Synthesis, structure, and magnetic properties of discrete d–f heterodinuclear complexes designed from tetrahedrally distorted [Cu(salabza)] (H₂salabza = *N,N′*-bis(salicylidene)-2-amino-benzylamine) and [Ln(hfac)₃] (Hhfac = 1,1,1,5,5,5-hexafluoro-acetylacetone, Ln = Gd or Lu)

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A tetrahedrally distorted mononuclear copper(II) complex, [Cu(salabza)] **1**, and two dinuclear CuLn complexes, [Cu(salabza)Ln(hfac)₃] (Ln = Gd **2** or Lu **3**), were synthesized and their molecular structures determined, where H₂salabza and Hhfac denote *N,N′*-bis(salicylidene)-2-aminobenzylamine and 1,1,1,5,5,5-hexafluoroacetylacetone, respectively. In complex **1** the deviations of the four co-ordinating atoms (O(1), O(2), N(1) and N(2)) of salabza²⁻ and the copper atom from the least-squares equatorial plane O(1)O(2)N(1)N(2) indicate the tetrahedral distortion around Cu. In **2** and **3** the Cu^{II} and Ln^{III} are bridged by the two phenolic oxygens of salabza²⁻. The Cu · · · Ln distances are 3.2481(8) Å for **2** and 3.1825(7) Å for **3**. The structures of **2** and **3** were found to consist of a perfectly discrete dinuclear CuLn unit, the shortest intermolecular Cu · · · Cu, Cu · · · Ln and Ln · · · Ln distances being 6.002(1), 7.522(1) and 8.507(1) Å for **2**, and 5.998(1), 7.509(1) and 8.584(1) Å for **3**, respectively. Cryomagnetic susceptibility measurements of **2** in the region of 2 K to room temperature indicated the operation of a ferromagnetic interaction between Cu^{II} and Gd^{III}, with $J = +0.8$ cm^{-1} based on $H = -2JS_{Cu} \cdot S_{Gd}$. This was confirmed by measurements of the field dependence of magnetization at 2 K.

Introduction

Since the reports of heteronuclear CuLn and NiLn complexes (Ln = lanthanide) by Vidali and co-workers[1] and Abid and Fenton[2] in 1984, a number of d–f heteronuclear complexes comprising a d-transition metal ion and a lanthanide ion have been studied to develop new functions and for magnetic and structural interests. Most such complexes structurally analysed so far are polynuclear complexes including Cu₂Gd, Cu₂Gd₂, Cu₃Gd, Cu₄Gd₂, Cu₄Pr₂, Cu₅Ln, Cr₂Nd₃, Cr₃Nd, NiYb₂ or NiLu₂ cores or similar complexes,[3–21] and very few reports[21–25] are available on the structural determination of a discrete d–f dinuclear complex. These few discrete dinuclear complexes are classified into three types. The first type includes the CuGd complexes reported by Costes *et al.*[22–24] using dinucleating compartmental Schiff base ligands with methyl group(s) on the lateral diiminoalkane chain in order to give a steric effect. The second type includes the CuGd complexes by Kahn and co-workers[21] and Costes *et al.*,[23] in which 1-methyl-imidazole,[21] methanol[23] or acetone[23] co-ordinates to a square planar copper(II) complex as a fifth apical ligand to prevent the dinuclear CuGd units from being brought close together. The third is the NiLa complex by Winpenny and co-workers,[25] in which the dinuclear NiLa unit is wholly encapsulated by a tripodal ligand prepared by the condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-methylphenol. Thus, the number of discrete d–f dinuclear complexes is very limited, in spite of the general view that such complexes are desirable

for understanding the very weak magnetic interaction between d-transition metal and lanthanide ions. Very recently, we reported the structure of the dinuclear complex [Cu(salabza)-Gd(hfac)₃] (H₂salabza = *N,N′*-bis(salicylidene)-2-aminobenzyl-amine, Hhfac = 1,1,1,5,5,5-hexafluoroacetylacetone).[26] This complex is a new type of discrete d–f heterodinuclear complex. Our synthetic strategy is based on the following two factors: (i) the co-ordination environment around the Cu^{II} is highly distorted from square planar geometry even if the Cu^{II} is four-co-ordinated; and (ii) the ligand co-ordinating to lanthanide is sterically bulkier so that dinuclear CuLn units are located far from each other and the intermolecular spin–spin coupling can be neglected. Along this line, we were successful in the synthesis of a CuLu complex, [Cu(salabza)Lu(hfac)₃], as another example of a discrete d–f heterodinuclear complex. In the present paper the structure of these dinuclear complexes as well as of the mononuclear copper(II) complex [Cu(salabza)] **1** will be reported. Further, the spin–spin interaction between Cu^{II} and Gd^{III} was also investigated by measuring the cryo-magnetic susceptibilities and the field dependence of magnetiz-ation.

