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Ferromagnetic interaction in a polynuclear gadolinium complex: structure and magnetic studies

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Acetylsalicylic acid reacts with gadolinium(III) ions to yield a new gadolinium complex (**1**) displaying a chain structure which has been determined by single crystal X-ray crystallography: monoclinic $P2_1/n$ (no. 14), $a = 13.5709(13)$, $b = 6.7141(9)$, $c = 22.7232(17)$ Å, $\beta = 99.705(14)°$, $Z = 4$. The thermal dependence of the $\chi_M T$ product (χ_M = molar magnetic susceptibility) has been measured and analysed according to the analytical expression of an infinite chain of classical spins derived by Fisher. The Gd ··· Gd interaction is weak but surprisingly is ferromagnetic with a magnitude of 0.037 cm^{-1}. Modelling of the field dependence of the magnetization at 2 K corroborates this result. It should be emphasized that (**1**) is the first example of a polynuclear gadolinium complex displaying a ferromagnetic Gd ··· Gd interaction and having a fully determined structure.

Introduction

Less attention has been paid to the magnetic properties of di- or poly-nuclear lanthanide complexes than to complexes associating d and f ions. This situation results from difficulties in obtaining pure and well-characterized (f, f′) complexes (f′ being identical or different from f) and in analysing their magnetic behaviour because of the orbital contribution of most of the f ions. In fact studies comprising structural investigations in support of the magnetic analysis are essentially limited to homopolynuclear gadolinium(III) complexes.[1–10] Until recently all the known complexes were found to be antiferromagnetic. The exchange coupling J operating between adjacent gadolinium ions and defined by the Hamiltonian $H = -2JS_aS_b$, varies from −0.045 to −0.2 cm^{-1}. Lately we have reported two dinuclear (Er, Er) and (Gd, Gd) complexes which show a ferromagnetic behaviour unambiguously attributable to lanthanide–lanthanide interaction. In the case of the (Gd, Gd) pair the exchange coupling constant J is equal to 0.05 cm^{-1}.[11] Otherwise, a semi-empirical qualitative analysis leads to the conclusion that the interaction operating in (Ln, Ln′) pairs may be either ferromagnetic ((Gd, Nd), (Gd, Ce), (Yb, Gd)) or antiferromagnetic ((Gd, Dy) and (Gd, Er)).[12] In very recent papers, it has been shown that ferromagnetism can be observed in homodinuclear triple-decker complexes involving Tb, Dy and Ho[13] and in a ferrocenecarboxylato-bridged gadolinium dimer.[14]

The present paper reports on an original gadolinium complex $[Gd(H_2L)(HL)(L)\cdot H_2O]_n$ (**1**) displaying a chain structure and ferromagnetic behaviour. It is closely related to a previously reported[11] dinuclear complex $[Gd(HL)_3(H_2O)]_2$ (**2**) which involves the same ligand (H_2L = salicylic acid). Seemingly these complexes differ by the nuclearity and the behaviour of the ligands. In the dinuclear species (**2**) the three ligands are monodeprotonated at the carboxylic site while, in the title complex (**1**), one ligand remains undeprotonated, the second and the third ones being mono- and di-deprotonated, respectively. Generally the attention given to carboxylate complexes of lanthanide ions is related to their potential utility as luminescent and sensory materials.[2,4,15–25] Diverse organic carboxylate ligands have been used, such as benzoic acid[18] or derivatives,[22,23] isonicotinic acid,[19] 3-hydroxybenzoic acid,[25] malonic acid,[15] and polyacids,[16,17] but there are only a few reports concerning salicylic acid or its derivatives.[11,20] Furthermore, the magnetic properties of these carboxylate complexes have been scarcely studied.[2,4,11,15]

Results and discussion

The differences between (**1**) and (**2**) originate in their respective preparation mode. (**2**) was obtained starting from salicylic acid and an equivalent amount of lithium hydroxide while acetylsalicylic acid was used in the case of the polynuclear entity (**1**). In the latter reaction the basic reagent, LiOH, causes cleavage of the acetyl group and deprotonation of the carboxylic function. Furthermore (**1**) was obtained as single crystals suitable for an X-ray diffraction study.

