A cyclic tetranuclear Cu_2Gd_2 complex with an $S = 8$ ground state derived from ferromagnetic spin-coupling between copper(II) and gadolinium(III) ions arrayed alternately

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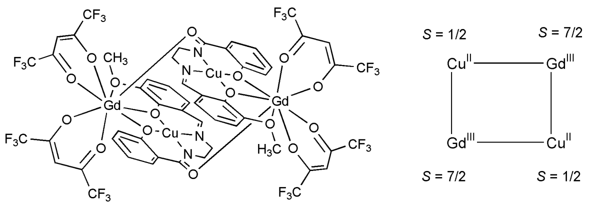
A cyclic tetranuclear $Cu^{II}_2Gd^{III}_2$ complex, in which Cu^{II} and Gd^{III} ions are arrayed alternately, has an $S = 8$ spin ground state, due to the ferromagnetic spin coupling between $S_{Gd} = 7/2$ and $S_{Cu} = 1/2$.

The field of molecular-based magnetic compounds has shown spectacular advances in the last two decades, especially in the metal-complex based magnetic materials.[1] Hetero-metal assembly complexes with multi-dimensional extended structures and versatile magnetic behavior[1] as well as single molecule magnets derived from large ground spin state and large magnetic anisotropy[2] have attracted special attention. These interesting magnetic materials consist of a d-transition metal ion, and the magnetic chemistry of d–f and f–f transition metal complexes is the forthcoming target in this field. Since ferromagnetic coupling between Cu^{II} and Gd^{III} ions was first observed in 1985 in a trinuclear complex,[3] several polynuclear Cu_2Gd_2, Cu_2Gd and other d–f complexes have been reported.[4] However, the coexisting antiferromagnetic coupling such as within a Cu_2 pair often concealed the weak ferromagnetic coupling and resulted in net antiferromagnetic behavior. Thus, recent efforts have been focused on strictly binuclear d–f complexes,[5] in order to obtain accurate information on the magnetic properties. If a d–f cluster compound without the d–d and the f–f magnetic interactions was synthesized, it could be a single molecule with a large spin state.[6] If a d–f extended multi-dimensional compound without d–d and the f–f magnetic interactions was synthesized, it would be a magnetic material exhibiting spontaneous magnetization.[7] Here we report a cyclic tetranuclear Cu_2Gd_2 complex $[CuLGd(hfac)_2]_2$, where H_3L = 1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane[8] and Hhfac = hexafluoroacetylacetone. The tetranuclear Cu_2Gd_2 complex assumes an $S = 8$ ground state derived from ferromagnetic spin-coupling between Cu^{II} and Gd^{III} ions arrayed alternately, in which the Cu^{II}–Cu^{II} and Gd^{III}–Gd^{III} magnetic interactions are weak.

The copper(II) complex K[CuL] was used as a '*ligand complex*' in order to construct an alternate array of Cu^{II} and Gd^{III} ions, because it is well-known that phenoxo-, methoxy- and amido-oxygen atoms can coordinate to a lanthanide ion,[9] and further it is expected that the amido oxygen atom at the opposite side serves as a bridge to provide an alternate array of the d–f metal ions.[10] As a counterpart, the gadolinium(III) complex $[Gd(hfac)_3(H_2O)_2]$ was used, because the hexafluoroacetylacetonato (hfac) ion can be easily substituted with external donor atoms and can also function as a capping or terminal ligand. The reaction of K[CuL] with an equimolar amount of $[Gd(hfac)_3(H_2O)_2]$ in methanol at ambient temperature produced dark reddish purple crystals of $[CuLGd(hfac)_2]$.[11]



Scheme 1

The structure was determined by a single-crystal X-ray diffraction analysis.[12] Fig. 1 shows an ORTEP drawing of the cyclic Cu_2Gd_2 tetranuclear structure, in which the Cu^{II} and Gd^{III} ions are arrayed alternately and the molecule has an inversion center. The Cu^{II} ion has square planar coordination geometry with the N_2O_2 donor atoms of the unequivalent tetradentate ligand (see chemical structure). The Cu–N and Cu–O distances of the 2-oxybenzamido moiety (Cu–N1 = 1.913(4), Cu–O2 = 1.903(4) Å) are considerably shorter than the corresponding values of the 2-oxy-3-methoxybenzaldehyde moiety (Cu–N2 = 1.931(4), Cu–O3 = 1.952(3) Å). In the cyclic structure, the Cu(II) complex functions as a '*ligand complex*' with the two Gd^{III} ions. The two phenoxo (O2 and O3) and the methoxy (O4) atoms at the one side of the planar Cu(II) complex coordinate to a Gd^{III} ion as a tridentate ligand with the distances of Gd–O2 = 2.468(3), Gd–O3 = 2.350(3), Gd–O4 = 2.550(3) Å, and Cu–Gd = 3.433(1) Å. The amido oxygen atom (O1) at the opposite side of the Cu(II) complex coordinates to another Gd ion as a monodenate ligand with the distance of Gd–O1 = 2.274(3) and Cu–Gd = 5.618(2) Å. Including the coordination of the two hfac ions as a bidentate chelate ligand (Gd–O = 2.347(4)–2.405(4) Å), the Gd^{III} ion has an octacoordinate geometry with the O_8 oxygen atoms. It should be noted that the Gd–O bond distance with the amido oxygen is the shortest among the eight Gd–O bonds. In a cyclic structure, there is no bridging ligand between the two Cu^{II} ions or between the two Gd^{III} ions. The Cu–Cu and Gd–Gd distances in the cyclic structure are 4.952(2) and 7.885(3) Å, respectively, indicating that each metal ion pair is well separated.