Experimental

Measurements

Elemental analyses of C, H and N were carried out at the Service Centre of Elemental Analysis, Kyushu University,

Table 1 Crystal data for complexes **1**, **2** and **3**

	1	**2**	**3**
Chemical formula	$C_{21}H_{16}CuN_2O_2$	$C_{36}H_{19}CuF_{18}GdN_2O_8$	$C_{36}H_{19}CuF_{18}LuN_2O_8$
M	391.92	1170.32	1188.04
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
$a/\text{Å}$	11.516(2)	17.354(3)	17.312(2)
$b/\text{Å}$	8.972(2)	14.050(3)	14.030(1)
$c/\text{Å}$	16.562(2)	17.780(3)	17.765(2)
$\beta/°$	98.86(1)	105.45(1)	106.093(7)
$U/\text{Å}^3$	1690.8(6)	4178(1)	4145.7(6)
Z	4	4	4
μ(Mo-Kα)/cm^{-1}	13.10	22.19	30.14
No. reflections collected	4260	10321	10240
No. unique reflections	4126	10007	9922
R_{int}	0.030	0.046	0.036
R	0.035	0.034	0.032
R'	0.026	0.040	0.026

Japan. Magnetic measurements were carried out in the range of 2.0 K to room temperature with a Quantum Design MPMS-5S SQUID magnetometer at the Institute for Molecular Science, Japan. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$, where χ_m is the magnetic susceptibility per CuGd unit corrected for diamagnetism of the constituting atoms using Pascal's constants.

Materials and syntheses

All chemicals were of reagent grade and used as commercially purchased; $Gd(NO_3)_3 \cdot 6H_2O$ and $Lu(NO_3)_3 \cdot 6H_2O$ were prepared, in the usual way, by evaporating a solution of the corresponding oxide in HNO_3 to dryness. The ligand H$_2$salabza was obtained by mixing warm ethanolic solutions of salicylaldehyde and of 2-aminobenzylamine in 2:1 molar ratio. The complexes [Gd(hfac)$_3$]·2H$_2$O and [Lu(hfac)$_3$]·2H$_2$O were prepared by the literature method.[27]

[Cu(salabza)] 1. Copper(II) acetate monohydrate (0.998 g, 5.0 mmol) was dissolved in the minimum volume of water and added to H$_2$salabza (1.652 g, 5.0 mmol) in warm methanol (90 cm^3). Soon dark green crystals were precipitated. After the mixture was warmed with stirring for 15 min, crystals were collected by suction filtration, washed with methanol and diethyl ether, and then dried in the open air. Yield: 1.646 g (84%) (Found: C, 64.40; H, 4.09; N, 7.16. Calc. for C$_{21}$H$_{16}$-CuN$_2$O$_2$: C, 64.36; H, 4.11; N, 7.15%).

[Cu(salabza)Gd(hfac)$_3$] 2. The complex [Gd(hfac)$_3$]·2H$_2$O (0.408 g, 0.5 mmol) in methanol (1 cm^3) was added to an equivalent amount of [Cu(salabza)] (0.196 g, 0.5 mmol) in chloroform (40 cm^3). After the mixture was refluxed for 2 h and filtered, the filtrate was allowed to stand at room temperature for 5 d to give dark green crystals suitable for X-ray analysis. Yield: 0.369 g (63%) (Found: C, 37.16; H, 1.73; N, 2.40. Calc. for C$_{36}$H$_{19}$CuF$_{18}$GdN$_2$O$_8$: C, 36.95; H, 1.64; N, 2.39%).