Structural study

The most salient feature of the structure of (**1**) is the formation of chains involving alternately bridging ligands and gadolinium ions. The way in which the metal ions and ligands are held together is best illustrated in Fig. 1 that represents a piece of the

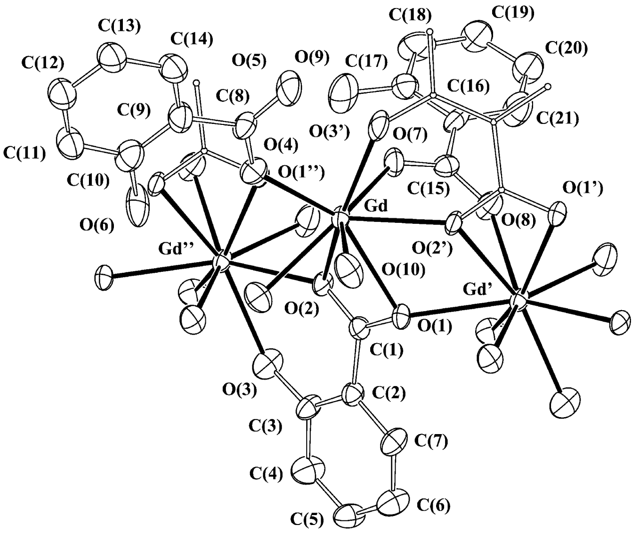

Fig. 1 ZORTEP view of complex $[Gd(H_2L)(HL)(L)\cdot H_2O]_n$ (**1**) with ellipsoïds drawn at the 50% probability level. Symmetry codes: ′(½ − x, −½ + y, ½ − z) and ″(½ − x, ½ + y, ½ − z).

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Table 1 Selected bond lengths (Å), distances (Å) and angles (°) for $[Gd(H_2L)(HL)(L){\cdot}H_2O]_n$ (**1**)

Gd–O(1)	2.565(3)	Gd–O(3′)	2.411(3)
Gd–O(2)	2.545(3)	Gd–O(4)	2.462(3)
Gd–O(1″)	2.490(3)	Gd–O(7)	2.338(3)
Gd–O(2′)	2.439(3)	Gd–O(8″)	2.415(3)
Gd–O(10)	2.377(3)	Gd″–O(3)	2.411(3)
Gd′–O(1)	2.490(3)	Gd″–O(2)	2.439(3)
Gd′–O(8)	2.415(3)	Gd′ ··· Gd″	6.7141(9)
O(1)–Gd–O(2)	50.49(9)	O(1″)–Gd–O(7)	71.07(10)
O(1)–Gd–O(1″)	114.17(6)	O(1″)–Gd–O(8″)	81.36(10)
O(1)–Gd–O(2′)	64.38(9)	O(1″)–Gd–O(10)	141.50(11)
O(1)–Gd–O(3′)	130.27(10)	O(2′)–Gd–O(3′)	65.96(10)
O(1)–Gd–O(4)	149.83(10)	O(2′)–Gd–O(4)	126.66(11)
O(1)–Gd–O(7)	85.63(10)	O(2′)–Gd–O(7)	75.06(11)
O(1)–Gd–O(8″)	80.96(10)	O(2′)–Gd–O(8″)	128.81(11)
O(1)–Gd–O(10)	83.41(11)	O(2′)–Gd–O(10)	72.06(12)
O(2)–Gd–O(1″)	63.98(9)	O(3′)–Gd–O(4)	69.46(11)
O(2)–Gd–O(2′)	108.81(7)	O(3′)–Gd–O(7)	79.43(11)
O(2)–Gd–O(3′)	153.96(11)	O(3′)–Gd–O(8″)	135.71(11)
O(2)–Gd–O(4)	123.97(10)	O(3′)–Gd–O(10)	84.15(12)
O(2)–Gd–O(7)	74.65(11)	O(4)–Gd–O(7)	123.35(11)
O(2)–Gd–O(8″)	68.51(10)	O(4)–Gd–O(8″)	71.03(11)
O(10)–Gd–O(2)	119.52(11)	O(4)–Gd–O(10)	75.77(12)
O(1″)–Gd–O(2′)	146.08(10)	O(7)–Gd–O(8″)	140.95(11)
O(1″)–Gd–O(3′)	105.20(10)	O(7)–Gd–O(10)	146.94(12)
O(1″)–Gd–O(4)	73.12(10)	O(8″)–Gd–O(10)	67.36(12)
Gd–O(1)–Gd′	111.85(10)	Gd–O(2)–Gd″	114.31(11)

