Synthesis, Molecular Structure, and Magnetic Properties of a Cu_2Gd Complex†

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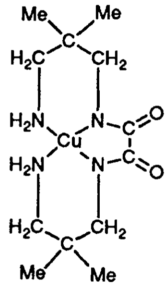
The compound $[Gd(CuL)_2(H_2O)_4][NO_3]_3 \cdot 2H_2O$ [H_2L = *N,N'*-bis(3-amino-2,2-dimethylpropyl)-oxamide] was prepared and characterised by means of structural and magnetic measurements. The crystals are monoclinic, space group $P2_1/c$, with a = 11.358(5), b = 16.932(4), c = 23.625(2) Å, β = 103.47(3)°, and Z = 4. The structural unit consists of a trinuclear tripositive cation, three nitrate anions and two lattice water molecules. The central gadolinium and terminal copper metal ions are ferromagnetically coupled, $J = -0.77$ cm^{-1}, while an antiferromagnetic coupling was detected between the terminal copper metal ions, $J = 0.42$ cm^{-1}.

With the aim of clarifying the role of the exchange interaction between 4f and 3d metal ions modulating the properties of magnetic materials containing rare-earth metals, in the last few years several compounds were synthesised where a lanthanide ion was coupled to different paramagnetic centres like copper(II) ions or stable organic radicals.[1–6] The analysis of the magnetic properties of the compounds where gadolinium(III) is present showed that in all the reported systems a ferromagnetic coupling involving Gd^{III} was operative.[7] A model based on a spin polarisation mechanism was proposed to account for this behaviour, as through this type of exchange is it possible even to justify the constant presence of an antiferromagnetic coupling between the copper(II) ions or organic radicals when more than one paramagnetic centre is interacting with gadolinium(III).[8,9] Very recently the possibility of a ferromagnetic gadolinium(III)–copper(II) coupling through an extended bridge like an oxamato group has been reported, although it was not possible to determine accurately the intensity of the interaction.[10]

We report here the synthesis, the crystal structure determination and the analysis of the magnetic properties of the trinuclear compound $[Gd(CuL)_2(H_2O)_4][NO_3]_3 \cdot 2H_2O$ where the magnetic interaction seems to operate through an extended bridge like an oxamidato group. The paramagnetic ligand is the copper compound illustrated.



CuL

Experimental

All chemicals were reagent grade and used as received. The Cu_2Gd complex was prepared by treating at 0 °C diethyl oxalate (1 mol) in absolute ethanol (140 cm^3) with 2,2-dimethylpropane-1,3-diamine (2 mol) in ethanol (240 cm^3). The mixture was kept at 100 °C for 30 min. A solution of $CuSO_4 \cdot 5H_2O$ (1 mol) in water (5 cm^3) was added and the mixture was treated with NaOH (2 mol) in water (50 cm^3). A violet precipitate was formed, which was filtered off and washed with water.[11] A suspension of the compound in water was then dissolved in the minimum volume of $MeCO_2H$; a solution (0.1 mol dm^{-3}) of NaOH was added until the violet solution turned red; slowly a precipitate was formed (Found: C, 45.75; H, 7.65; N, 17.40. Calc. for $C_{12}H_{24}CuN_4O_2$: C, 45.05; H, 7.55; N, 17.50%). A 1 mol amount of the precipitate suspended in water was treated with stirring with solid $Gd(NO_3)_3 \cdot 5H_2O$ (1 mol). The solution was filtered and left under vacuum with P_2O_5. Within 1 week ruby-violet crystals were formed (Found: C, 26.35; H, 5.55; N, 13.95. Calc. for $C_{24}H_{60}Cu_2GdN_{11}O_{19}$: C, 26.40; H, 5.55; N, 14.10%).

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured in the range 2.5–200 K with a Metronique Ingegnerie SQUID. Data were corrected for the contribution of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.[12] Magnetisation was measured at 2.65 K using the same apparatus at various magnetic fields in the range 0.5–6 T. The compound $Gd_2(SO_4)_3$ (Aldrich, 99.99+%) was used to calibrate the external magnetic fields.

Crystal-structure Determination.—Ruby-violet crystals were obtained by slow crystallisation of the reaction mixture. They were defined by three pairs of pinacoids. X-Ray data were collected at room temperature on an automated Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å).