[Cu(salabza)Lu(hfac)$_3$] 3. The synthetic method was similar to that for complex **2**, except for the use of [Lu(hfac)$_3$]·2H$_2$O instead of [Gd(hfac)$_3$]·2H$_2$O. Yield: 0.327 g (55%) (Found: C, 36.32; H, 1.59; N, 2.46. Calc. for C$_{36}$H$_{19}$CuF$_{18}$LuN$_2$O$_8$: C, 36.40; H, 1.61; N, 2.36%).

X-Ray structural analyses of complexes 1, 2 and 3

Each single crystal of complex **1**, **2** and **3** was mounted on a glass fiber and coated with epoxy resin. All the measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a 12 kW

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cu–O(1)	1.900(2)	Cu–O(2)	1.889(2)
Cu–N(1)	1.961(3)	Cu–N(2)	1.949(3)
O(1)–Cu–O(2)	87.28(10)	O(1)–Cu–N(1)	93.0(1)
O(1)–Cu–N(2)	160.3(1)	O(2)–Cu–N(1)	157.7(1)
O(2)–Cu–N(2)	93.7(1)	N(1)–Cu–N(2)	93.4(1)

rotating anode generator. The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0° at a scan speed 8.0° min^{-1} (in omega). The intensities of representative reflections were measured after every 150 s. Over the course of the data collection they decreased by −0.7, −24.0 and −0.8%, respectively and a linear correction factor was applied to account for this. An empirical absorption correction based on azimuthal scans of several reflections was made. Intensity data were corrected for Lorentz-polarization effects. The structures were solved by the direct method and expanded using the Fourier technique. The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the structure factor calculations but not refined. The final cycle of full-matrix least-squares refinement of **1**, **2** and **3** was based on 2303, 6226 and 6763 observed reflections ($I > 3.00\sigma(I)$), and 284, 650 and 704 variable parameters, respectively. Crystallographic parameters are summarized in Table 1. Neutral atom scattering factors were taken from Cromer and Waber.[28] All calculations were performed using the TEXSAN package.[29]

CCDC reference number 186/1761.

See http://www.rsc.org/suppdata/dt/a9/a907423f/ for crystallographic files in .cif format.

Results and discussion

Molecular structure of the mononuclear complex [Cu(salabza)] 1

The molecular structure of [Cu(salabza)] is shown in Fig. 1, together with the atomic numbering scheme. Interatomic distances and angles relevant to the co-ordination sphere around copper are given in Table 2. The Cu–O bond lengths (1.900(2) and 1.889(2) Å) fall in the range of those (1.886–1.92 Å) for the chloroform adduct[31] and the 4-nitrophenol adduct[32] of [N,N-bis(salicylidene)ethylenediaminato]copper(II) [Cu(salen)]. The Cu–N bond lengths (1.961(3) and 1.949(3) Å) are slightly longer, compared with those (1.904–1.95 Å) for the above adducts of [Cu(salen)]. The equatorial plane can be defined by the two oxygen and two nitrogen atoms of salabza^{2-}. The deviations of these four atoms and the copper atom from this least-squares equatorial plane are −0.322(2) Å for O(1), 0.349(2) Å for O(2), 0.370(3) Å for N(1), −0.348(3) Å for N(2), and −0.009 Å for Cu, whereas, in the chloroform adduct of [Cu(salen)][31]
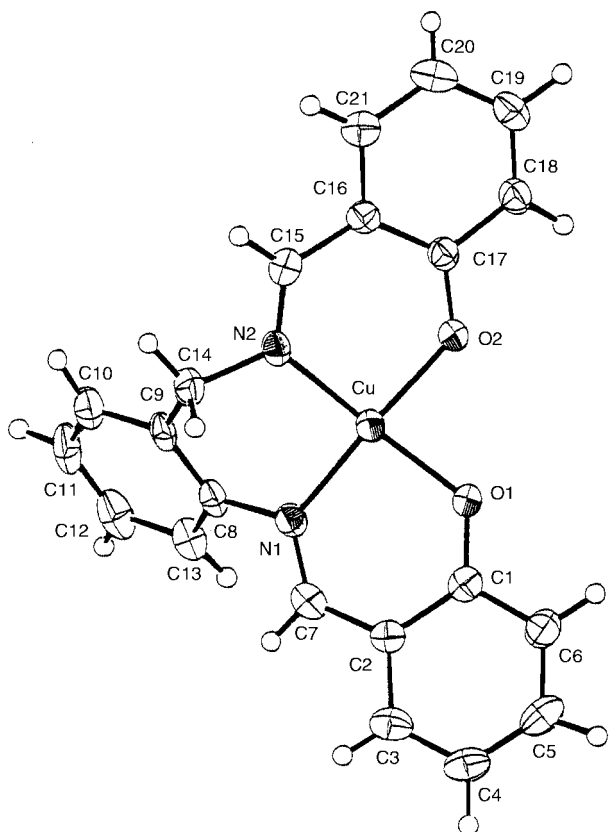
Fig. 1 An ORTEP[30] drawing of [Cu(salabza)] **1** with the atom numbering scheme.
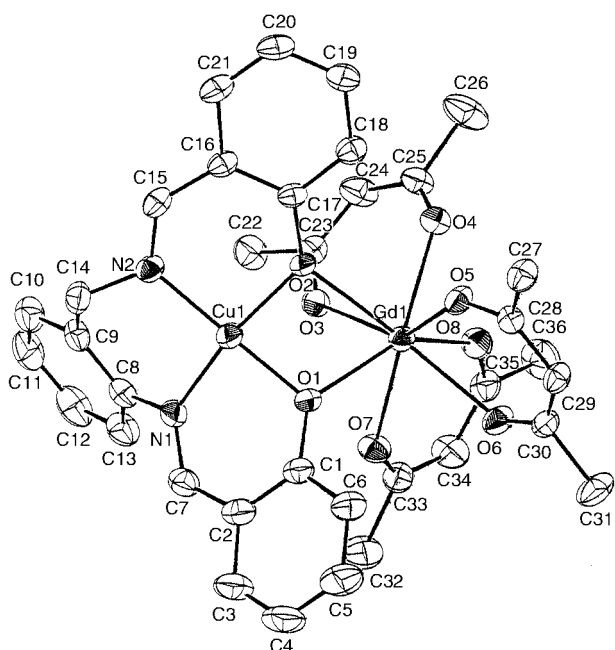

