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Ferromagnetic Coupling in the Three-Dimensional Malonato-Bridged Gadolinium(III) Complex $[Gd_2(mal)_3(H_2O)_6]$ (H_2mal = Malonic Acid)

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The novel gadolinium(III) complex of formula $[Gd_2(mal)_3(H_2O)_6]$ (**1**) (H_2mal = 1,3-propanedioic acid) has been prepared and characterized by X-ray diffraction analysis. Crystal data for **1**: monoclinic, space group $I2/a$, $a = 11.1064(10)$ Å, $b = 12.2524(10)$ Å, $c = 13.6098(2)$ Å, $\beta = 92.925(10)°$, $U = 1849.5(3)$ Å^3, $Z = 4$. Compound **1** is a three-dimensional network made up of malonate-bridged gadolinium(III) ions where the malonate exhibits two bridging modes, η^5-bidentate + unidentate and $\eta^3{:}\eta^3$ + bis(unidentate). The gadolinium atom is nine-coordinate with three water molecules and six malonate oxygen atoms from three malonate ligands forming a distorted monocapped square antiprism. The shortest metal–metal separations are 4.2763(3) Å [through the oxo-carboxylate bridge] and 6.541(3) Å [through the carboxylate in the *anti–syn* coordination mode]. The value of the angle at the oxo-carboxylate atom is 116.8(2)°. Variable-temperature magnetic susceptibility measurements reveal the occurrence of a significant ferromagnetic interaction through the oxo-carboxylate pathway ($J = +0.048(1)$ cm^{-1}, $H = -JS_{Gd(1)}\cdot S_{Gd(1a)}$).

Coordination compounds with lanthanide cations have attracted the interest of researchers in materials science because of their luminescence[2,3] and/or magnetic properties.[4−18] The rather large magnetic moment of most of the lanthanide(III) cations [Ln(III)] together with their anisotropy makes these ions very appealing in the preparation of magnetic materials. A great number of 4f−3d or 4f−organic radical systems have been described. Recent studies concerning the use of malonate (dianion of 1,3-propanedioic acid, mal^{2-}) as a ligand toward 3d[19,20] and 4f[19,21] cations have shown that a great variety of polymeric structures can be obtained due to the different coordination modes adopted by this ligand.[22]

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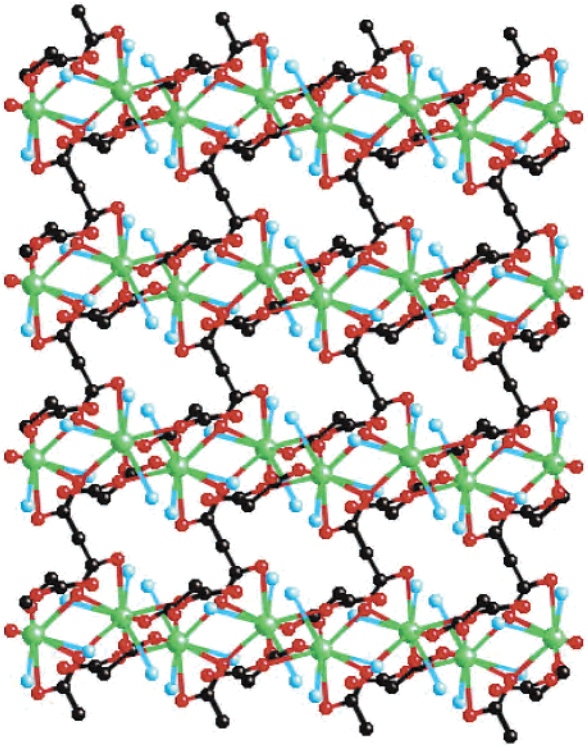
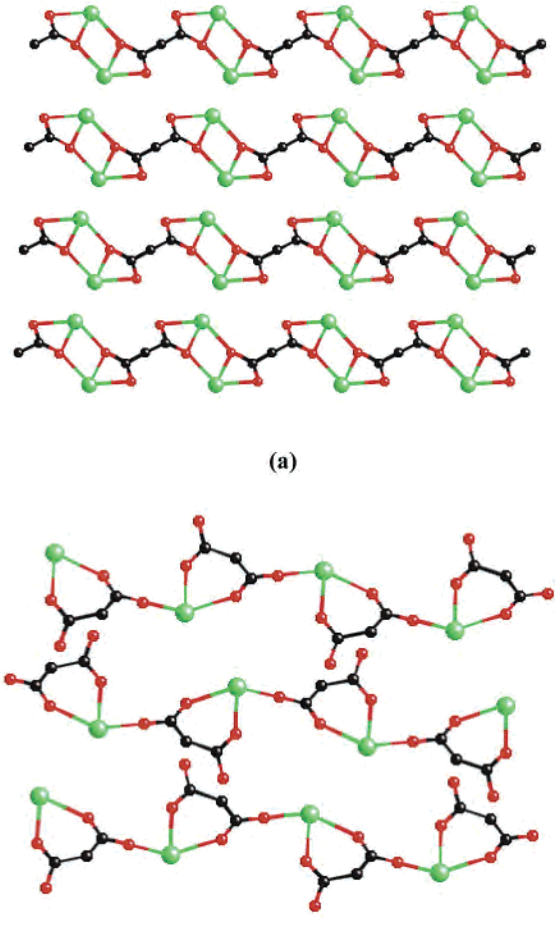


Figure 1. View of the three-dimensional structure of compound **1** along the *b* axis.