Crystal data. $C_{24}H_{60}Cu_2GdN_{11}O_{19}$, M = 1091.15, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 11.358(5), b = 16.932(4), c = 23.625(5) Å, β = 103.47(3)°, U = 4418.4(4) Å^3, Z = 4, D_c = 1.64 (D_m = 1.65 by flotation) g cm^{-3}, $F(000)$ = 2220, μ(Mo-Kα) = 22.7 cm^{-1}, crystal dimensions *ca.* 0.25 × 0.30 × 0.20 mm.

Unit-cell parameters were derived by least-squares fitting to the setting angles of 25 intense reflections in the range θ 7–14°. The intensity data were collected at room temperature with the ω–2θ scan technique in the range 1–26°, at a scan speed range of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\chi_M(\text{emu}) = (10^6/4\pi)\chi_M(\text{SI})$.

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations(e.s.d.s) in parentheses

O(1)–Gd	2.398(9)	O(2)–Gd	2.416(9)	N(7)–Cu(2)	1.95(1)	N(8)–Cu(2)	2.02(1)
O(3)–Gd	2.317(9)	O(4)–Gd	2.43(1)	C(2)–O(1)	1.21(1)	C(1)–O(3)	1.28(2)
O(5)–Gd	2.31(1)	O(6)–Gd	2.443(9)	C(12)–O(4)	1.28(2)	C(8)–O(5)	1.27(2)
O(7)–Gd	2.42(1)	O(8)–Gd	2.41(1)	C(2)–N(1)	1.32(2)	C(1)–N(3)	1.29(2)
N(1)–Cu(1)	1.97(1)	N(2)–Cu(1)	2.00(1)	C(8)–N(6)	1.29(2)	C(12)–N(7)	1.30(2)
N(3)–Cu(1)	1.94(1)	N(4)–Cu(1)	1.99(1)	C(2)–C(1)	1.60(2)	C(12)–C(8)	1.50(2)
N(5)–Cu(2)	2.02(2)	N(6)–Cu(2)	1.96(1)				
O(2)–Gd–O(1)	135.6(3)	O(3)–Gd–O(1)	68.8(3)	N(8)–Cu(2)–N(6)	172.9(7)	N(8)–Cu(2)–N(7)	93.1(6)
O(3)–Gd–O(2)	74.6(3)	O(4)–Gd–O(1)	74.7(3)	C(2)–O(1)–Gd	119.1(9)	C(1)–O(3)–Gd	119.9(9)
O(4)–Gd–O(2)	76.2(3)	O(4)–Gd–O(3)	82.2(3)	C(12)–O(4)–Gd	113.9(8)	C(8)–O(5)–Gd	120.0(8)
O(5)–Gd–O(1)	86.6(4)	O(5)–Gd–O(2)	112.9(4)	C(2)–N(1)–Cu(1)	115.9(9)	C(6)–N(1)–Cu(1)	131(1)
O(5)–Gd–O(3)	146.3(4)	O(5)–Gd–O(4)	68.8(3)	C(6)–N(1)–C(2)	113(1)	C(7)–N(2)–Cu(1)	122(1)
O(6)–Gd–O(1)	77.4(3)	O(6)–Gd–O(2)	145.0(3)	C(1)–N(3)–Cu(1)	114.2(9)	C(4)–N(3)–Cu(1)	129.1(9)
O(6)–Gd–O(3)	120.3(3)	O(6)–Gd–O(4)	133.8(3)	C(4)–N(3)–C(1)	116(1)	C(15)–N(4)–Cu(1)	118(1)
O(6)–Gd–O(5)	73.4(3)	O(7)–Gd–O(1)	106.9(5)	C(20)–N(5)–Cu(2)	120(1)	C(8)–N(6)–Cu(2)	113(1)
O(7)–Gd–O(2)	84.3(5)	O(7)–Gd–O(3)	72.3(5)	C(11)–N(6)–Cu(2)	130(1)	C(11)–N(6)–C(8)	117(1)
O(7)–Gd–O(4)	151.3(4)	O(7)–Gd–O(5)	139.3(4)	C(9)–N(7)–Cu(2)	129(1)	C(12)–N(7)–Cu(2)	114(1)
O(7)–Gd–O(6)	72.6(4)	O(8)–Gd–O(1)	153.0(4)	C(18)–N(8)–Cu(2)	121(1)	N(3)–C(1)–O(3)	129(1)
O(8)–Gd–O(2)	70.6(4)	O(8)–Gd–O(3)	136.0(5)	C(2)–C(1)–O(3)	115(1)	C(2)–C(1)–N(3)	116(1)
O(8)–Gd–O(4)	113.9(6)	O(8)–Gd–O(5)	74.1(6)	N(1)–C(2)–O(1)	134(1)	C(1)–C(2)–O(1)	116(1)
O(8)–Gd–O(6)	79.0(5)	O(8)–Gd–O(7)	78.0(8)	C(1)–C(2)–N(1)	109(1)	C(5)–C(3)–C(4)	107(1)
N(2)–Cu(1)–N(1)	93.0(5)	N(3)–Cu(1)–N(1)	83.9(5)	N(6)–C(8)–O(5)	128(1)	C(12)–C(8)–O(5)	116(1)
N(3)–Cu(1)–N(2)	174.7(5)	N(4)–Cu(1)–N(1)	171.4(6)	C(12)–C(8)–N(6)	116(1)	C(23)–C(9)–N(7)	119
N(4)–Cu(1)–N(2)	89.3(5)	N(4)–Cu(1)–N(3)	94.4(5)	C(13)–C(11)–N(6)	114(1)	N(7)–C(12)–O(4)	128(1)
N(6)–Cu(2)–N(5)	93.6(6)	N(7)–Cu(2)–N(5)	172.4(7)	C(8)–C(12)–O(4)	119(1)	C(8)–C(12)–N(7)	113(1)
N(7)–Cu(2)–N(6)	82.8(5)	N(8)–Cu(2)–N(5)	91.1(7)				

