sup> Semiempirical absorption corrections<sup>17</sup> based on  $\psi$  scans were applied. The structure was solved using a Patterson procedure with the SHELXS-

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**Table 2.** Selected Bond Lengths (Å) and Distances (Å) for  $[\text{L}_3\text{Gd}_3(\text{OH})_2(\text{NO}_3)_2(\text{OH}_2)_4](\text{NO}_3)_2(\text{H}_2\text{O})_4$ 

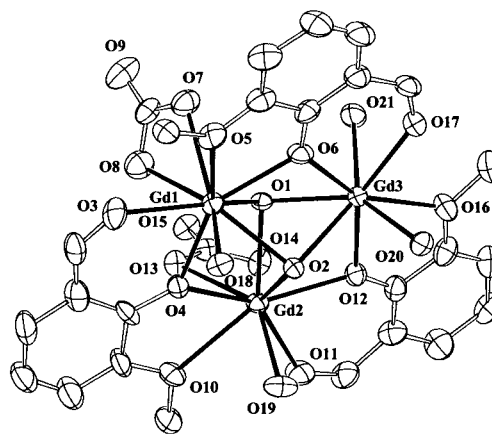
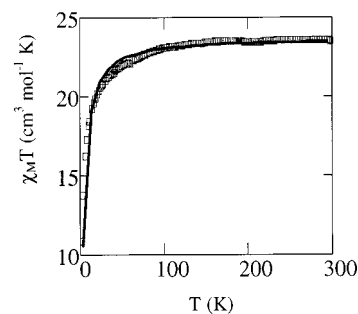
Gd(1)–O(1)	2.370(4)	Gd(2)–O(1)	2.374(4)
Gd(1)–O(2)	2.412(4)	Gd(2)–O(2)	2.408(4)
Gd(1)–O(3)	2.364(5)	Gd(2)–O(4)	2.345(4)
Gd(1)–O(4)	2.336(4)	Gd(2)–O(10)	2.552(4)
Gd(1)–O(5)	2.556(4)	Gd(2)–O(11)	2.362(4)
Gd(1)–O(6)	2.349(4)	Gd(2)–O(12)	2.358(4)
Gd(1)–O(7)	2.480(5)	Gd(2)–O(13)	2.530(5)
Gd(1)–O(8)	2.602(5)	Gd(2)–O(14)	2.510(5)
Gd(1)–O(18)	2.396(5)	Gd(2)–O(19)	2.390(5)
Gd(3)–O(1)	2.346(4)	Gd(3)–O(16)	2.542(6)
Gd(3)–O(2)	2.365(4)	Gd(3)–O(17)	2.348(5)
Gd(3)–O(6)	2.351(5)	Gd(3)–O(20)	2.368(4)
Gd(3)–O(12)	2.355(4)	Gd(3)–O(21)	2.318(4)
Gd(1)···Gd(2)	3.5591(4)	Gd(1)···Gd(3)	3.5591(5)
Gd(2)···Gd(3)	3.5730(4)		

97 program<sup>18</sup> and refined against all  $F_o^2$  (SHELXL-97)<sup>19</sup> with a weighting scheme  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$  where  $3P = (F_o^2 + 2F_c^2)$  and  $a$  and  $b$  are constants adjusted by the program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model, except those bonded to the water molecules which were allowed to vary, with  $U$  equal to 1.1 times the  $U_{\text{eq}}$  of the atom of attachment. Atomic scattering factors were taken from a standard source.<sup>20</sup> The structure was drawn with the ZORTEP<sup>21</sup> program. Selected bond lengths are listed in Table 2.

## Results and Discussion

The first observation of the Gd<sub>3</sub> complex was completely fortuitous. A powder sample of the mononuclear precursor L'Gd (L' being the deprotonated form of tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-butenyl]amine)<sup>9</sup> was dissolved in dichloromethane and added to an alcohol–water (1/1) solution of Gd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in an attempt to obtain well-shaped crystals of the related L'Gd<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> complex. A crystalline product was isolated, but it presented analytical data that did not fit the expected binuclear formula. Considering the mass spectral data (FAB<sup>+</sup>) (cf. experimental data) we were led to the conclusion that the ligand L' was hydrolyzed with subsequent formation of bi- and trinuclear complexes of the L ligand. Genuine samples of the trinuclear complex are readily and directly prepared from 3-methoxysalicylaldehyde (HL), Gd(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, and CsOH·H<sub>2</sub>O. Indeed their analytical and spectroscopic data are similar to the data obtained with the crystallized sample.

