

## Synthesis and Magnetism of $\mu$ -Oxamido-Bridged $\text{Cu}_2^{\text{II}}\text{Ln}^{\text{III}}$ -type Heterotrinnuclear Complexes (Ln = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er)

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Eight new  $\text{Cu}_2^{\text{II}}\text{Ln}^{\text{III}}$ -type (Ln = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er) heterotrinnuclear complexes bridged by N,N'-bis(2-aminopropyl)oxamidocopper(II) [Cu(oxdn)], namely  $\text{Cu}_2(\text{oxdn})_2\text{Ln}(\text{NO}_3)_3$ , have been synthesized and characterized by elemental analyses, molar conductivity measurements and spectroscopic (IR, UV, ESR) studies. Magnetic susceptibility measurements (4.2–300 K) and studies of  $\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_3$  complex have revealed that the central gadolinium(III) and terminal copper(II) ions are ferromagnetically coupled with the exchange integral  $J_{(\text{Cu}-\text{Gd})} = +2.98 \text{ cm}^{-1}$ , while an anti-ferromagnetic coupling is detected between the terminal copper(II) metal ions with the exchange integral  $J_{(\text{Cu}-\text{Cu})} = -0.75 \text{ cm}^{-1}$ , on the basis of the spin Hamiltonian operator  $[\hat{H} = -2J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Gd}} + \hat{S}_{\text{Cu2}} \cdot \hat{S}_{\text{Gd}}) - 2J'(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu2}})]$ .

**Key words:** copper(II)–lanthanide(III)–copper(II), heterotrinnuclear complexes, ferromagnetic spin-coupling, synthesis

Studies on synthesis and magnetic properties of heteropolynuclear complexes containing different paramagnetic centers have been an active field of research in recent years [1–3]. Interest in this area is fundamental not only for gaining some insight into the structural and electronic factors governing ferromagnetic interaction between paramagnetic centers [3], but also for obtaining information about designing and synthesizing molecule-based magnets [2] and investigating the spin-exchange mechanism between paramagnetic metal ions [1]. Compared with the studies dealing with heteropolynuclear systems comprising d-transition metal ions [1,4–9], relatively few studies dealing with heterometal complexes containing d-transition metal ions and lanthanide(III) ions (so-called d-f heteronuclear complexes) have been reported, especially for heterotrinnuclear complexes of this kind, due to the very weak interaction and a large anisotropic effect of lanthanide ions [10–13]. However, the fact that the d-f mixed oxides have been used in many functional materials and/or have been expected as promising functional materials [14], stimulated us to develop d-f heteronuclear complexes, possessing new functions associated with some d-f heterometal centers [15–17]. In continuation of our earlier work, in this paper, eight new heterotrinnuclear complexes,  $\text{Cu}_2(\text{oxdn})_2\text{Ln}(\text{NO}_3)_3$  (Ln = Ce, Nd, Sm, Eu, Gd, Tb,

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Dy, Er) have been prepared by the reaction of N,N'-bis(2-aminopropyl)oxamido-copper(II) (abbreviated as Cu(oxdn)) with lanthanide(III) ions. The ESR and magnetic properties of the  $\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_3$  complex have been studied in detail. The main result is that the copper(II) and gadolinium(III) ions are coupled in a ferromagnetic fashion *via* isotropic coupling ( $J = +2.98 \text{ cm}^{-1}$ ), thus, indicating that weak coupling can be established between transition-metal and rare-earth ions.

## EXPERIMENTAL

**Materials:** All the reagents used were of analytical grade. The hydrated lanthanide nitrates were prepared by general methods. The starting material N,N'-bis(2-aminopropyl)oxamidocopper(II), Cu(oxdn), was synthesized as previously described in [5].

