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Synthesis, structure and magnetic properties of a linear Cu(II)Cu(II)Gd(III) complex

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Abstract

A dimetallic trinuclear Cu(II)$_2$Gd(III) complex, [Cu$_2$(L)][Gd(hfac)$_3$] (**1**: H$_4$L = 3,3′-(1,2-ethanediyldinitrilo)bis(1-*o*-hydroxyphenyl-1-butaneonato), hfac$^-$ = hexafluoroacetylacetonate ion) has been synthesized, and structurally and magnetically characterized. [Cu$_2$(L)] unit coordinates to [Gd(hfac)$_3$] through two phenolate oxygen atoms to afford a linear Cu(II)–Cu(II)–Gd(III) system. Its magnetic property is dominated by the antiferromagnetic interaction between two Cu^{2+} ions, and the Gd^{3+} ion behaves like a magnetically isolated ion.

Keywords: Gadorinium; Copper; Trinuclear complex; Magnetic property; Crystal structure

1. Introduction

Magnetostructural studies of oligonuclear metal complexes, particularly those of heterometallic systems, are current research targets in the field of coordination chemistry, with a hope to gain fundamental bases for developing molecular-based magnetic materials [1–5]. Recently, we are focusing on magnetic studies of heterometallic systems containing a lanthanide ion as one constituent, because high utility of lanthanide ions in advanced materials has been recognized in magnetic materials, light emitting diode, luminescent materials, etc. 3d–4f heteronuclear complexes of different types have been synthesized and their physicochemical properties have been studied [6–19]. Of particular magnetic properties of Cu(II)–Gd(III) complexes have been extensively studied to indicate a ferromagnetic spin-exchange interaction between the metal ions. In this study we have prepared a linear Cu(II)Cu(II)Gd(III) complex, [{Cu$_2$(L)}{Gd(hfac)$_3$}] (**1**), by the reaction between [Cu$_2$(L)] (H$_4$L = the Schiff base derived from the [2:1] condensation between 1-(*o*-hydroxyphenyl)-1,3-butanedione and 1,3-propanediamine) and [Gd(hfac)$_3$] (hfac$^-$ = hexafluoroacetylacetonate ion). The crystal structure and magnetic property of **1** are described. The chemical structure of H$_4$L is shown in Chart 1.

2. Experimental

2.1. Synthesis

H$_4$L [20–24] and [Gd(hfac)$_3$]·2H$_2$O [25] were prepared according to literature methods.

2.1.1. [Cu$_2$(L)]·0.5CHCl$_3$

To a CHCl$_3$ solution (50 ml) of H$_4$L (395 mg, 1 mmol) was added dropwise a methanol solution (150 ml) of

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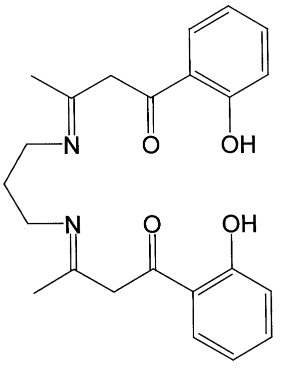


Chart 1.

$Cu(CH_3COO)_2 \cdot H_2O$ (400 mg, 2 mmol) and the mixture was heated with stirring for 6 h. The resulting green precipitate was collected suction filtration. $[Cu_2(L)] \cdot 0.5CHCl_3$ was obtained as green needles by recrystallization from DMF-ether mixture. Yield: 375 mg (65%). *Anal.* Calc. for $C_{23.5}H_{22.5}Cl_{1.5}Cu_2N_2O_4$: C, 48.90; H, 3.93; N, 4.85; Cu, 22.0%. Found: C, 48.70; H, 3.99; N, 4.81; Cu, 21.6%. IR (KBr disk): $\nu = 1597, 1523\ cm^{-1}$.