A single-crystal X-ray diffraction study shows that the trinuclear entity is dicationic and corresponds to the formula  $[\text{L}_3\text{Gd}_3(\text{OH})_2(\text{NO}_3)_2(\text{OH}_2)_4]^{2+}$ . In addition to the dication which is represented in Figure 1 the structure contains two uncoordinated nitrate and four water molecules. In the (Gd<sub>3</sub>O<sub>5</sub>) core, the three lanthanide ions are held together by a multiple bridging network supported by five oxygen atoms. Each of the two hydroxo ions is simultaneously bound to the three gadolinium ions, which otherwise are linked two by two by monatomic and tetrameric bridges afforded by the L ligands. The monatomic bridges are formed by the phenolato oxygens while the polyatomic pathways go through the phenolato and methoxo groups. The aldehyde oxygen atoms bind terminally to the metal

**Figure 1.** ZORTEP plot for  $[\text{L}_3\text{Gd}_3(\text{OH})_2(\text{NO}_3)_2(\text{OH}_2)_4](\text{NO}_3)_2(\text{H}_2\text{O})_4$  with ellipsoids drawn at the 50% probability level.**Figure 2.** Thermal dependence of  $\chi_{\text{M}}T$  for  $[\text{L}_3\text{Gd}_3(\text{OH})_2(\text{NO}_3)_2(\text{OH}_2)_4](\text{NO}_3)_2(\text{H}_2\text{O})_4$  at 0.1 T. The full line corresponds to the best data fit.

ions. To achieve their environment two lanthanide ions (Gd(1) and Gd(2)) make use of a water molecule and a bidentate nitrate ion while the third metal ion, Gd(3), resorts to two water molecules. The two first ions are nine-coordinated and the third one eight-coordinated.

There is a general trend for the Gd(3)–O distances being shorter than the Gd(1)–O and Gd(2)–O ones whatever the nature (bridging or terminal) of the oxygen atom (Table 2). Considering the bridging Gd–O bond lengths, the mean values are 2.354(4) Å for Gd(3)–O, 2.363(4) Å for Gd(1)–O, and 2.371(4) Å for Gd(2)–O. The OGD and GdOGd angles do not afford any clear distinction between the Gd ions. Identical values (3.5591(4) Å) are observed for the Gd(1)···Gd(2) and Gd(1)···Gd(3) separations, the related Gd(2)···Gd(3) distance being slightly larger (3.5730(4) Å). These Gd···Gd distances are slightly shorter than those reported in the literature.<sup>6,11,12</sup> Finally we note that the hydroxo ions, the coordinated and the uncoordinated water molecules, and the uncoordinated nitrate ions participate in an extended network of hydrogen bonds. However, this does not result in a significant shortening of the intermolecular contacts. The intermolecular Gd···Gd distances vary from 8.1884(5) to 9.7346(2) Å and thus are much larger than the related intramolecular values.

The magnetic behavior of the trinuclear cluster is represented in Figure 2 in the form of the thermal dependence of the  $\chi_{\text{M}}T$  product,  $\chi_{\text{M}}$  being the molar susceptibility. At 300 K,  $\chi_{\text{M}}T$  is equal to 23.30 cm<sup>3</sup> mol<sup>-1</sup> K, which does not differ from the value expected for three noninteracting gadolinium ions (23.6 cm<sup>3</sup> mol<sup>-1</sup> K). On lowering the temperature  $\chi_{\text{M}}T$  decreases. The variation is thin over the 300–100 K temperature range ( $\chi_{\text{M}}T = 22.9$  cm<sup>3</sup> mol<sup>-1</sup> K). Below 100 K,  $\chi_{\text{M}}T$  starts to decrease slowly till 50 K ( $\chi_{\text{M}}T = 21.8$  cm<sup>3</sup> mol<sup>-1</sup> K) and then more

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rapidly below 50 K, reaching a value of  $10.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K. The resulting profile of the  $\chi_{\text{M}}T$  vs  $T$  curve is indicative of an overall antiferromagnetic interaction.