**Synthesis of  $\text{Cu}_2(\text{oxdn})_2\text{Ln}(\text{NO}_3)_3$  (Ln = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er) complexes:** All the eight heterotrinnuclear complexes were prepared in a similar fashion and only the typical preparation of  $\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_3$  is given here. To a solution of Cu(oxdn) (580.2 mg, 2.2 mmol) stirred in absolute ethanol (15  $\text{cm}^3$ ) was added successively a solution of  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (451.4 mg, 1 mmol) in absolute ethanol (20  $\text{cm}^3$ ), followed by a solution of ethyl orthofomate (10  $\text{cm}^3$ ). The stirring was continued at room temperature for a further 12 h to give purple microcrystals which were removed by filtration, washed several times with ethanol, water and diethyl ether and dried over  $\text{P}_2\text{O}_5$  under reduced pressure. The elemental analyses confirmed the compositions given (see Table 1). Some important data of these complexes are collected in Table 1.

**Table 1.** Compositions, yields, colors and melting points (M.p) of the heterotrinnuclear complexes.

Complex	Empirical formula (Formula weight)	Color	Yield (%)	M.p. (C)
(1)	$\text{Cu}_2\text{CeC}_{16}\text{H}_{34}\text{N}_{11}\text{O}_{14}$ (871.72)	pale-red	80	329
(2)	$\text{Cu}_2\text{NdC}_{16}\text{H}_{32}\text{N}_{11}\text{O}_{13}$ (857.83)	purple-brown	77	267
(3)	$\text{Cu}_2\text{SmC}_{16}\text{H}_{36}\text{N}_{11}\text{O}_{15}$ (900.02)	violet	56	285
(4)	$\text{Cu}_2\text{EuC}_{16}\text{H}_{32}\text{N}_{11}\text{O}_{13}$ (865.55)	violet	68	332
(5)	$\text{Cu}_2\text{GdC}_{16}\text{H}_{32}\text{N}_{11}\text{O}_{13}$ (870.84)	purple	83	346
(6)	$\text{Cu}_2\text{TbC}_{16}\text{H}_{32}\text{N}_{11}\text{O}_{13}$ (872.52)	pale-brown	69	279
(7)	$\text{Cu}_2\text{DyC}_{16}\text{H}_{34}\text{N}_{11}\text{O}_{14}$ (894.10)	violet-red	72	321
(8)	$\text{Cu}_2\text{ErC}_{16}\text{H}_{32}\text{N}_{11}\text{O}_{13}$ (880.85)	purple-brown	54	344

(1) =  $\text{Cu}_2(\text{oxdn})_2\text{Ce}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ ,

(2) =  $\text{Cu}_2(\text{oxdn})_2\text{Nd}(\text{NO}_3)_3$ ,

(3) =  $\text{Cu}_2(\text{oxdn})_2\text{Sm}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ ,

(4) =  $\text{Cu}_2(\text{oxdn})_2\text{Eu}(\text{NO}_3)_3$ ,

(5) =  $\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_3$ ,

(6) =  $\text{Cu}_2(\text{oxdn})_2\text{Tb}(\text{NO}_3)_3$ ,

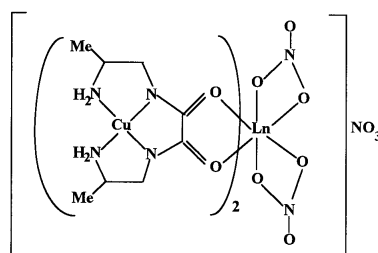
(7) =  $\text{Cu}_2(\text{oxdn})_2\text{Dy}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ ,

(8) =  $\text{Cu}_2(\text{oxdn})_2\text{Er}(\text{NO}_3)_3$ .

**Physical measurements:** Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. Metal contents were determined by EDTA titration. IR spectra were recorded with a Nicolet FT-IR 5DX spectrometer using KBr pellets. The electronic spectra were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Variable temperature magnetic susceptibilities (4–300 K) were measured at the Institute of Physics, Chinese Academy of Sciences, using a vibrating magnetometer Model CF-1 (sensitivity  $m = 10^{-4}$  emu.). Diamagnetic corrections were made with Pascal's constants [18] for all the constituent atoms and effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$ , where  $\chi_{\text{M}}$  is the molar magnetic susceptibility corrected for diamagnetism of the constituting atoms. The ESR spectra were measured with a JES-FEIXG ESR-apparatus using the X-band.