The magnetic susceptibilities were measured under a 1 T applied magnetic field in the 2–300 K temperature range.[13] The

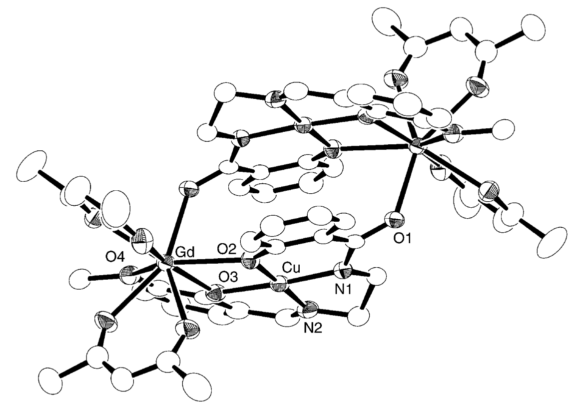


Fig. 1 ORTEP view of the cyclic Cu_2Gd_2 tetranuclear complex with 30% thermal probability ellipsoids and selected atom labeling scheme. The hydrogen and fluorine atoms are omitted for clarity.

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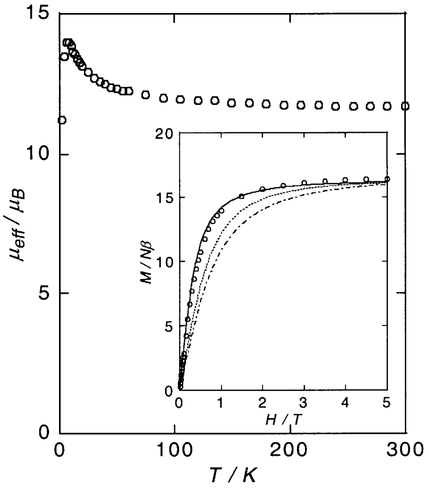

Fig. 2 Plot of the effective magnetic moment (μ_{eff}) per Cu_2Gd_2 *vs.* temperature. The inserted figure shows the field dependence of the magnetization at 2 K. The solid line represents the theoretical curve for $g = 2.02$ and $S = 8$ spin state produced by ferromagnetic coupling of the spin system (1/2, 7/2, 1/2, 7/2). The dotted and broken lines represent the theoretical curves for two isolated $S = 4$ spin states and for an isolated spin state of (1/2, 7/2, 1/2, 7/2).

magnetic behavior is shown in Fig. 2, as the μ_{eff} *vs.* T plot, where μ_{eff} is the effective magnetic moment per Cu_2Gd_2. The μ_{eff} at 300 K is 11.61 μ_B, which is slightly larger than the spin-only value of 11.49 μ_B expected for independently existing two Cu^{II} ($S = 1/2$) and two Gd^{III} ($S = 7/2$) ions and $g = 2.00$. On lowering the temperature, the μ_{eff} increases gradually to reach a maximum value, 13.98 μ_B, at 8.0 K and then decreases abruptly. The increase at the higher temperature region indicates the operation of ferromagnetic interaction between the Cu^{II} and Gd^{III} ions. The maximum value of the μ_{eff} is larger than the spin-only value, 12.65 μ_B, expected for two isolated $S = 4$ spins resulting from ferromagnetic coupling between the Cu^{II} and Gd^{III} ions of the binuclear complex, although the value is smaller than the spin-only value, 16.97 μ_B, expected for an $S = 8$ spin. The abrupt decrease in the μ_{eff} at the lower temperature region can be ascribed to weak intermolecular antiferromagnetic interaction.

