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# Synthesis and Magnetic Studies of [$Cu_3^{II}Ln^{III}$] Heterotetranuclear Complexes with N,N′-Bis(3-amino-2,2-dimethylpropyl)oxamidocopper(II)

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Eleven new oxamido-bridged $Cu_3^{II}Ln^{III}$-type (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb) heterotetranuclear complexes, namely $Cu_3(Me_2oxpn)_3Ln(NO_3)_3$, where $Me_2oxpn$ denotes N,N′-bis(3-amino-2,2-dimethylpropyl)oxamido dianion, have been synthesized and characterized by elemental analyses, molar conductivity measurements, and spectroscopic (IR, UV, ESR) studies. Cryomagnetic measurements (4.2~300 K) and studies of $Cu_3(Me_2oxpn)_3Gd(NO_3)_3$ complex have revealed that the gadolinium(III) and copper(II) ions are ferromagnetically coupled with the exchange integral $J = +3.88\ cm^{-1}$, on the basis of the spin Hamiltonian operator $[\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_0 + \hat{S}_2 \cdot \hat{S}_0 + \hat{S}_3 \cdot \hat{S}_0)]$.

**Key words:** heterotetranuclear complexes, oxamido-bridge, copper(II), lanthanide(III), synthesis, magnetic properties

The interest in bridged heteropolymetallic complexes containing different paramagnetic centers has risen considerably in recent years [1–3]. The synthesis, spectroscopic and magnetic investigations of new heteropolynuclear complexes are 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 due to the very weak interaction and a large anisotropic effect of lanthanide ions [10–14]. 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 [15], stimulated us to develop d-f heteronuclear complexes, possessing new functions associated with some d-f heterometal centers. In continuation of our earlier work [16,17], in this paper, eleven new μ-oxamido-bridged $Cu_3^{II}Ln^{III}$-type heterotetranuclear complexes (Ln = La, Ce, Pr, Nd, Sm, Eu,

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Gd, Tb, Ho, Er, Yb), where copper(II) ions lie at the corners of a triangle with a lanthanide(III) ion at the center, have been prepared by the reaction of N,N′-bis(3-amino-2,2-dimethylpropyl)oxamidocopper(II) (abbreviated as Cu(Me$_2$oxpn)) with lanthanide(III) ions. The ESR and magnetic properties of the $Cu_3(Me_2oxpn)_3Gd(NO_3)_3$ 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 ($J = +3.88$ 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(3-amino-2,2-dimethylpropyl)oxamidocopper(II), Cu(Me$_2$oxpn), was synthesized as previously described in the literature [14] method.

**Synthesis of $Cu_3(Me_2oxpn)_3Ln(NO_3)_3$ complexes:** The preparations of the eleven heterotetranuclear complexes were identical and are exemplified by $Cu_3(Me_2oxpn)_3Gd(NO_3)_3$. To a solution of Cu(Me$_2$oxpn) (991.7 mg, 3.1 mmol) stirred in absolute ethanol ( 20 cm$^3$) was added successively a solution of $Gd(NO_3)_3·6H_2O$ (451.4 mg, 1 mmol) in absolute ethanol (15 cm$^3$), followed by a solution of ethyl orthofomate (15 cm$^3$). The stirring was continued at room temperature for a further 10 h to give violet-red microcrystals which were removed by filtration, washed several times with ethanol, water and diethyl ether and dried over $P_4O_{10}$ under reduced pressure. Colors, yields and melting points of these heterotetranuclear complexes are listed in Table 1.