## RESULTS AND DISCUSSION

**Synthetic route and coordination environment:** Use of metal complexes that contain a potential donor group capable of coordinating to another metal ion as a ligand is one of the effective methods for synthesizing hetero-metal polynuclear complexes [4,19]. In this study, our purpose was to obtain Cu(II)–Ln(III)–Cu(II) hetero-trinuclear complexes, therefore, this synthetic method was adopted and N,N'-bis(2-aminopropyl)oxamidocopper(II), [Cu(oxdn)], was chosen as a bidentate fragment because it can coordinate to another metal ion through the carbonyl oxygens of oxamido group to afford bi- and tri- nuclear complexes. Indeed, elemental analyses and physical data (see Tables 1 and 2) indicate that the reaction of Cu(oxdn) with  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$ ) in *ca.* 2:1 mole ratio yielded the heterotrinnuclear complexes of the general formula  $\text{Cu}_2(\text{oxdn})_2\text{Ln}(\text{NO}_3)_3$ , as expected. These complexes are the first examples Cu(II)–Ln(III)–Cu(II) heterotrinnuclear complexes bridged by N,N'-bis(2-aminopropyl)oxamido group. Based on the conductivity measurements, spectroscopic (IR, ESR and UV) characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.



**Figure 1.** Plausible coordination environment of the complexes ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$ ).

**General properties of the trinuclear complexes:** These trinuclear complexes are very soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature; moderately soluble in water, methanol and acetone, and practically insoluble in carbon tetrachloride, chloroform and benzene. The  $\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_3$  complex can be recrystallized from a DMF/ethanol (1:1) mixture. The solid Cu(II)–Ln(III)–Cu(II) trinuclear complexes are fairly stable in air so as to facilitate physical measurements.

For the eight Cu(II)–Ln(III)–Cu(II) trinuclear complexes, the observed molar conductance values in DMF solution (in the range 70~85  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) are given in Table 2. These values are indicative of the 1:1 electrolytic nature [20], which indicates that only one nitrate anion is outside and the two nitrate anions inside coordination sphere. This is consistent with the measured IR data of the heterotrinnuclear complexes.

**Infrared spectra:** In order to clarify the mode of bonding, the IR spectra of the mononuclear fragment [Cu(oxdn)] and Cu(II)–Ln(III)–Cu(II) heterotrinnuclear complexes were studied and assigned on the basis of a careful comparison of the latter with the former. The most relevant IR absorption bands of the trinuclear complexes and the mononuclear fragment [Cu(oxdn)] along with their assignments are shown in Table 2. We will only discuss some selected infrared bands. It is noteworthy that the carbonyl stretching vibration at 1615  $\text{cm}^{-1}$  for the mononuclear fragment [Cu(oxdn)] was considerably shifted towards higher frequencies (*ca.* 20~40  $\text{cm}^{-1}$ ) in the trinuclear complexes. Therefore, when the deprotonated amide nitrogen is coordinated to the metal ion, its amide I band shifts considerably towards lower wavenumbers. In the case of an oxamide dianion, coordinated to metal ions as a bridging ligand, the amide I band reverts to near its original position (in the protonated species) [19]. Although the amide I is due to a composite N–C=O vibration, it can essentially be seen as  $\nu(\text{C}=\text{O})$ . It is likely that the bond order of C=O (carbonyl) in the trinuclear complexes is higher than that in the corresponding mononuclear complex [Cu(oxdn)]. This shift has often been used as a definite proof of oxamido-bridged structures [19]. The  $-\text{NH}_2$  stretching vibration for Cu(oxdn) observed at 3175  $\text{cm}^{-1}$  in their trinuclear complexes further supports this view. In addition, the C=O deformation vibration at 720  $\text{cm}^{-1}$  of the complex ligand, [Cu(oxdn)], disappeared in the spectra of the trinuclear complexes. This may be attributed to the coordination of the carbonyl oxygens to the Ln(III) ion [16]. This coordination mode of the complex ligand, [Cu(oxdn)], has been revealed by X-ray diffraction analysis of an analogous complex [21]. On the other hand, the spectra of the trinuclear complexes exhibit characteristic vibrational frequencies of coordinated nitrate group, which is suggested by two bands observed around 1490 and 1310  $\text{cm}^{-1}$  due to the  $\nu_4$  and  $\nu_1$  vibrations of the nitrate group of  $C_{2v}$  symmetry [22]. The medium band at 1030  $\text{cm}^{-1}$  due to the  $\nu_2$  vibration of the nitrate group ( $C_{2v}$ ) stands as additional evidence for the presence of coordinated nitrate group. The difference in wave numbers between the two highest frequency bands ( $\nu_4 - \nu_1$ ) of nitrate ( $C_{2v}$ ) is about 180  $\text{cm}^{-1}$ , suggesting that the nitrate groups are attached bidentately to the Ln(III) ions [23]. Furthermore, the absorption band observed at 1380~1385  $\text{cm}^{-1}$  is due to the ionic nitrate in the trinuclear complexes. This indicates that these trinuclear complexes have both ionic and coordinated nitrate groups. Thus, the above spectral observations, together with the molar conductance data, confirm that these trinuclear complexes may be formulated as  $[\text{Cu}_2(\text{oxdn})_2\text{Ln}(\text{NO}_3)_2]\text{NO}_3$  (Ln = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er).