Table 2 Final fractional coordinates of $[Gd(CuL)_2(H_2O)_4][NO_3]_3\cdot 2H_2O$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Gd	0.232 91(7)	0.536 87(5)	0.464 82(3)	N(8)	0.279(2)	0.144(1)	0.587(1)
Cu(1)	0.431 4(2)	0.578 4(1)	0.706 97(8)	N(9)	0.454(2)	0.747(1)	0.860 2(8)
Cu(2)	0.186 4(2)	0.214 2(1)	0.522 0(1)	N(10)	0.655(2)	0.441(1)	0.736 8(8)
O(1)	0.189 1(9)	0.524 8(7)	0.559 2(4)	N(11)	0.638(3)	0.538(2)	0.917(1)
O(2)	0.414 2(9)	0.540 7(8)	0.427 5(4)	C(1)	0.377(1)	0.593 4(9)	0.588 5(7)
O(3)	0.374 9(9)	0.603 4(7)	0.534 9(5)	C(2)	0.264(1)	0.548(1)	0.601 8(6)
O(4)	0.347 5(9)	0.422 2(7)	0.509 3(5)	C(3)	0.628(1)	0.711(1)	0.671 8(7)
O(5)	0.123(1)	0.421 2(7)	0.441 0(5)	C(4)	0.563(2)	0.657(1)	0.621 5(8)
O(6)	0.019 4(9)	0.573 3(6)	0.445 8(5)	C(5)	0.736(2)	0.746(1)	0.655 4(9)
O(7)	0.220(1)	0.677(1)	0.440 8(9)	C(6)	0.179(2)	0.498(1)	0.674 0(9)
O(8)	0.177(1)	0.533(2)	0.359 1(6)	C(7)	0.295(2)	0.494(2)	0.781(1)
O(9)	0.435(1)	0.774 9(9)	0.906 2(6)	C(8)	0.159(1)	0.358 6(9)	0.468 3(7)
O(10)	0.542(2)	0.770(1)	0.843 4(6)	C(9)	0.442(2)	0.289(1)	0.572 6(9)
O(11)	0.382(1)	0.696 6(9)	0.831 6(7)	C(10)	−0.203(2)	0.217(2)	0.384(1)
O(12)	0.576(1)	0.463(1)	0.693 1(5)	C(11)	−0.021(2)	0.291(1)	0.430 0(8)
O(13)	0.759(2)	0.427(1)	0.734 3(8)	C(12)	0.285(1)	0.360(1)	0.507 1(7)
O(14)	0.625(2)	0.437(1)	0.784 2(7)	C(13)	−0.073(2)	0.206(1)	0.418 1(9)
O(15)	0.523(2)	0.539(2)	0.913(1)	C(14)	0.192(2)	0.482(1)	0.736(1)
O(16)	0.706(2)	0.504(2)	0.956(1)	C(15)	0.671(2)	0.664(1)	0.727(1)
O(17)	0.667(3)	0.583(2)	0.885(1)	C(16)	0.086(2)	0.439(2)	0.750(1)
O(1H)	0.646(2)	0.025(2)	0.427(1)	C(17)	0.539(2)	0.778(1)	0.681(1)
O(2H)	0.888(2)	0.472(1)	0.869 0(9)	C(18)	0.402(3)	0.160(2)	0.616(1)
N(1)	0.279(1)	0.537(1)	0.658 1(5)	C(19)	0.000(2)	0.166(2)	0.377(1)
N(2)	0.400(1)	0.529 3(9)	0.779 3(5)	C(20)	−0.065(3)	0.156(2)	0.469(1)
N(3)	0.459(1)	0.615 2(8)	0.633 4(5)	C(21)	0.371 5	0.280 3	0.662 8
N(4)	0.573(1)	0.636(1)	0.755 0(6)	C(22)	0.138 9	0.562 2	0.745 4
N(5)	0.056(2)	0.132(1)	0.497 8(9)	C(23)	0.461 0	0.241 1	0.631 4
N(6)	0.100(1)	0.293 1(8)	0.466 7(6)	C(24)	0.588 9	0.241 9	0.671 7
N(7)	0.315(1)	0.293 0(9)	0.534 4(7)				