Fig. 2 An ORTEP drawing of [Cu(salabza)Gd(hfac)₃] **2** with the atom numbering scheme.

the deviations of the two oxygen atoms, the two nitrogen atoms and the copper atom from the N_2O_2 least-squares plane are reported to be 0.032 and −0.033 Å for the oxygens, −0.033 and 0.034 Å for the nitrogens, and 0.049 Å for Cu. These results apparently indicate that the co-ordination sphere around the Cu^{II} of the present [Cu(salabza)] is largely distorted toward tetrahedral, compared with that of [Cu(salen)]. Such a large distortion from square planar geometry may be one of the factors which make it possible to form the discrete dinuclear CuLn complex without adding a fifth apical ligand.

Table 3 Selected bond lengths (Å) and angles (°) for complexes **2** and **3**

| 2		3	
Cu(1)–Gd(1)	3.2481(8)	Cu(1)–Lu(1)	3.1825(7)
Cu(1)–O(1)	1.925(3)	Cu(1)–O(1)	1.928(3)
Cu(1)–O(2)	1.923(3)	Cu(1)–O(2)	1.927(3)
Cu(1)–N(1)	1.965(4)	Cu(1)–N(1)	1.957(4)
Cu(1)–N(2)	1.914(4)	Cu(1)–N(2)	1.922(4)
Gd(1)–O(1)	2.345(3)	Lu(1)–O(1)	2.262(3)
Gd(1)–O(2)	2.514(3)	Lu(1)–O(2)	2.481(3)
Gd(1)–O(3)	2.369(3)	Lu(1)–O(3)	2.287(3)
Gd(1)–O(4)	2.353(3)	Lu(1)–O(4)	2.279(3)
Gd(1)–O(5)	2.369(3)	Lu(1)–O(5)	2.290(3)
Gd(1)–O(6)	2.383(3)	Lu(1)–O(6)	2.306(3)
Gd(1)–O(7)	2.391(3)	Lu(1)–O(7)	2.322(3)
Gd(1)–O(8)	2.367(4)	Lu(1)–O(8)	2.298(3)
O(1)–Cu(1)–O(2)	81.5(1)	O(1)–Cu(1)–O(2)	80.6(1)
O(1)–Cu(1)–N(1)	92.1(2)	O(1)–Cu(1)–N(1)	92.4(1)
O(2)–Cu(1)–N(2)	95.7(1)	O(2)–Cu(1)–N(2)	95.7(1)
N(1)–Cu(1)–N(2)	93.9(2)	N(1)–Cu(1)–N(2)	94.3(2)
O(1)–Cu(1)–N(2)	168.7(2)	O(1)–Cu(1)–N(2)	168.4(1)