2.1.2. [{$Cu_2(L)$}{Gd(hfac)$_3$}] (**1**)

A solution of $[Cu_2(L)] \cdot 0.5CHCl_3$ (289 mg, 0.5 mmol) in $CHCl_3$ (200 ml) was added to a solution of $[Gd(hfac)_3] \cdot 2H_2O$ (405 mg, 0.5 mmol) in methanol (10 ml), and the mixture was refluxed for 2 days. The resulting green solution was allowed to stand for several days to give green crystals. They were collected by suction filtration, washed with methanol and dried in air. Yield: 402 mg (62%). *Anal.* Calc. for $C_{38}H_{25}Cu_2F_{18}GdN_2O_{10}$: C, 35.22; H, 1.94; N, 2.16; Cu, 9.8; Gd, 12.1%. Found: C, 35.20; H, 1.98; N, 2.21; Cu, 10.1; Gd, 12.2%. IR (KBr disk): $\nu = 1653, 1597, 1530, 1257, 1206, 1145\ cm^{-1}$; UV/Vis (acetonitrile) $\lambda_{max} = 652^{br}$ nm; (powdered sample) $\lambda_{max} = 595^{br}$ nm; FAB MS: m/z: 1089.5 $\{[Cu_2(L)][Gd(hfac)_2]\}^+$.

2.2. X-ray crystallography

Crystal data for **1**: $C_{38}H_{25}Cu_2F_{18}GdN_2O_{10}$, F.W. = 1295.94; green plates, crystal dimensions $0.22 \times 0.33 \times 0.11\ mm^{-3}$, triclinic, space group $P\bar{1}$, $a = 12.426(1)$, $b = 16.558(1)$, $c = 11.882(1)$ Å, $\alpha = 102.934(6)°$, $\beta = 108.905(3)°$, $\gamma = 78.972(3)°$, $V = 2235.5(3)$ Å^3, $Z = 2$, $D_{calc} = 1.925\ g\ cm^{-3}$, μ (Mo Kα) $= 25.45\ cm^{-1}$, $R = 0.073$, $R_w = 0.138$, $R_1 = 0.046$. R (for all data) $= \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$, $R_w = [(\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)]^{1/2}$, R_1 (for $I > 2.0\sigma(I)) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Data collection: Rigaku Raxis-Rapid Imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Indexing was performed from three oscillations which were exposed for 5 min. The data were collected at -90 ± 1 °C to a maximum 2θ value of 55.0°. A symmetry-related absorption correction using the program ABSCOR was applied. The structure was solved by direct method, expanded using Fourier techniques and refined anisotropically on F^2. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [26]. Of the 18 457 reflections which were collected, 9819 were unique ($R_{int} = 0.043$); equivalent reflections were merged. The final cycle of full-matrix least-squares refinement was based on 9819 all reflections and 712 variable parameters. Hydrogen atoms were included but not refined.

3. Result and discussion

3.1. Preparation and general properties

Compound **1** was prepared by the reaction of $[Cu_2(L)]$ and $[Gd(hfac)_3] \cdot 2H_2O$ in the 1:1 molar ratio. The metal ratio (Cu:Gd = 2:1) is confirmed by Rigaku ZSX-100S X-ray fluorescence spectrometer. IR spectrum shows ν_{CN}, ν_{CO} and ν_{CF} bands at 1530, 1653 and 1257 cm^{-1}, respectively.

The result of the molar conductance measurement indicates that compound **1** is non-electrolyte in acetonitrile. FAB MS spectra for **1** show a dominant ion peak at $m/z = 1089.5$ which corresponds to a fragment, $\{[Cu_2(L)][Gd(hfac)_2]\}^+$. These results suggest that the Cu_2Gd trinuclear core is stable in solution. Compound **1** shows no remarkable redox activity. It shows a broad band around 650 nm which is attributed to a superposition of d–d bands due to the two ions in the dissimilar N_2O_2 and O_4 cavities.

3.2. Crystal structure

ORTEP drawings with atom numbering scheme are shown in Figs. 1 and 2. Selected bond distances and angles are listed in Table 1.

The asymmetric unit consists of one $[Cu_2(L)]$ and one $[Gd(hfac)_3]$ units. Two Cu ions locate in N_2O_2 and O_4 sites of L^{4-} with a dihedral angle (between N1, N2, O2, O3 plane and O1, O2, O3, O4 plane) of 14.9(1)°. The Cu···Cu separation bridged by two enolate oxygen atoms (O2 and O3) is 3.000(1) Å. The Cu1–O2–Cu2 and Cu1–O3–Cu2 angles are 102.8(2)° and 101.1(2)°, respectively. The geometry of each Cu is square plane. The dihedral angle between the plane defined by Cu1, O1 and O4 and the plane defined by Cu1, O2 and O3 is 9.906°. The dihedral angle between the plane defined by Cu2, O2 and O3 and the plane defined by Cu2, N1 and N2 is 14.218°. The Cu1-to-ligand and Cu2-to-ligand bond distances fall in the range of 1.870(4)–1.903(4) and