1.5–3.3° $\min^{-1}$, with a scan width 1.0° + 0.35 tanθ. Two standard reflections were measured every hour, and the intensities showed no significant changes. Of 9158 collected reflections, 4051 had $I > 3.0\sigma(I)$ (after merge $R = 0.029$); number of parameters 357. All data were corrected for Lorenz and polarisation effects, and an empirical absorption correction, based on the ψ scan, was applied[13] (maximum, minimum transmission factors = 0.99, 0.94).

The structure was solved by direct methods, which afforded the positions of the metal atoms; all the remaining non-hydrogen atoms were located by subsequent Fourier difference syntheses. The refinement was carried out by least-squares calculations including the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms. The hydrogen atoms bonded to C and N atoms were placed in calculated positions. The refinement of the hydrogen atoms was completed as follows: (*i*) all the atoms in the ligands were given a constant thermal parameter ($U = 0.1$ Å^2) and allowed to ride on their respective carrier atoms; (*ii*) atoms belonging to the co-ordinated and lattice water were not considered because they were not detected.

The final Fourier difference map showed maximum peaks of residual electron density of 1.8 e Å^{-3} near the heavy atoms, and not exceeding 1 e Å^{-3} elsewhere. This model converged at R = 0.063 and R' = 0.064, where $w = 1.3/[\sigma^2(F) + 0.001F_o^2]$. Complex neutral-atom scattering factors[14] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76[15] program package and the ORTEP[16] plotting program. Selected bond distances and bond angles are given in Table 1, atomic coordinates in Table 2. The cation exhibits some evidence of disorder, which shows up as abnormal dimensions for some carbon atoms of the methyl groups.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structure.—The structural unit of the complex consists of trinuclear tripositive complex cations, three nitrate anions and two lattice water molecules involved in a network of hydrogen bridges. An analysis of the crystal packing reveals no features of chemical relevance.

The geometry of the cation is depicted in Fig. 1. The central Gd^{3+} ion is eight-co-ordinated by two pairs of oxamidate oxygens in *cis* positions and four water molecules. The gadolinium and copper chelate rings are planar with maximum deviation from the average planes not exceeding 0.09 and 0.04 Å respectively. The Gd–O distances are in the range 2.317(9)–2.443(9), with average values Gd–O(aqua) 2.422 and Gd–O(oxamidate) 2.364 Å. Although the range of values is quite high the average values provide evidence for different strengths of the chemically non-equivalent Gd–O interactions. The found *cis* co-ordination geometry (referring to oxamidate) around the central gadolinium ion in the complex is indicative of the greater stability of this isomer with respect to the *trans* one. A possible explanation is that bonding interactions between oxamidate oxygens and gadolinium orbitals are favoured when the weaker donor water oxygens are placed *trans* to them.