O(2)–Cu(1)–N(1)	160.7(2)	O(2)–Cu(1)–N(1)	160.8(1)
O(1)–Gd(1)–O(2)	62.2(1)	O(1)–Lu(1)–O(2)	63.27(10)
O(3)–Gd(1)–O(4)	74.1(1)	O(3)–Lu(1)–O(4)	77.1(1)
O(5)–Gd(1)–O(6)	70.6(1)	O(5)–Lu(1)–O(6)	72.7(1)
O(7)–Gd(1)–O(8)	71.1(1)	O(7)–Lu(1)–O(8)	73.2(1)
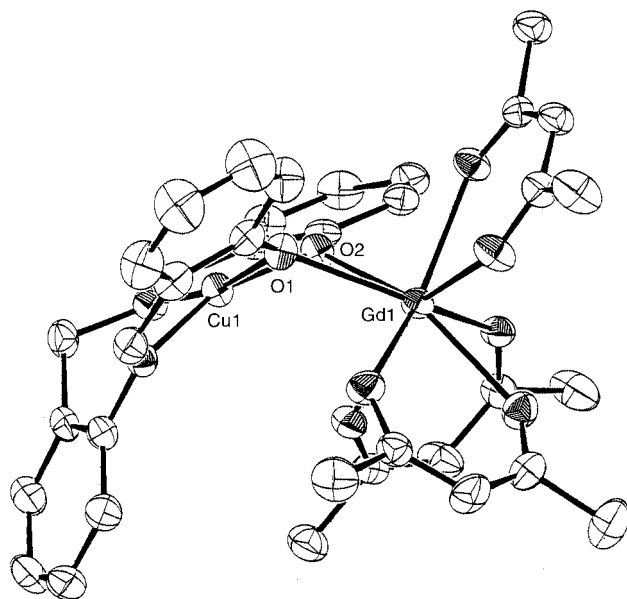
Fig. 3 Side view of the molecular structure of [Cu(salabza)-Gd(hfac)₃] **2**.

Molecular structure of [Cu(salabza)Gd(hfac)₃] 2

The shortest intermolecular Cu···Cu, Cu···Gd, and Gd···Gd distances are 6.002(1), 7.522(1), and 8.507(1) Å, respectively. The intermolecular Cu···Cu distance is much longer compared with that (3.630 Å)[21] of [Cu(salen)Gd(hfac)₃] reported to be a Cu_2Gd_2 tetranuclear complex by Kahn and co-workers, indicating that the structure of the present complex consists of a discrete dinuclear CuGd unit. The ORTEP drawing of the complex is given in Fig. 2, together with the atomic numbering scheme, and a side view in Fig. 3. The Cu^{II} and Gd^{III} are bridged by the two phenolic oxygens, and the Cu···Gd distance is 3.2481(8) Å (Table 3), which is close to that (3.252(4) Å)[21] of the complex of Kahn and co-workers but shorter than those (3.428(1)–3.5231(4) Å) of the complexes of Costes *et al.*[22,23] because of their use of phenol-based dinucleating ligands, which are derived from 3-methoxysalicylaldehyde and diamines and hence difficult to distort from the planar structure by their chemical structures. The Cu^{II} is bound to the two imino
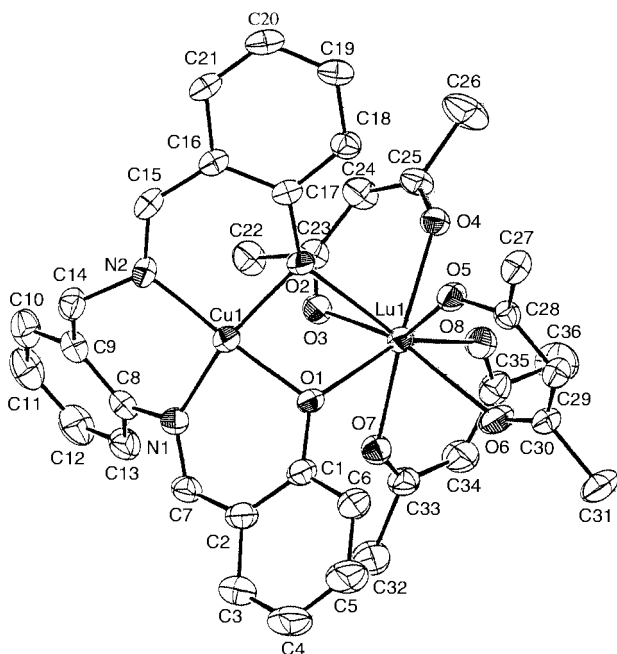
Fig. 4 An ORTEP drawing of [Cu(salabza)Lu(hfac)$_3$] **3** with the atom numbering scheme.