To confirm the spin ground state of the cyclic tetranuclear complex, the field dependence of the magnetization was measured up to 5 T at several temperatures. The inserted plots in Fig. 2 show the experimental values of $M/N\beta$ *vs.* H at 2 K, together with the theoretical curves for the sum of the Brillouin functions of isolated two Cu^{II} ($S = 1/2$) and two Gd^{III} ($S = 7/2$) ions, for sum of two $S = 4$ spins, and for an $S = 8$ spin derived from the ferromagnetic coupling of the spin-system (1/2, 7/2, 1/2, 7/2), respectively. The magnetization data are larger than those for two independent $S = 4$ spins and for a magnetically isolated (1/2, 7/2, 1/2, 7/2) system. The magnetization data are well reproduced by the Brillouin function with $S = 8$ and $g = 2.02$. The slight difference is due to an incomplete population of the $S = 8$ state.

This study revealed that a discrete molecule with a large spin could be easily synthesized even in a d–f transition metal complex. The analogous synthetic approach should produce single molecules with larger spin states and with magnetic anisotropy. Magnets with an extended multidimensional structure can be obtained by substitution of the terminal ligand.

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Notes and references

1 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.

2 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141.

3 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128.

4 C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1750; C. Benelli, A. C. Fabretti and A. Giusti, *J. Chem. Soc., Dalton Trans.*, 1993, 409; A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1986, **25**, 572; M. L. Kahn, C. Mathoniere and O. Kahn, *Inorg. Chem.*, 1999, **38**, 3692; C. Benelli, M. Murrier, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1999, 4125; R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447.

5 J.-P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, 2000, **39**, 165; J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 2000, **39**, 169; J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 1997, **36**, 3429; J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 1997, **39**, 4284; M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohba and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 2000, 259.

6 Recently, the same synthetic approach has been developed: J.-P. Costes and F. Dahan, *C. R. Seances Acad. Sci.*, accepted in special issue number dedicated to the late Olivier Kahn, 'Assembling ferromagnetically coupled (Cu, Gd) pairs: toward higher spin entities'.

7 O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batail and M. Guillot, *Inorg. Chem.*, 1992, **31**, 110.

8 H_3L was synthesized by the 1 : 1 : 1 condensation of methyl salicylate, ethylenediamine and 3-methoxysalicylaldehyde. The crude product was washed well with dichloromethane. K[CuL] was obtained as reddish purple crystals by the reaction of H_3L, copper(II) acetate monohydrate and potassium *tert*-butoxide in the molar ratio of 1 : 1 : 3 in methanol.

9 J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Chem. Eur. J.*, 1998, **4**, 1616.

10 Y. Sunatsuki, T. Matsuo, M. Nakamura, F. Kai, N. Matsumoto and J.-P. Tuchagues, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2611; Y. Sunatsuki, M. Mimura, H. Shimada, F. Kai and N. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 167.

11 Synthesis of [CuLGd(hfac)$_2$]: a methanolic solution (20 mL) of K[CuL] (104 mg, 0.25 mmol) was added to a methanolic solution (20 mL) of [Gd(hfac)$_3$(H_2O)$_2$] (204 mg, 0.25 mmol) at ambient temperature. The mixture was allowed to stand for several days. Meanwhile, dark reddish purple crystals which formed were collected (205 mg). Anal.: calcd. for $C_{27}H_{17}N_2O_8F_{12}CuGd$: C 34.27, H 1.81, N, 2.96; found: C 34.37, H 1.85, N, 2.95%.

12 *Crystal data*: $C_{27}H_{17}N_2O_8F_{12}CuGd$, $M = 946.22$, triclinic, space group $= P1$ (no. 2), $a = 11.054(4)$, $b = 16.173(4)$, $c = 10.284(3)$ Å, $\alpha = 105.96(2)$, $\beta = 114.61(2)$, $\gamma = 80.47(3)$°, $V = 1604(1)$ Å^3, $Z = 2$, $F(000) = 916$, $D_c = 1.958$ g cm^{-3}, $D_m = 1.91$ g cm^{-3}, $\lambda = 0.71069$ Å, $T = 20 \pm 1$ °C, μ(Mo-Kα) = 28.37 cm^{-1}, $R = 0.033$, $R_w = 0.034$, ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$). Data were collected over the 2θ range 2.5–50° on a Rigaku AFC-7R X-ray diffractometer with Mo-Kα radiation. A total of 5981 reflections were collected, of which 5661 were independent. Convergence to the final R values was achieved using 5060 unique reflections ($R_{int} = 0.012$) with $I > 2.00\ \sigma(I)$ and a maximum/residual peak of −0.61/0.91 e Å^{-3}. CCDC 182/1792. See http://www.rsc.org/suppdata/cc/b0/b006445i/ for crystallographic files in .cif format,

13 Magnetic susceptibilities were measured with a MPMS5 SQUID susceptometer (Quantum Design, Inc.) in the 2–300 K temperature range under an external magnetic field of 1 T. The calibrations were done with palladium. Corrections for diamagnetism were applied using Pascal's constants. Effective magnetic moments were calculated with the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per tetrameric molecule.