In a more quantitative approach we use the isotropic HDVV exchange Hamiltonian for a triangular spin ( $S_i$ ) system.<sup>22</sup> To avoid overparametrization the Gd(1)–Gd(2) and Gd(1)–Gd(3) coupling constants are assumed to be equal ( $J$ ) but different from the Gd(2)–Gd(3) one ( $\alpha J$ ). This hypothesis is consistent with the structural data. The appropriate Hamiltonian is

$$H = -2J(S_1S_2 + S_1S_3 + \alpha S_2S_3)$$

or, after introduction of  $S^* = S_2 + S_3$  and  $S_{\text{T}} = S_1 + S^*$ ,

$$H = -J[S_{\text{T}}(S_{\text{T}} + 1) - (1 - \alpha)S^*(S^* + 1) - (1 + 2\alpha)S(S + 1)]$$

There are 48 possible spin states specified by the ( $S_{\text{T}}$ ,  $S^*$ ) values. The energy of each state is given by  $E(S_{\text{T}}, S^*) = -J[S_{\text{T}}(S_{\text{T}} + 1) - (1 - \alpha)S^*(S^* + 1)]$  neglecting a constant term  $(1 + 2\alpha)S(S + 1)$  ( $S = 7/2$ ). Substituting the  $E$  expressions into Van Vleck's equation yields a formula to which the experimental  $\chi_{\text{M}}T$  values are fitted. The best fit is obtained for  $2J = -0.20 \pm 0.01 \text{ cm}^{-1}$ ,  $\alpha = 1.00 \pm 0.01$ , and  $g = 2.003(3)$ . These data correspond to identical values for  $J$  and  $J'$ . An analysis of the experimental results on the basis of a spin-only Hamiltonian for an isotropic exchange  $H = -2J(S_1S_2 + S_1S_3 + S_2S_3)$  gives a  $2J$  value of  $-0.19 \text{ cm}^{-1}$ , with  $g = 2.003$  and  $R = 1.0 \times 10^{-3}$  ( $R = \sum[(\chi_{\text{M}}T)_{\text{obs}} - (\chi_{\text{M}}T)_{\text{calc}}]^2 / \sum[(\chi_{\text{M}}T)_{\text{obs}}]^2$ ) (Figure 2). As the actual symmetry of the spin array is  $C_{3v}$  and not  $C_i$  as initially assumed, the number of distinct states, which

are labeled  $E(S_{\text{T}})$ , reduces from 48 to 11. The total spread of these exchange split states is narrow,  $\Delta(E) = |E(21/2) - E(1/2)| = 11.4 \text{ cm}^{-1}$  so that several low-lying spin states are populated, even at 2 K. This may explain why the experimental  $\chi_{\text{M}}T$  value observed at 2 K is higher than expected for a  $S_{\text{T}} = 1/2$  ground state. Indeed  $E(3/2)$ ,  $E(5/2)$ , and  $E(7/2)$  are separated from the ground state  $E(1/2)$  by ca. 0.29, 0.76, and  $1.42 \text{ cm}^{-1}$ , respectively (compare with the  $kT$  value of ca.  $1.4 \text{ cm}^{-1}$  at 2 K).

The magnetic behavior of the trinuclear complex is consistent with those of the previously quoted polynuclear gadolinium(III) complexes. In all these cases the magnetic interaction within a (Gd, Gd) couple is antiferromagnetic with a magnitude varying from  $0.045$  to  $0.21 \text{ cm}^{-1}$ . The value observed for the trinuclear cluster ( $|2J| = 0.19 \text{ cm}^{-1}$ ) corresponds to the largest ones. The relatively high value of the interaction parameter  $J$  may be attributed to the occurrence of three exchange pathways. However, due to the paucity of the reported complexes, a magnetostructural correlation cannot be done at the moment.

**Acknowledgment.** We thank Dr. A. Mari for his contribution to the magnetic measurements and Dr. S. Richelme (Service Commun de Spectroscopie de Masse) for her contribution to the mass spectral data. The authors are greatly indebted to Dr. J. P. Laurent for fruitful discussion and comments.

**Supporting Information Available:** X-ray crystallographic files including the structural data for  $[\text{L}_3\text{Gd}_3(\text{OH})_2(\text{NO}_3)_2(\text{OH}_2)_4](\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_4$  in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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