nitrogens and the two phenolic oxygens of salabza^{2-}. Its deviation from the least-squares N$_2$O$_2$ plane formed by the four co-ordinating atoms is -0.059 Å. The deviations of the co-ordinating atoms from the least-squares plane are $-0.202(3)$ Å for O(1), 0.190(3) for O(2), 0.292(4) Å for N(1), and -0.267 (4) Å for N(2), and the dihedral angle between the CuO(1)N(1) and CuO(2)N(2) planes is 160.13°, also here indicating the large tetrahedral distortion of the geometry around the Cu^{II}. The Gd^{III} is eight-co-ordinated, with six oxygens of three hfac$^-$ and two phenolic oxygens of salabza^{2-}. The four atoms Cu, Gd, O(1), and O(2) do not lie on the same plane, as can be seen from Fig. 3. The dihedral angle between the CuO(1)O(2) and GdO(1)O(2) planes is 132.61°.

From the above results, the success in the synthesis of a discrete dinuclear complex without adding a fifth apical ligand may result from the larger distortion of the geometry around the Cu^{II} toward a tetrahedral structure. Thus, the present work gives a new strategy for obtaining discrete d–f dinuclear complexes comprising a d-transition metal ion and a lanthanide ion.

Molecular structure of [Cu(salabza)Lu(hfac)$_3$] 3

The structure of this complex is essentially similar to that of **2**. The shortest intermolecular Cu···Cu, Cu···Lu, and Lu···Lu distances are 5.998(1), 7.509(1), and 8.584(1) Å, respectively, showing that also the structure of **3** consists of a discrete dinuclear CuLu unit. The ORTEP drawing is given in Fig. 4, together with the atomic numbering scheme. The Cu···Lu distance is 3.1825(7) Å. The deviation of the Cu^{II} from the least-squares N$_2$O$_2$ plane formed by the four co-ordinating atoms is -0.055 Å. The deviations of the co-ordinating atoms from the least-squares plane are $-0.196(3)$ Å for O(1), 0.198(3) Å for O(2), 0.276(4) Å for N(1), and $-0.265(4)$ Å for N(2), and the dihedral angle between the CuO(1)N(1) and CuO(2)N(2) planes is 160.56°. The Lu^{III} is eight-co-ordinated with six oxygens of three hfac$^-$ and two phenolic oxygens of salabza^{2-}. The dihedral angle between the CuO(1)O(2) and LuO(1)O(2) planes is 131.15°.

Magnetic properties of [Cu(salabza)Gd(hfac)$_3$] 2

The ground state of Gd^{III} is $^8S_{7/2}$, and the lowest excited energy level is very high. Thus, the contributions of the orbital angular
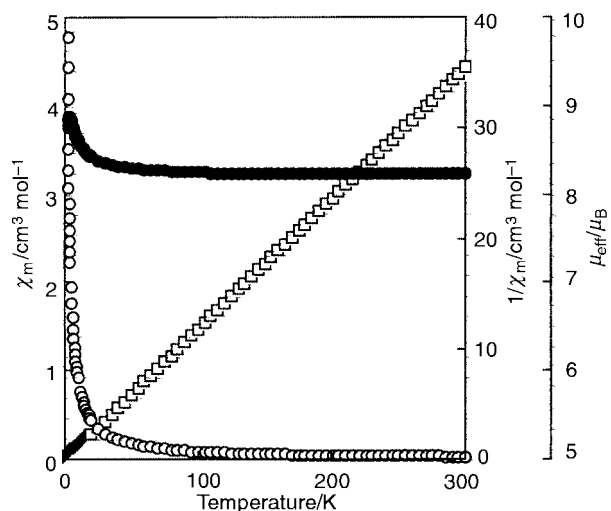
Fig. 5 Temperature dependence of χ_m (○), $1/\chi_m$ (□), and μ_{eff} (●) for complex **2**, where χ_m and μ_{eff} are magnetic susceptibility and effective magnetic moment per CuGd unit, respectively.

momentum and the anisotropic effect do not need to be taken into consideration when the properties of its complexes are discussed on the basis of electronic configuration. This makes it simple to interpret the magnetic properties of heteronuclear complexes comprising d-transition metal and lanthanide ions.