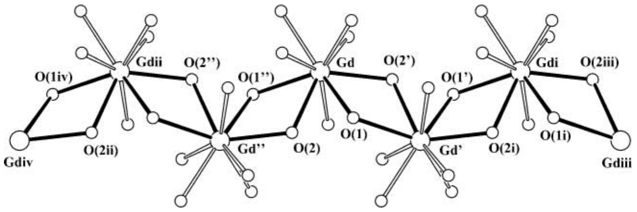

Fig. 2 Simplified view of the chain.

chain involving three metal ions. Representative bond lengths and angles are reported in Table 1. The structural results confirm that the complex is best represented by a formula associating one gadolinium ion, one water molecule and three ligands. In accordance with charge balance considerations, the three ligands differ in their protonation states. They are respectively undeprotonated (H_2L) and monodeprotonated (HL^-) at the carboxylic function and dideprotonated at the carboxylic and phenol functions (L^{2-}). They also display different coordination modes. H_2L acts as a monodentate ligand through the O4 oxygen atom of its carboxylic group. HL^- links according to a two-fold screw-axis symmetry two adjacent ions (Gd(x, y, z) with Gd′(½ − x, −½ + y, ½ − z) or Gd″(½ − x, ½ + y, ½ − z)) through the oxygen atoms (O7 and O8 or O8″ and O7″) of the carboxylato groups thus participating in a three atomic bridge of the Z,Z-type (η^1:η^1:μ). The coordination behaviour of the dideprotonated species (L^{2-}) is more complex and rather unusual. The carboxylato oxygen atoms (O1 and O2) chelate the Gd ion (η^2 mode) and, simultaneously, form monoatomic bridges with the neighbouring Gd′ and Gd″ ions according to an η^1:η^1:μ mode. The phenolato oxygen O3 of L^{2-} binds to the Gd″ ion creating an additional pentaatomic bridge between Gd and Gd″. It should be emphasized that each L^{2-} ligand is linked to three different Gd ions according to an η^2:η^2:η^1:μ_3 mode and may be considered as the cornerstone of the chain structure. To sum up the bridging framework, we note that two adjacent lanthanide ions (Gd and Gd′ for instance) are related by two monoatomic (O1 and O2′), one triatomic (O7, C15, O8) and one pentaatomic (O3′, C3′, C2′, C1′, O2′) bridge. In addition each metal ion is linked to its two next neighbours through carboxylate groups acting as η^1:η^1 bridging groups in the E,E conformation as exemplified by the (Gd″, O2, C1, O1, Gd′) pathway. Finally stabilization of the chain structure is achieved by three hydrogen bonds which involve the water molecule with the phenol or phenolate groups of H_2L or HL^- species and the carboxylic function of H_2L with the carboxylate of HL^-. Furthermore there are three additional hydrogen bonds that do not participate in stabilizing the chain since they involve intramolecular hydrogen bonds in H_2L and HL^- species (Table 2). A simplified view of the chain is given in Fig. 2. Along the chain, the Gd ··· Gd separation is equal to 4.1871(2) Å. This distance is slightly shorter than the in the dinuclear species (4.25 Å)[11] but larger than in previously reported trinuclear complexes (3.5730(4) Å),[5] (3.743(1) Å)[4] or dinuclear complexes obtained with tripodal ligands (3.984(4) Å),[6a] 3.636(4) Å)[6b] or simpler ligands (3.755(9) Å).[8] The difference could be due to the steric crowding of the ligands positioned at the periphery of the chain. This effect also ensures a good insulation of the chains, the shortest Gd ··· Gd interchain distance being equal to 12.2677(3) Å. The gadolinium ion is nine-coordinate and its geometry can be considered as a monocapped square antiprism, the capping position being occupied by the water oxygen atom. Out of the nine oxygen atoms intervening in the coordination sphere five are afforded by three different dideprotonated L^{2-} ligands, two from two different monodeprotonated HL^- ligands, and one from the undeprotonated H_2L salicylic acid, the last one being afforded by the water molecule. The Gd–O bond lengths vary from 2.338(3) to 2.565(3) Å. The shorter ones involve the HL^- ligand. In the case of the L^{2-} ligand, the bond lengths are longer, except for the η^2 chelating part involving the phenolate oxygen. As a whole these bond lengths are in the range commonly observed for gadolinium–acetate bonds.[2,25]