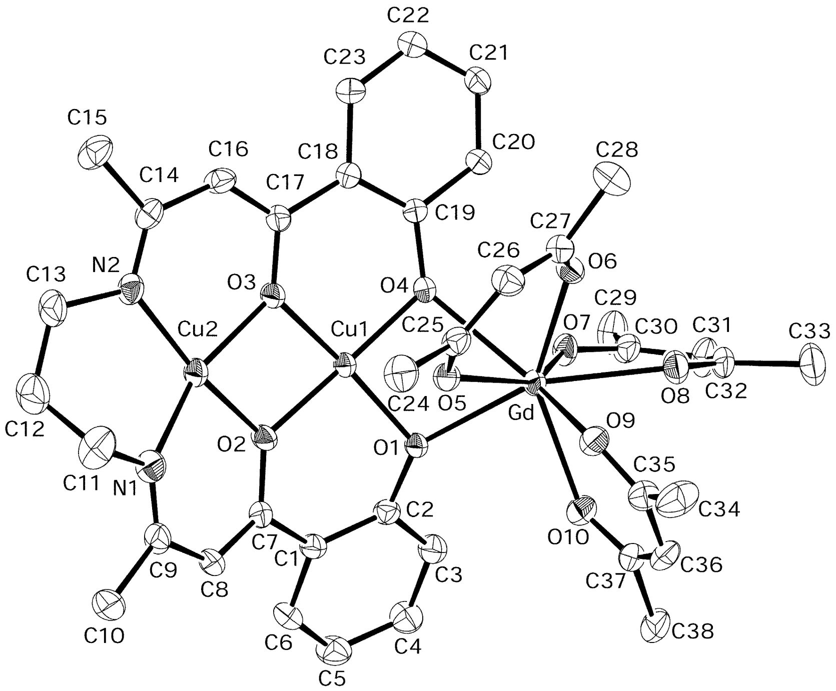


Fig. 1. An ORTEP drawing of [{Cu_2(L)}{Gd(hfac)$_3$}] (**1**) with atom numbering scheme (top view).

1.932(5)–1.983(4) Å, respectively. The displacement of Cu1 and Cu2 from the basal least-squares plane is 0.119 and 0.021 Å, respectively. Phenolic oxygen atoms (O1 and O4) coordinate to Gd ion with the bond distance of 2.375(4) and 2.470(4) Å, respectively. The Cu1–O1–Gd and Cu1–O4–Gd angles are 96.6(1)° and 94.4(1)°, respectively. The Gd ion has an eight-coordine environment with oxygen atoms. The Gd–O bond distances fall in the range of 2.343(4)–2.470(4) Å. The Cu1O_4 plane and the GdO_2 plane forms a dihedral angle of 123.5(1). The Gd deviates by 1.375(5) Å from the plane defined by O1, O2, O3 and O4. The Cu1···Gd and Cu2···Gd separations are 3.210(1) and 5.889(1), respectively. Two phenol rings twist due to the coordination to Gd ion with a dihedral angle (between C1–C6 and C18–C23 rings) of 29.7(2)° (Fig. 3).

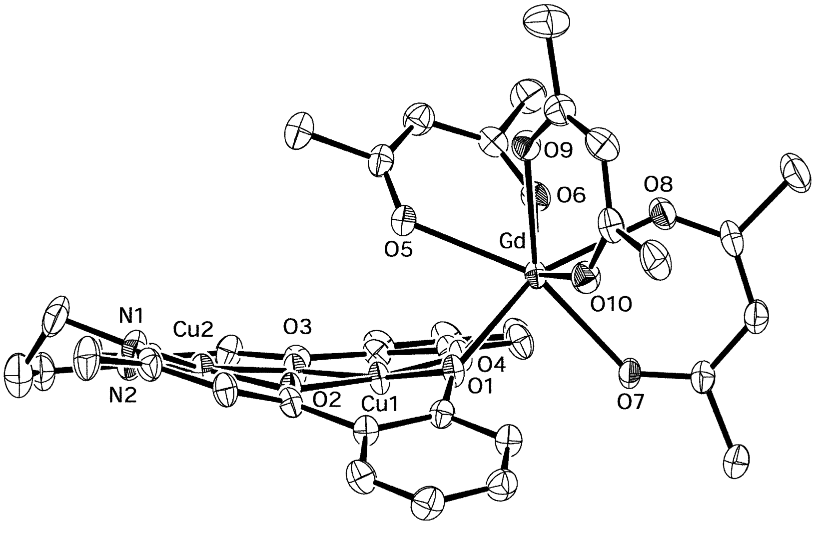


Fig. 2. An ORTEP drawing of [{Cu_2(L)}{Gd(hfac)$_3$}] (**1**) (side view).