Two oxamidate anions act as bridges between the central and the outer metal ions. They are flat and the bridged metal ions are contained in the same plane (maximum deviation from the average plane 0.03 Å). The distances between contiguous metal centres are as follows: Gd ··· Cu(1), Gd ··· Cu(2) 5.684 and 5.681(1) Å. The copper ions form with the gadolinium ion an ideal angle of 85.22(1)° with the shortest distance Cu ··· Cu of 7.694 Å. The oxamidate anions are functionalized by two *N*-bonded three-carbon chains dimethyl substituted at the central carbon and terminating with amino groups. The resulting *N*-tetradentate ligands co-ordinate in a planar geometry two copper(II) ions. Each complex unit $M^{II}N_2$(amidate)-N_2(amine) contains three chelate rings: a five-membered ring which is part of the flat system metal(eight-co-ordinated)–oxamidate–metal(square) and two puckered six-membered rings. The four six-membered rings in each cation exhibit a half-chair conformation in which the substituted carbon atom (*para* to the metal atom) is out of the average plane described by the other five atoms [C(3) 0.62, C(13) −0.53, and C(23) 0.57 Å]; C(14) deviates from this plane by 0.13 Å only, probably due to the packing constraint.

The square-planar co-ordination polyhedra are substantially flat with deviations from the average planes in the range −0.11 to +0.11 Å. These slight deviations from planarity are tetrahedral like and the N(amidate)–M–N(amine) angles are between 171 and 175°. The average bond distances are as follows: M–N(amidate) 1.955; M–N(amine) 2.008 Å. The M–N(amidate) interactions are stronger than the M–N(amine) ones, being 0.05 Å shorter.

Magnetic Properties.—The effective magnetic moment of $[Gd(CuL)_2(H_2O)_4][NO_3]_3$ increases on lowering the temperature in the range 2.5–100 K as shown in Fig. 2. Assuming that the two copper(II) ions are equivalent as regards the magnetic interaction and considering that all the interacting ions have a non-degenerate ground state, it is possible to describe the coupling exchange by using the isotropic spin Hamiltonian (1)

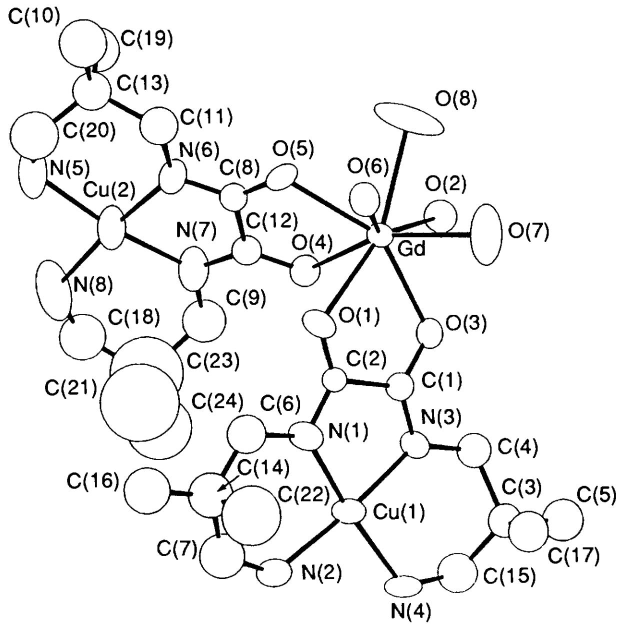

Fig. 1 An ORTEP drawing of the $[Gd(CuL)_2(H_2O)_4]^{3+}$ cation with the adopted numbering scheme. The hydrogen atoms, the nitrate groups and the lattice water molecules are not represented for clarity

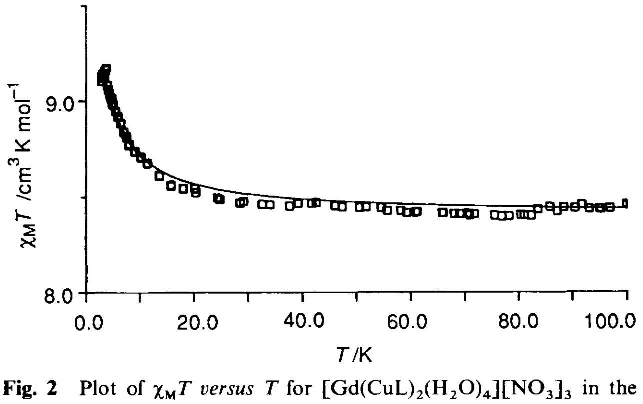

Fig. 2 Plot of $\chi_M T$ *versus* T for $[Gd(CuL)_2(H_2O)_4][NO_3]_3$ in the range 2.35–100 K

$$\mathscr{H} = J_{Gd-Cu}(S_{Gd}S_{Gd-Cu(1)} + S_{Gd}S_{Gd-Cu(2)}) + J_{Cu-Cu}S_{Cu(1)}S_{Cu(2)} \quad (1)$$