**Table 2.** Physical data for the Cu(II)–Ln(III)–Cu(II) heterotrinnuclear complexes.

Complex	$\Lambda_M^*$	IR (cm <sup>-1</sup> )						UV (nm)			
		$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{NO}_3^-)$		$\nu(\text{NO}_3^-)$ (coordinated)		d-d	f-f	Assignment	CT
				(ionic)	$\nu_4$	$\nu_1$	$\nu_2$				
Cu(oxdn)		3175	1615					513			
(1)	82	3175	1650	1380	1490	1310	1030	535			328
(2)	85	3175	1650	1382	1492	1315	1032	541	736	( <sup>4</sup> I <sub>9/2</sub> → <sup>7</sup> F <sub>7/2</sub> )	330
(3)	80	3175	1640	1381	1490	1310	1030	548	420	( <sup>4</sup> H <sub>5/2</sub> → <sup>4</sup> I <sub>9/2</sub> )	325
(4)	72	3175	1640	1385	1491	1308	1032	543			312
(5)	80	3175	1658	1384	1490	1310	1031	538			317
(6)	78	3175	1655	1382	1491	1305	1033	532	455	( <sup>7</sup> F <sub>6</sub> → <sup>5</sup> F <sub>4</sub> )	315
(7)	83	3175	1650	1380	1490	1312	1032	530	425	( <sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> I <sub>15/2</sub> )	327
(8)	80	3175	1650	1383	1492	1306	1032	540	652	( <sup>4</sup> I <sub>15/2</sub> → <sup>7</sup> F <sub>9/2</sub> )	320

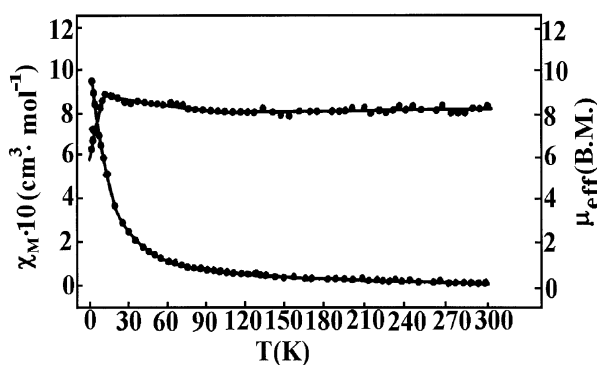
\*Values for  $1 \times 10^{-3}$  mol L<sup>-1</sup> DMF solution, unit:  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