**Table 1.** Yields, colors and melting points (M.p.) of the heterotrinuclear complexes.

| Complex | Empirical Formula (Formula Weight) | Color | Yield (%) | M.p. (°C) |
|---|---|---|---|---|
| **(1)** | $Cu_3LaC_{36}H_{74}N_{15}O_{16}$<br>(1302.61) | violet | 89 | 320 |
| **(2)** | $Cu_3CeC_{36}H_{74}N_{15}O_{16}$<br>(1303.83) | purple | 75 | 261 |
| **(3)** | $Cu_3PrC_{36}H_{72}N_{15}O_{15}$<br>(1286.59) | violet | 52 | 299 |
| **(4)** | $Cu_3NdC_{36}H_{74}N_{15}O_{15}$<br>(1291.95) | pale-red | 64 | 335 |
| **(5)** | $Cu_3SmC_{36}H_{72}N_{15}O_{15}$<br>(1296.09) | purple-brown | 86 | 304 |
| **(6)** | $Cu_3EuC_{36}H_{72}N_{15}O_{15}$<br>(1297.65) | pale-violet | 61 | 331 |
| **(7)** | $Cu_3GdC_{36}H_{72}N_{15}O_{15}$<br>(1302.94) | violet-red | 77 | 327 |
| **(8)** | $Cu_3TbC_{36}H_{72}N_{15}O_{15}$<br>(1304.62) | ruby-violet | 55 | 348 |
| **(9)** | $Cu_3HoC_{36}H_{72}N_{15}O_{15}$<br>(1310.59) | red-brown | 79 | 297 |
| **(10)** | $Cu_3ErC_{36}H_{72}N_{15}O_{15}$<br>(1312.95) | red-brown | 71 | 320 |
| **(11)** | $Cu_3YbC_{36}H_{74}N_{15}O_{16}$<br>(1336.71) | violet | 88 | 312 |

**(1)** = $Cu_3(Me_2oxpn)_3La(NO_3)_3·H_2O$, **(2)** = $Cu_3(Me_2oxpn)_3Ce(NO_3)_3·H_2O$, **(3)** = $Cu_3(Me_2oxpn)_3Pr(NO_3)_3$,
**(4)** = $Cu_3(Me_2oxpn)_3Nd(NO_3)_3·H_2O$, **(5)** = $Cu_3(Me_2oxpn)_3Sm(NO_3)_3$, **(6)** = $Cu_3(Me_2oxpn)_3Eu(NO_3)_3$,
**(7)** = $Cu_3(Me_2oxpn)_3Gd(NO_3)_3$, **(8)** = $Cu_3(Me_2oxpn)_3Tb(NO_3)_3$, **(9)** = $Cu_3(Me_2oxpn)_3Ho(NO_3)_3$,
**(10)** = $Cu_3(Me_2oxpn)_3Er(NO_3)_3$, **(11)** = $Cu_3(Me_2oxpn)_3Yb(NO_3)_3·H_2O$.

**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 spectrophotometer 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 using a Quantum Design MPMS-5 SQUID magnetometr. Diamagnetic corrections were made with Pascal's constants [18] for all the constituent atoms and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where $\chi_M$ is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms. The ESR spectra were measured with a JES-FEIXG ESR-apparatus using the X-band.

## RESULTS AND DISCUSSION

**Synthesis and coordination environment of the heterotetranuclear complexes:** One of the best strategies to design and synthesize polynuclear species is the "complex as ligand" approach, *i.e.* using mononuclear complexes that contain potential donor groups capable of coordinating to another metal ion [4,19]. A good example is represented by the use of the Cu(II) complexes of N,N′-disubstituted oxamides as ligands [16,17,19–22]. In this study, our purpose was to obtain $Cu_3^{II}Ln^{III}$ heterotetranuclear complexes, therefore, this synthetic method was adopted and N,N′-bis(3-amino-2,2-dimethylpropyl)oxamidocopper(II), [$Cu(Me_2oxpn)$], was chosen as a bidentate mononuclear fragment because it can coordinate to another metal ion through the carbonyl oxygens of oxamido group to afford polynuclear complexes [14]. Indeed, elemental analyses and physical data (see Tables 1 and 2) indicate that the reaction of $Cu(Me_2oxpn)$ with $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb) in *ca.* 3:1 mole ratio yielded the heterotetranuclear complexes of the general formula $Cu_3(Me_2oxpn)_3Ln(NO_3)_3$, as expected. These complexes are the first examples $Cu_3^{II}Ln^{III}$ heterotetranuclear complexes bridged by N,N′-bis(3-amino-2,2-dimethylpropyl)oxamido group. Based on the conductivity measurements, spectroscopic (IR, UV and ESR) characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