In the present work, we report the preparation,[23] X-ray structural analysis,[24] and variable-temperature magnetic study of the first example of a three-dimensional malonate-bridged compound of Gd(III) which exhibits ferromagnetic coupling between pairs of Gd(III) ions.

The structure of **1** consists of a three-dimensional arrangement of triaquagadolinium(III) units bridged by malonate groups (see Figure 1) which results from the cross-linking of the single chains running parallel to the *c* axis (Figure 2a) and the double *zigzag* chains which grow in the *ab* plane (Figure 2b). Extensive hydrogen bonds involving carboxylate groups and water molecules [2.731(3) and 2.723(3) Å for O(1W)•• O(2a) and O(2W)•••O(4b), respectively] contribute to the stabilization of the crystal structure.

The gadolinium atoms in [$Gd_2(mal)_3(H_2O)_6$] are surrounded by nine oxygen atoms: six oxygen atoms from three malonate ligands and three coordinated water molecules build a distorted monocapped square antiprism surrounding. Similar geometries are observed in other malonate-containing lanthanide complexes.[25−30] Three aspects concerning the Gd−O bond distances are to be outlined: (i) the average value of the Gd(1)−O(mal) bonds is 2.454(2) Å; (ii) there exists a long bond between Gd(1) and the O(6) carboxylate-oxygen [2.597(2) Å] which is involved in the formation of the oxo-bridge Gd(1)−O(6)−Gd(1a) (see Figure 3); (iii) the Gd−O(w) bond lengths vary in the range 2.456(2)−2.509(2) Å, values which are slightly longer than those of gadolinium to carboxylate oxygens [2.308−2.597 Å].


(a)

(b)

Figure 2. (a) Projection of the double chains down the *b* axis. (b) Projection of the single chains down the *c* axis. Water molecules, malonate ligands [L1 in part a and L2 in part b], and hydrogen atoms have been omitted for clarity.

There are two crystallographically independent malonate units with different arrangements which are noted as L1 and L2 in Chart 1. The L1 mode links two gadolinium atoms acting simultaneously as bidentate chelate and monodentate. The chelate ring of L1 has a boat conformation, and its carboxylate bridge adopts the *anti*−*syn* conformation. The malonate ligand of the L2 unit links four gadolinium atoms through two bidentate four-membered chelate rings and two monodentate interactions with the *anti*−*anti* conformation. The average C−O bond distances and O−C−O bond angles in L1 and L2 are 1.262(17) Å and 121.8(4)°, respectively. These values are in agreement with the previously reported malonate-containing lanthanide complexes. The shortest

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(23) The formation of this gadolinium malonate is accomplished by the reaction between malonic acid and gadolinium nitrate in a sodium metasilicate gel.

(24) Crystallographic analysis for **1** follows. Monoclinic, space group $I2/a$, $a = 11.1064(10)$ Å, $b = 12.2524(10)$ Å, $c = 13.6098(10)$ Å, $\beta = 92.925(10)°$, $U = 1849.5(3)$ Å^3, $Z = 4$, $\mu = 7.201$ mm^{-1}, R1 = 0.0200, wR2 = 0.0527 for 2389 observed reflections, 2637 of them with $I > 2\sigma(I)$.

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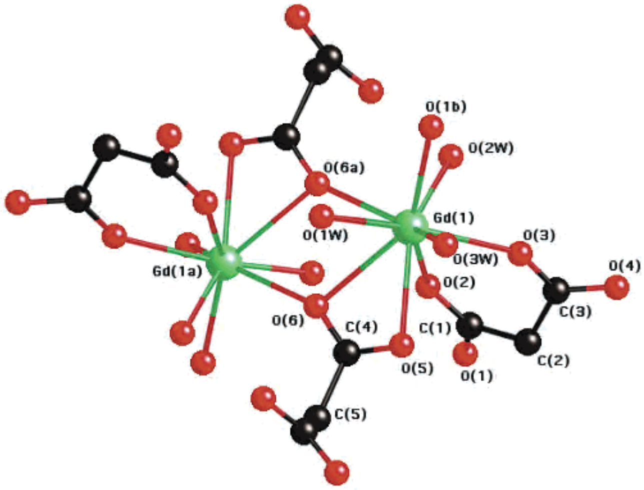
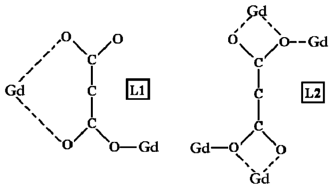


Figure 3. Coordination geometry of the gadolinium cation in **1**. Symmetry codes: (a) = $^1/_2 - x$, $^1/_2 - y$, $^1/_2 - z$; (b) = $1 - x$, $^1/_2 + y$, $^1/_2 - z$.