**Electronic spectra:** The electronic absorption spectral data of the eight trinuclear complexes in acetonitrile solutions are listed in Table 2. As shown in this table the electronic spectra of the eight trinuclear complexes are similar to each other. The electronic spectra of all the complexes exhibit a band at 530–548 nm, which may be attributed to the d-d transition of the “inside” copper(II) in a square-planar environment. The frequency is lower than that for the mononuclear copper(II) complex (513 nm). Such a red-shift of copper(II) ion in the d-d band may be attributed to the decreased planarity of the [CuN<sub>4</sub>] chromophore on forming a trinuclear complex with Ln(III) ion. In addition, a strong absorption in the short wavelength range (see Table 2) may be attributed to the charge-transfer absorption band, which may be due to the spin-exchange interaction between the copper(II) and lanthanide(III) ions through the  $\pi$ -path orbital set up by an oxamido bridge [19]. Further investigation of these and similar systems is required in order to obtain more detailed assignment for charge transfer. Besides, in the electronic spectra of Cu<sub>2</sub>(oxdn)<sub>2</sub>Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = Sm, Tb, Nd, Dy, Er), f-f transitions of Ln(III) were obtained. These data are listed in Table 2 along with their assignments [24]. Other f-f transitions which are expected to appear may be concealed by d-d, charge-transfer, or intraligand transitions.

In spite of our many efforts, single crystals suitable for X-ray crystallography have not yet been obtained for these complexes. However, based on the composition of these complexes, their IR, ESR, electronic spectra and conductivity measurements, magnetic characterization (*vide infra*) and the crystal structure of the analogous complex [21], these complexes are proposed to have an extended oxamido-bridged trinuclear structure and to contain a lanthanide(III) ion and two copper(II) ions, which have the presumed coordination environment as shown in Fig. 1. The plausible structure is further supported by the following ESR and magnetic studies.

**ESR spectra:** In order to obtain further structural information, the X-band powder ESR spectra of the  $[\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_2]\text{NO}_3$  and  $[\text{Cu}(\text{oxdn})]$  have been recorded at room temperature. The spectrum of the former is obviously different from that of the latter and exhibits a dissymmetric broad band around  $g = 2.0$ , which indicates a magnetic spin-exchange interaction between Gd(III) and Cu(II) ions [13]. Since there is a lack of structural data for this complex, it is difficult to interpret quantitatively this broad band. Qualitatively, however, it is clear that these features reflect the exchange coupling between gadolinium(III) and copper(II). According to Kambe's approach [25], the three spins  $S_{\text{Gd}} = 7/2$  and  $S_{\text{Cu1}} = S_{\text{Cu2}} = 1/2$  coupled to yield the total spin states of one  $S = 9/2$ , one  $S = 5/2$  and two  $S = 7/2$ . On basis of Boltzmann distribution, all these states are a thermal population at room temperature, owing to very weak interaction (*vide infra*). Thus, the dissymmetric broad signals may be ascribed to the complex in these spin states [13].

**Magnetic property of  $[\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_2]\text{NO}_3$ :** From the above discussion of the ESR spectra we have shown that a spin-coupled interaction exists between copper(II) and gadolinium(III) ions. In order to understand quantitatively the magnitude of the spin-exchange interaction, the variable-temperature (4.2~300 K) magnetic susceptibility data were collected for  $[\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_2]\text{NO}_3$  complex, as an example, and the results are shown in Fig. 2 as plots of  $\chi_M$  vs. T and  $\mu_{\text{eff}}$  vs. T, where  $\chi_M$ ,  $\mu_{\text{eff}}$  and T denote magnetic susceptibility per molecule, effective magnetic moment per molecule, and absolute temperature, respectively. The choice of gadolinium is because Gd(III) ion and its complexes are quite simple for a magnetic study, since the ground state of Gd(III) is  $^8S_{7/2}$  and the energy level of the lowest excited state is very high, that is, the magnetic data usually can be interpreted without considering the contribution of the orbital angular momentum and the anisotropic effect [13,15]. Based on the inherent nature of the Gd(III), the  $[\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_2]\text{NO}_3$  complex is an ideal model for the magnetic interaction between Cu(II) and Ln(III) ions among the eight heterotrinnuclear complexes. As shown in Fig. 2, the observed magnetic moment at room temperature for  $[\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_2]\text{NO}_3$  complex is higher than the spin-only