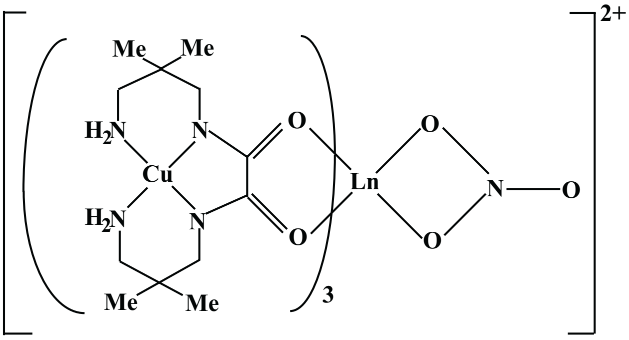

**Figure 1.** Plausible coordination environment of the complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb).

**Solubility and molar conductances of the heterotetranuclear complexes:** These tetranuclear complexes are very soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature, moderately soluble in ethanol and acetone; and practically insoluble in carbon tetrachloride, chloroform and benzene. The $Cu_3(Me_2oxpn)_3Gd(NO_3)_3$ complex can be recrystallized from a DMF/ethanol (1:2) mixture. The solid $Cu^{II}_3Ln^{III}$ tetranuclear complexes are fairly stable in air so as to facilitate physical measurements. For the eleven $Cu^{II}_3Ln^{III}$ tetranuclear complexes, the observed molar conductance values in DMF solution (in the range 140~155 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) are given in Table 2. These values are indicative of the 1:2 electrolytic nature [23], which indicates that only one nitrate anion is inside and the two nitrate anions outside coordination sphere. This is consistent with the measured IR data of the heterotetranuclear complexes.

**Infrared spectra:** In order to clarify the mode of bonding, the IR spectra of the mononuclear fragment $[Cu(Me_2oxpn)]$ and $Cu^{II}_3Ln^{III}$ heterotetranuclear 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 tetranuclear complexes and the mononuclear fragment $[Cu(Me_2oxpn)]$, along with their assignments are listed in Table 2. We will only discuss some selected infrared bands. It is noteworthy that the carbonyl stretching vibration at 1605 $cm^{-1}$ for the mononuclear fragment $[Cu(Me_2oxpn)]$ was considerably shifted towards higher frequencies (*ca.* 30~60 $cm^{-1}$) in the tetranuclear 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 $\upsilon(C{=}O)$. It is likely that the bond order of C=O (carbonyl) in the tetranuclear complexes is higher than that in the corresponding mononuclear complex $[Cu(Me_2oxpn)]$. This shift has often been used as a definite proof of oxamido-bridged structures [19]. The $-NH_2$ stretching vibration for $Cu(Me_2oxpn)$ observed at 3285 $cm^{-1}$ in the spectra of tetranuclear complexes further supports this view. In addition, the C=O deformation vibration at 715 $cm^{-1}$ of the complex ligand, $[Cu(Me_2oxpn)]$, disappeared in the spectra of the tetranuclear 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, $[Cu(Me_2oxpn)]$, has been revealed by X-ray diffraction analysis of an analogous complex [14]. On the other hand, the spectra of the tetranuclear complexes exhibit characteristic vibrational frequencies of coordinated nitrate group, which is suggested by two bands observed around 1490 and 1310 $cm^{-1}$ due to the $\upsilon_4$ and $\upsilon_1$ vibrations of the nitrate group of $C_{2v}$ symmetry [24]. The medium band at 1030 $cm^{-1}$ due to the $\upsilon_2$ 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 ($\upsilon_4$–$\upsilon_1$) of nitrate ($C_{2v}$) is about 180 $cm^{-1}$, suggesting that the nitrate groups are attached bidentately to the Ln(III) ions [25]. Furthermore, the absorption band observed at 1380~1385 $cm^{-1}$ is due to the ionic nitrate in the tetranuclear complexes. This indicates that these tetranuclear complexes have both ionic and coordinated nitrate groups. Thus, the above spectral observations, together with the molar conductance data, confirm that these tetranuclear complexes may be formulated as $[Cu_3(Me_2oxpn)_3$-$Ln(NO_3)](NO_3)_2$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb).

**Electronic spectra:** The electronic absorption spectral data of the eleven tetranuclear complexes in DMF solutions are listed in Table 2. As shown in this table the electronic spectra of the eleven tetranuclear complexes are similar. The electronic spectra of all the complexes exhibit a band at 540~545 nm, which may be attributed to the d-d transition of the "inside" copper(II) in a square-planar environment. The frequency is higher than that for the mononuclear copper(II) complex (605 nm). Such a blue-shift of copper(II) ion in the d-d band may be attributed to the increased ligand field strength for the $[CuN_4]$ chromophore on forming a tetranuclear complex with a lanthanide(III) ion [16,17]. 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 π-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 $Cu_3(Me_2oxpn)_3Ln(NO_3)_3$ (Ln = Nd, Sm, Tb, Ho, Er), f-f transitions of Ln(III) were also observed. These data are shown in Table 2 along with their assignments [26]. Other f-f transitions which are expected to appear may be concealed by d-d, charge-transfer, or intraligand transitions.