Chart 1



metal−metal separations are 4.2763(3) Å for Gd(1)···Gd(1a) [through the O(6) oxo-carboxylate oxygen atom] and 6.541(3) Å for Gd(1)···Gd(1b) [through the O(2)C(1)O(1)-carboxylate group].

The temperature dependence of the $\chi_M T$ product for **1** [χ_M is the magnetic susceptibility per two Gd(III) ions] is shown in Figure 4. At room temperature, $\chi_M T$ is ca. 15.75 cm^3 mol^{-1} K, a value which is as expected for two magnetically isolated $S = {}^7/_2$ local spins with $g = 2.0$. This value remains practically constant when cooling to 60 K, and further, it sharply increases to 18.6 cm^3 mol^{-1} K at 2.0 K. This curve is typical of a weak but significant ferromagnetic interaction between two gadolinium(III) ions. Although two exchange pathways are possible (oxo-carboxylato and carboxylato bridges), the shorter metal−metal separation through the oxo-carboxylate bridge, together with its greater efficiency to mediate exchange interactions versus that of the more extended carboxylato bridge, allows us to discard the latter one. Consequently, we analyze the magnetic properties of **1** through a simple dimer law deduced from the isotropic spin Hamiltonian $H = -JS_{Gd(1)}\cdot S_{Gd(1a)}$. The best-fit parameters are the following: $J = +0.05$ cm^{-1}, $g = 2.0$, and $R = 1.5 \times 10^{-5}$ (R is the agreement factor defined as $\sum[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{obs}]^2$). The magnetization plot per two Gd(III) ions (see inset of Figure 4) at 2.0 K closely follows the Brillouin function per two magnetically isolated Gd(III) ions with $g = 2.0$ because of the weak ferromagnetic interaction; the population of the ground spin state $S = 7$ in our experimental conditions is very small. To our knowledge, this is the first time that a ferromagnetic interaction is observed between two gadolinium(III) ions in a structurally characterized complex. Previous results on structurally characterized homopolynuclear Gd(III) complexes with an oxygen bridge (see S2 and references included) reveal the occurrence of antiferromagnetic interactions varying in the range −0.05 to −0.21 cm^{-1}. Only in a very recent report concerning the compound of formula $[GdL_3(H_2O)_2]_2$ (HL = salicylic acid) was a ferromagnetic coupling of the same magnitude of that of **1** observed, but the structure of this compound remains unknown.[31]

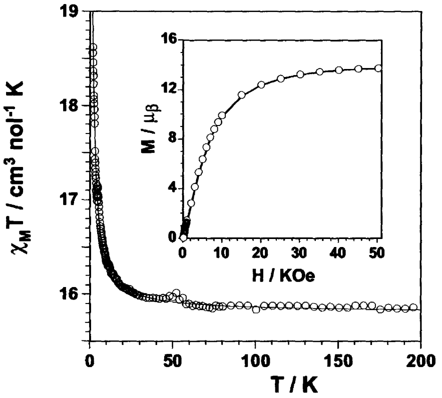


Figure 4. Temperature dependence of the $\chi_M T$ product of **1**: (○) experimental data; (—) best-fit curve (see text). The inset shows the M (○) versus H plot at 2 K [the solid line (—) is the Brillouin function for two magnetically isolated Gd(III) ions with $g = 2.0$].

At this stage, we can only suggest that the ferromagnetic coupling observed in **1** is most likely due to the accidental orthogonality between the magnetic orbitals of the two interacting Gd(III) ions, the value of the angle at the oxo-bridge, and the Gd···Gd separation through it, which plays the major role. This situation remains that of the di-μ-hydroxodicopper(II) family where the intradimer magnetic coupling is ferro- or antiferromagnetic depending mainly on the value of the angle at the hydroxo bridge.[32] The occurrence of more than one possible exchange pathway in **1** (carboxylate and oxo) makes difficult the identification of crucial factors governing the ferromagnetic coupling. Further work is in progress (magneto-structural studies and DFT type calculations) to design and characterize new examples of ferromagnetically coupled oxo-bridged Gd(III) compounds in order to clarify the exchange mechanism in these systems.

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Supporting Information Available: Experimental details (synthesis, X-ray crystallography and magnetic measurements), bond distances [Å] and angles [deg] of the coordination geometry of the gadolinium cation (S1) and structurally characterized homopolynuclear complexes with an oxygen bridge (old Table 1, new S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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