**Figure 2.** Magnetic susceptibility ( $\chi_M$ ) and effective magnetic moment ( $\mu_{\text{eff}}$ ) vs T for  $[\text{Cu}_2(\text{oxdn})_2\text{Gd}(\text{NO}_3)_2]\text{NO}_3$  complex. The solid line denotes the least-squares fit the data to equation (2) given in the text.

value (8.31 B.M.) in the absence of the magnetic interaction of Cu(II)–Gd(III)–Cu(II) spin-system ( $S_{\text{Cu1}} = S_{\text{Cu2}} = 1/2$ ,  $S_{\text{Gd}} = 7/2$ ) and increased steadily upon cooling down. This is typical of a ferromagnetic coupling between the Cu(II) and Gd(III) ions within this complex.

In order to understand the spin-exchange interaction, the magnetic analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator

$$\hat{H} = -2J(\hat{S}_{\text{Gd}} \cdot \hat{S}_{\text{Cu1}} + \hat{S}_{\text{Gd}} \cdot \hat{S}_{\text{Cu2}}) - 2J'\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu2}} \quad (1)$$

where the exchange integral  $J$  is the Cu(II)–Gd(III) coupling constant,  $J'$  denotes the Cu(II)–Cu(II) coupling constant. For the Cu(II)–Gd(III)–Cu(II) trinuclear system ( $S_{\text{Cu1}} = S_{\text{Cu2}} = 1/2$ ,  $S_{\text{Gd}} = 7/2$ ), the theoretical expression of magnetic susceptibility is given in (2):

$$\chi_{\text{M}} = \frac{N\beta^2 g^2}{6kT} \left[ \frac{495\exp(-8x) + 252\exp(-7x/2) + 105 + 252\exp(-9x/2 + y)}{10\exp(-8x) + 8\exp(-7x/2) + 6 + 8\exp(-9x/2 + y)} \right] \quad (2)$$

where  $x = -2J/kT$ ,  $y = -2J'/kT$ ,  $\chi_{\text{M}}$  denotes the molecular susceptibility per binuclear complex and the other symbols have their usual meanings. As shown in Fig. 2, good least-square fits to the experimental data were attained with equation (2). The best fit yielded  $J = +2.98 \text{ cm}^{-1}$ ,  $J' = -0.75 \text{ cm}^{-1}$  and  $g = 2.00$ . The agreement factor  $F$ , defined here as  $F = \Sigma[(\chi_{\text{M}})_{\text{obs.}} - (\chi_{\text{M}})_{\text{calc.}}]^2 / \Sigma(\chi_{\text{M}})_{\text{obs.}}$ , equals  $7.8 \times 10^{-5}$ . The results indicated that the positive sign of  $J$  corresponds to a ferromagnetic Gd(III)–Cu(II) interaction and the negative sign of  $J'$  to an antiferromagnetic Cu(II)–Cu(II) interaction. The small  $J$  value may account for the fact that 4f-electrons are shielded by the outershell electrons [26]. However, the ferromagnetic interaction existing in the present complex between Gd(III) and Cu(II), which was also observed in previously reported for  $\text{Cu}_2\text{Gd}$  clusters [10, 12], is interesting because gadolinium(III) has unpaired electrons in seven f orbitals and at least one of them or one linear combination can give a non-zero overlap with the magnetic orbitals on copper(II). Thus, this gives an anti-ferromagnetic coupling. One plausible mechanism, that cause a ferromagnetic coupling between Gd(III) and Cu(II) as proposed by Benelli [27] and Kahn [28] *et al.*, is the spin-polarization, that occurs when the magnetic orbital of Cu(II) overlaps with the empty 5d orbital [28] of Gd(III) through a filled bridging orbital. The fraction of unpaired electron, thus polarized from Cu(II) to Gd(III), is parallel to the f electrons due to Hund's rule, affording a ferromagnetic coupling between Cu(II) and Gd(III). The 4f orbital is shielded by the outer filled 5s and 5p orbitals, and lanthanide ions generally form complexes using 6s, 6p, and/or 5d orbitals, what further supports the spin-polarization mechanism.

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