Table 1
Selected bond distances (Å) and angles (°)

Bond lengths			
Cu(1)–O(1)	1.903(3)	Cu(1)–O(2)	1.903(4)
Cu(1)–O(3)	1.901(4)	Cu(1)–O(4)	1.870(4)
Cu(2)–O(2)	1.936(4)	Cu(2)–O(3)	1.983(4)
Cu(2)–N(1)	1.943(5)	Cu(2)–N(2)	1.932(5)
Gd–O(1)	2.375(4)	Gd–O(4)	2.470(4)
Gd–O(5)	2.431(4)	Gd–O(6)	2.343(4)
Gd–O(7)	2.354(4)	Gd–O(8)	2.395(4)
Gd–O(9)	2.382(4)	Gd–O(10)	2.357(4)
Bond angles			
O(1)–Cu(1)–O(2)	94.7(2)	O(1)–Cu(1)–O(3)	169.6(2)
O(1)–Cu(1)–O(4)	88.7(2)	O(2)–Cu(1)–O(3)	79.0(2)
O(2)–Cu(1)–O(4)	173.1(2)	O(3)–Cu(1)–O(4)	96.8(2)
O(2)–Cu(2)–O(3)	76.3(1)	O(2)–Cu(2)–N(1)	91.1(2)
O(2)–Cu(2)–N(2)	165.8(2)	O(3)–Cu(2)–N(1)	162.2(2)
O(3)–Cu(2)–N(2)	92.5(2)	N(1)–Cu(2)–N(2)	101.7(2)
O(1)–Gd–O(4)	65.9(1)	O(1)–Gd–O(5)	76.1(1)
O(1)–Gd–O(6)	137.8(1)	O(1)–Gd–O(7)	89.2(1)
O(1)–Gd–O(8)	148.7(1)	O(1)–Gd–O(9)	115.2(1)
O(1)–Gd–O(10)	78.5(1)	O(4)–Gd–O(5)	70.9(1)
O(4)–Gd–O(6)	77.1(1)	O(4)–Gd–O(7)	80.3(1)
O(4)–Gd–O(8)	131.3(1)	O(4)–Gd–O(9)	137.0(1)
O(4)–Gd–O(10)	141.4(1)		

3.3. Magnetic property

Magnetic susceptibilities were measured on Quantum Design MPMS-5XL in the temperature range of 2–300 K. The $\chi_M T$ vs. T plot shows no remarkable temperature-dependence below 200 K and a slight decrease at low-temperature region (Fig. 4). The $\chi_M T$ at room temperature is 8.15 cm^3 K mol^{-1} (8.07 μ_B), which is smaller than the expected value for magnetically uncoupled two Cu^{II} (S = 1/2) ions and one Gd^{III} (S = 7/2) ion (8.63 cm^3 K mol^{-1}; 8.30 μ_B). This suggests an operation of antiferromagnetic interaction. Indeed, dinuclear complex [Cu$_2$(L)(H$_2$O)] shows a strong antiferromagnetic interaction ($-J > 300$ cm^{-1}). The antiferromagnetic interaction between Cu ions in [Cu$_2$(L)] must be maintain in **1** because the dicopper core structure does not change on forming the trinuclear CuCuGd core.

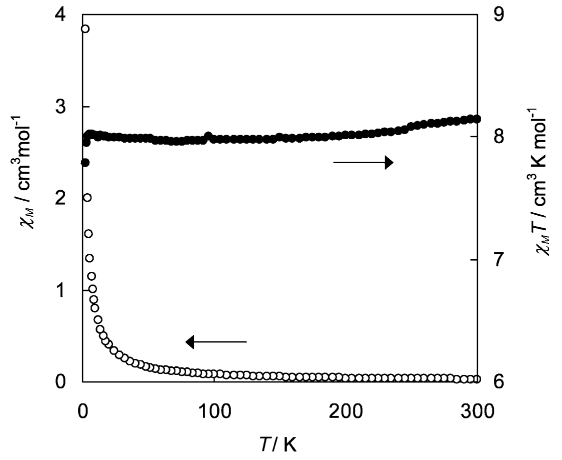
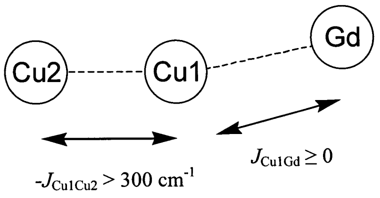


Fig. 4. Temperature-dependences of χ_M and $\chi_M T$ for **1**.