where J_{Gd-Cu} and J_{Cu-Cu} are the coupling constants which account for the gadolinium(III)–copper(II) and copper(II)–copper(II) interactions respectively. With this Hamiltonian it is possible to evaluate the energies of the four spin levels of the complex (one with $S = \frac{9}{2}$, two with $S = \frac{7}{2}$, and one with $S = \frac{5}{2}$) which are generated by the interaction of one spin $\frac{7}{2}$ with two $S = \frac{1}{2}$ spins.[3] Therefore, applying the appropriate Van Vleck equation modified to account for the presence of an external magnetic field,[17] it is possible to calculate the magnetic susceptibility, χ, of the trimer. A non-linear least-squares minimisation of the function $R = \{[S_i(\chi_i^{obs} - \chi_i^{calc})^2 T_i^2]/\Sigma_i(\chi_i^{calc}T_i)^2\}^{\frac{1}{2}}$ yielded as best-fit parameters $J_{Gd-Cu} = -0.77(3)$ cm^{-1} and $J_{Cu-Cu} = 0.42(4)$ cm^{-1} with $R = 3.9 \times 10^{-3}$, the g factors for Gd^{III} and Cu^{II} being fixed at 1.985 and 2.10 respectively. The reliability of these parameters was confirmed by measurements of the magnetisation of $[Gd(CuL)_2$-

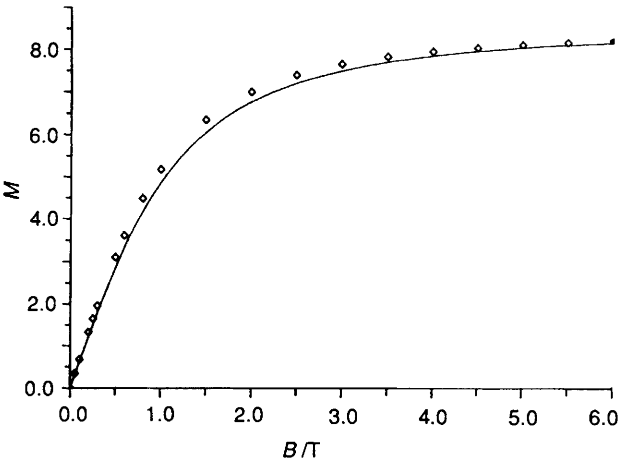

Fig. 3 Plot of magnetisation *versus* magnetic field for $[Gd(CuL)_2(H_2O)_4][NO_3]_3$. Magnetisation M is given in units $N\mu_B$ where N is Avogadro's number and μ_B is the Bohr Magneton.

$(H_2O)_4][NO_3]_3$ at 2.65 K varying the external magnetic field: as shown in Fig. 3, the agreement between the experimental data and the magnetisation curve calculated by using the best-fit parameters is good.

The analysis of the magnetic behaviour of the complex is in agreement with previous findings on the nature of the magnetic coupling in similar trinuclear units.[7] The presence of a ferromagnetic gadolinium(III)–copper(II) coupling together with an antiferromagnetic copper(II)–copper(II) one has been justified on the basis of a spin-polarisation mechanism.[8] The model assumes that there is a spin transfer of a fraction of an unpaired electron from a 3d orbital centred on a copper ion to the empty 6s orbital of gadolinium: the seven unpaired electrons of this ion are forced to align parallel to the transferred spin by Hund's rule and therefore the final result is a ferromagnetic gadolinium(III)–copper(II) coupling. At the same time, as the two copper ions are simultaneously interacting with the gadolinium, the two fractions of spins which are transferred in the 6s orbitals must be antiparallel and, consequently, the copper(II)–copper(II) coupling is antiferromagnetic in nature. As both these mechanisms are active in the complex, the magnetic properties of the system are determined by competing interactions and, therefore, a spin frustration is present in the nuclear unit.

This kind of mechanism essentially does not depend on the overlap of the magnetic orbitals and, consequently, the magnetic interactions should not be strongly influenced by the nature and geometry of the bridging ligands: therefore, the presence in our compound of couplings similar in nature and intensity to those found with different co-ordinations and bridging ligands seems to confirm the validity of the above described model. On the other hand the evidence that an extended bridge like the oxamidate group is able to transmit a magnetic interaction even in the presence of a 4f ion may offer another tool to chemists involved in the field of the synthesis of new molecular magnetic materials.

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