The Gd–O(water) bond is shorter than the mean bond lengths generally observed for this type of bond for nine-coordinate gadolinium ions (2.439 ± 0.040 Å). This shortening could be explained by the fact that in our case the bound water acts as a hydrogen-bond donor.[26]

Magnetic properties

The thermal variation of the $\chi_M T$ product (χ_M is the magnetic susceptibility per gadolinium centre) for (**1**) is shown in Fig. 3. At 300 K, $\chi_M T$ is equal to 7.83 $cm^3\ mol^{-1}$ K which is the value expected for an insulated Gd^{3+} ion in the $^8S_{7/2}$ ground state. As the temperature is lowered, $\chi_M T$ remains constant till 40 K, increases steadily from 40 to 10 K and then more sharply down to 2 K. Such a behavior is typical of a ferromagnetic interaction between the gadolinium ions. Here we are dealing with an infinite chain with a local spin equal to 7/2, and the simpler analytical expression for the magnetic susceptibility is that derived by Fisher[27] {eqn. (1), $u = \coth[JS(S+1)/kT] - [kT/JS(S+1)]$}.

$$\chi_M T = [Ng^2\beta^2 S(S+1)/3k][(1+u)/(1-u)] \qquad (1)$$

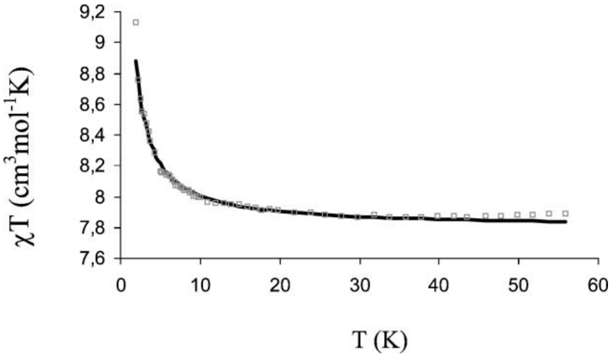

Fig. 3 Thermal dependence of $\chi_M T$ for $[Gd(H_2L)(HL)(L){\cdot}H_2O]_n$ (**1**). The solid line represents the best fit of the experimental data.

In this relation, the exchange interaction within a pair of adjacent Gd^{3+} ions is equal to $2J$. The best agreement between experimental and calculated data corresponds to $2J$ = 0.037

Table 2 Hydrogen bonds for $[Gd(H_2L)(HL)(L)\cdot H_2O]_n$ (**1**)

D	H	D–H/Å	A	H ··· A/Å	D ··· A/Å	D–H ··· A/°
O(5)	H(5A)	0.82	O(3′)	1.78	2.421(4)	133
O(6)	H(6A)	0.82	O(4)	1.85	2.533(5)	139
O(9)	H(9A)	0.82	O(7)	1.93	2.617(5)	141
O(10)	H(10A)	0.97(3)	O(9′)	2.13(4)	2.925(6)	138(3)
O(10)	H(10B)	0.96(4)	O(6i)	1.80(4)	2.669(5)	150(4)

Symmetry codes. ′: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; i: $x, -1 + y, z$.

cm^{-1} and $g = 1.99$ with an agreement factor R ($R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{obs}]^2$) of 1.2×10^{-4}. It appears that the Gd ··· Gd interaction is strongly reminiscent of that found in the dinuclear complex (**2**) which is ferromagnetic with $2J$ having a magnitude of *ca.* 0.05 cm^{-1}.[11] The nature of the Gd ··· Gd interaction in (**1**) is further supported by magnetization measurements in the 0–5 T range at 2 K (Fig. 4). The experimental values of M are fairly well reproduced by the Brillouin function corresponding to the parameters extracted from the static susceptibility data (Fig. 4, solid line). This conclusion contrasts with previous findings which unanimously document the occurrence of an antiferromagnetic ground state in homopolynuclear gadolinium complexes.[1–10] It may be underlined that the experimental data are well represented by a model comprising only one exchange coupling constant while two types of interaction would be foreseen from the structural data. Indeed chemical links transmitting magnetic interaction between adjacent gadolinium ions and between next-neighboring ions do exist. Such a situation may lead to spin frustration if the two interactions display different signs. However, owing to the lengths of the related bridging frameworks, the second interaction is more probably very weak and does not probably affect the magnetic behavior.