Scheme 1.

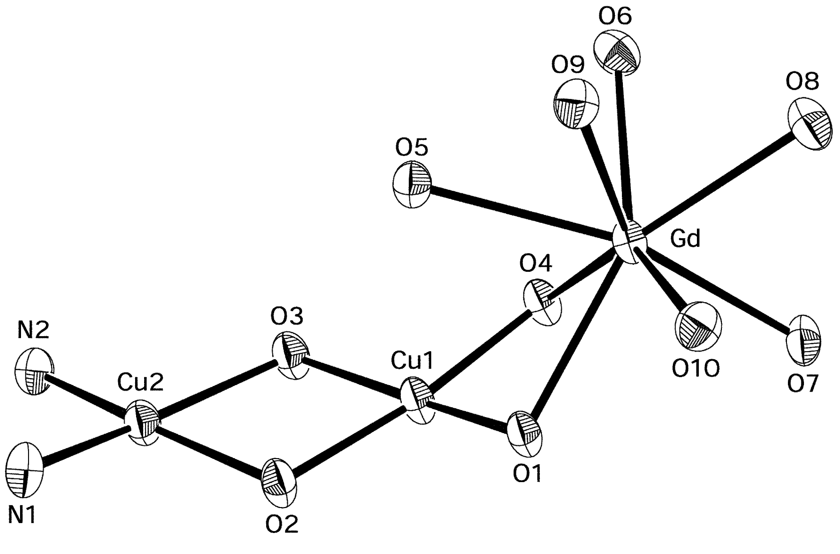


Fig. 3. Coordination structure of the Cu(II)Cu(II)Gd(III) tricuclear core.

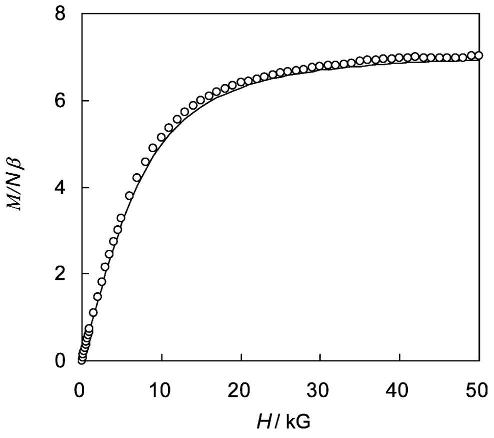


Fig. 5. Field-dependences of magnetization M for **1** at 2 K. Simulated curve is shown by solid line.

It is generally shown that a weak ferromagnetic interaction operates in di(μ-alkoxo) and di(μ-phenoxo) Cu(II)Gd(III) complexes. The structural result for **1** suggests that a ferromagnetic interaction can operate between Cu1 and Gd ions. However, the antiferromagnetic interaction between Cu1 and Cu2 ions is much larger than the ferromagnetic interaction between Cu1 and Gd ions in this case. Because of this reason there exist little spin on the Cu1 center, and the Gd ion behaves as an isolated magnetic center (Scheme 1).

The field-dependence of magnetization curve is given in Fig. 5. The M vs. H curve is well simulated by Brillouin function for $S_T = 7/2$ with $g = 2.00$, adding a support to that the Gd^{3+} is magnetically isolated.

4. Conclusion

A dimetallic trinuclear complex [$\{Cu_2(L)\}\{Gd(hfac)_3\}$] (**1**) has been prepared by the reaction of [$Cu_2(L)$] and [$Gd(hfac)_3$]$\cdot 2H_2O$ in the 1:1 molar ratio. It has a Cu(II)–Cu(II)–Gd(III) trinuclear core structure with keeping the Cu_2 core structure. Two Cu(II) ions antiferromagnetically coupled and magnetic interaction between Cu(II) and Gd(III) ions is negligible. The present complex can also be extended to other 3d–3d′–4f trimetallic system of magnetic significance. Researches along this line are in progress in this laboratory.

5. Supplementary material

Crystallographic data for **1** has been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-194477. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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