Fig. 5 shows the temperature dependences of the magnetic susceptibility (χ_m), the reciprocal magnetic susceptibility ($1/\chi_m$) and the effective magnetic moment (μ_{eff}). The plot of $1/\chi_m$ *vs.* T follows the Curie–Weiss law with the Weiss constant $\theta = +0.73$ K, indicating a weak ferromagnetic interaction. The effective magnetic moment at 300.4 K is 8.22 μ_B, which is very close to the spin-only value, 8.12 μ_B, calculated from the equation, $(\mu_{eff} = \mu_{Cu}^2 + \mu_{Gd}^2)^{1/2}$, derived by assuming that the spin–spin interaction is absent between Cu^{II} ($S_{Cu} = 1/2$) and Gd^{III} ($S_{Gd} = 7/2$). As the temperature is lowered the effective magnetic moment gradually increases to reach a maximum value, 8.88 μ_B, at 3.4 K. Such an increase in magnetic moment with lowering of temperature indicates that a ferromagnetic interaction operates between Cu^{II} and Gd^{III}, consistently with the positive Weiss constant, because the spin-only value for the total spin state $S = 4$ resulting from a ferromagnetic spin–spin coupling of the present spin system is 8.94 μ_B. Below 3.4 K the magnetic moment slightly decreases to 8.75 μ_B at 2.0 K. We tried to reproduce the magnetic susceptibility data by the spin-only equation (1) using the spin Hamiltonian $H = -2JS_{Cu} \cdot J_{Gd}$. The

$$\chi_m = \frac{4Ng^2\beta^2}{kT} \frac{15 + 7\exp(-8J/kT)}{9 + 7\exp(-8J/kT)} + N_\alpha \quad (1)$$

best fit parameters are $g = 2.02$, $J = +0.8$ cm^{-1}, and $N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. The positive J value indicates a ferromagnetic coupling between Cu^{II} and Gd^{III}.

The field dependence of the magnetization measured at 2.0 K is shown in Fig. 6 in the form of a *M vs. H* plot, where *M* and *H* are magnetization and applied magnetic field, respectively. It is expected from the above magnetic susceptibility data that only the ground state ($S = 4$) is significantly populated at 2 K. As expected, the magnetization behavior at 2 K follows the Brillouin function of $S = 4$ very well, indicating the operation of a ferromagnetic interaction between Cu^{II} and Gd^{III} to give the ground state of $S = 4$, which is almost completely populated at 2 K.

Thus, a ferromagnetic spin–spin interaction between Cu^{II} and Gd^{III} appears to operate in the present complex, as observed in the previously prepared CuGd complexes.[3–5,7,10–12,17,21–23,33–40]
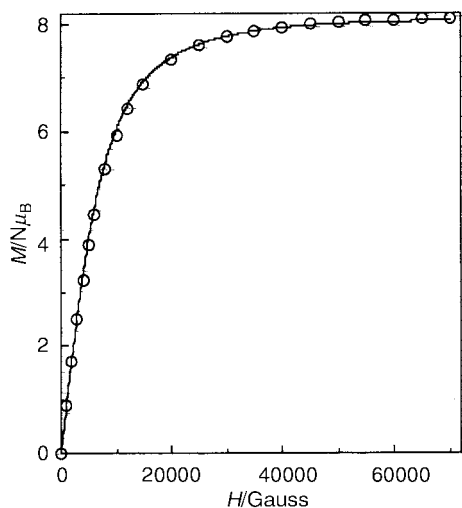
Fig. 6 Field dependence plot of magnetization for complex **2** at 2 K. The solid line represents the theoretical magnetization curve for $S_T = S_{Cu} + S_{Gd} = 4$ and $g = 2.02$.

Acknowledgements

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