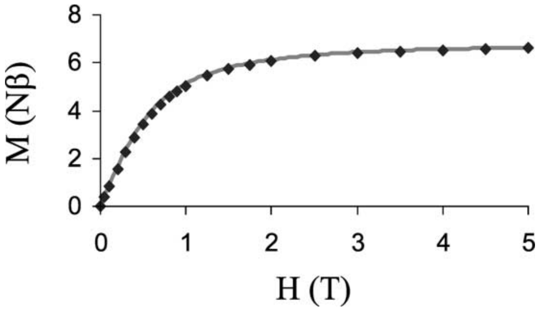

Fig. 4 Field dependence of the magnetization for complex $[Gd(H_2L)(HL)(L)\cdot H_2O]_n$ (**1**) at 2 K. The solid line represents the data computed with the set of parameters obtained from the best fit of the $\chi_M T$ curve shown in Fig. 3.

In conclusion the present work affords convincing proof that the Gd ··· Gd interaction may be ferromagnetic. At the present time we know several examples of well-characterized gadolinium complexes which present an antiferromagnetic interaction[1–10] while we describe here the first example of a polynuclear gadolinium complex displaying ferromagnetic Gd ··· Gd interactions and having a fully determined structure. More work is needed to more fully discuss the structural factors responsible for the nature of the Gd ··· Gd magnetic interaction.

Experimental

Materials and methods

All starting materials were purchased from Aldrich and used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). The polynuclear complex $[Gd(H_2L)(HL)(L)\cdot H_2O]_n$ (**1**) (H_2L = salicylic acid) was prepared by reacting a mixture of acetylsalicylic acid (1.80 g, 10 mmol) and $LiOH\cdot H_2O$ (0.42 g, 10 mmol) in absolute methanol (50 mL) with $Gd(NO_3)_3\cdot 6H_2O$ (1.50 g, 3.3 mmol). After gentle heating and reduction to half volume under stirring, the white precipitate which appeared was filtered off after cooling, and washed with methanol and diethyl ether. Yield 0.9 g (46%); elemental analysis: calc. for $C_{21}H_{17}GdO_{10}$: C 43.0, H 2.9; found: C 42.7, H 2.7%. The mass spectrum of the resulting species (FAB^+ mode, 3-nitrobenzyl alcohol matrix, dimethylformamide as solvent, Nermag R10–10 spectrometer) contains the major signal at m/z = 1016. Owing to its position and isotopic feature, it is attributed to the $[L_4Gd_3]^+$ ion. The main signals of the IR spectrum (KBr disk) are centred at 3287, 1683, 1623, 1567, 1480, 1465, 1428, 1388, 1244, 1216, 1146, 1032, 755, 704, 663, 572 and 529 cm^{-1}. Magnetic susceptibility data were collected on powdered samples with use of a SQUID-based sample magnetometer (QUANTUM Design Model MPMS instrument) in the 2–300 K range with a field of 0.1 T. Magnetization values were determined at 2 K for fields varying from 0.05 to 5 T. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants.[28]

X-Ray crystal structure determination

Light-pink crystals of $[Gd(H_2L)(HL)(L)\cdot H_2O]_n$ (**1**) suitable for X-ray determination were obtained by slow crystallization from the methanol mother-solution. $C_{21}H_{17}GdO_{10}$, M = 586.60, monoclinic, a = 13.5709(13), b = 6.7141(9), c = 22.7232(17) Å, β = 99.705(14)°, V = 2040.8(4) $Å^3$, T = 293 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 3.308 mm^{-1}, 4643 reflections measured, 4454 unique (R_{int} = 0.0304) which were used in all calculations. The final R values were $wR(F^2)$ = 0.068 (all data) and R = 0.029 [$F^2 > 2\sigma(F^2)$].

X-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using a ω–2θ scan mode with a variable scan speed. Data reduction was made with the MolEN package.[29] Absorption corrections from psi scans were applied (maximum and minimum transmission factors = 0.9994–0.6610).[30] The structure was solved by direct methods using SHELXS-97[31] and refined on F^2 by full-matrix least-squares using SHELXL-97[32] with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model, except those bonded to the water molecule that were allowed to vary. Isotropic U_H were 1.1 times higher than those of the atom to which they are bonded. Scattering factors were taken from ref. 33. The molecular plot was obtained using the ZORTEP program.[34]

CCDC reference number 199304

See http://www.rsc.org/suppdata/dt/b2/b212093c/ for crystallographic data in CIF or other electronic format.

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