**Table 2.** Physical data for the $Cu_3^{II}Ln^{III}$ heterotetranuclear complexes.

| Complex | $\Lambda_M$* | IR ($cm^{-1}$) | | | | | | UV (nm) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\upsilon(NH_2)$ | $\upsilon(C{=}O)$ | $\upsilon(NO_3^-)$ (ionic) | $\upsilon(NO_3^-)$ (coordinated) | | | d-d | f-f | Assignment | CT |
| | | | | | $\upsilon_4$ | $\upsilon_1$ | $\upsilon_2$ | | | | |
| $Cu(Me_2oxpn)$ | | 3285 | 1605 | | | | | 605 | | | |
| **(1)** | 150 | 3285 | 1652 | 1380 | 1490 | 1310 | 1030 | 545 | | | 318 |
| **(2)** | 155 | 3285 | 1650 | 1382 | 1492 | 1315 | 1032 | 541 | | | 326 |
| **(3)** | 140 | 3285 | 1645 | 1381 | 1490 | 1310 | 1030 | 540 | | | 311 |
| **(4)** | 142 | 3285 | 1640 | 1380 | 149 | 1308 | 1032 | 543 | 735 | $(^4I_{9/2} \rightarrow {}^7F_{7/2})$ | 319 |
| **(5)** | 145 | 3285 | 1658 | 1380 | 1490 | 1310 | 1031 | 542 | 420 | $(^4H_{5/2} \rightarrow {}^4I_{9/2})$ | 317 |
| **(6)** | 148 | 3285 | 1655 | 1382 | 1491 | 1305 | 1033 | 540 | | | 316 |
| **(7)** | 150 | 3285 | 1650 | 1380 | 1490 | 1312 | 1032 | 542 | | | 320 |
| **(8)** | 152 | 3285 | 1659 | 1382 | 1492 | 1306 | 1031 | 540 | 451 | $(^7F_6 \rightarrow {}^5F_4)$ | 328 |
| **(9)** | 140 | 3285 | 1650 | 1385 | 1495 | 1310 | 1032 | 545 | 642 | $(^5I_8 \rightarrow {}^4F_5)$ | 321 |
| **(10)** | 142 | 3285 | 1660 | 1383 | 1492 | 1306 | 1032 | 541 | 655 | $(^4I_{15/2} \rightarrow {}^7F_{9/2})$ | 312 |
| **(11)** | 154 | 3285 | 1665 | 1380 | 1494 | 1312 | 1030 | 544 | | | 310 |

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

Based on the composition of these complexes, their IR, ESR, UV spectra and conductivity measurements, magnetic characterization (*vide infra*) and the crystal structure of the analogous complex [14], these complexes are proposed to have an extended oxamido-bridged tetranuclear structure and to contain a lanthanide(III) ion and three copper(II) ions, which have the presumed coordination environment as shown in Figure 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 $[Cu_3(Me_2oxpn)_3Gd(NO_3)](NO_3)_2$ and $[Cu(Me_2oxpn)]$ 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 [27], the four spins $S_{Gd} = 7/2$, $S_{Cu1} = S_{Cu2} = S_{Cu3} = 1/2$ coupled to yield the total spin states of one S = 5, three S = 4, three S = 3, one S = 2 and one S = 1. On basis of Boltzmann distribution, all these states are in a thermal population at room temperature, due to very weak interaction (*vide infra*). Thus, the dissymmetric broad signals may be ascribed to the complex in these spin states [13].

**Magnetic properties of $[Cu_3(Me_2oxpn)_3Gd(NO_3)](NO_3)_2$:** From the above discussion of the ESR spectra it is noted 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 further collected for $[Cu_3(Me_2oxpn)_3Gd(NO_3)](NO_3)_2$ complex, as an example, and the results are shown in Figure 2 as plots of $\chi_M$ *vs*. T and $\mu_{eff}$ *vs*. T, where $\chi_M$, $\mu_{eff}$ and T denote magnetic susceptibility per molecule, effective magnetic moment per molecule, and absolute temperature, respectively. The reason for 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 gadolinium(III), the $[Cu_3(Me_2oxdn)_3Gd(NO_3)](NO_3)_2$ complex is an ideal model for the magnetic interaction between Cu(II) and Ln(III) ions among the eleven heterotetranuclear complexes. As shown in Figure 2, the observed magnetic moment at room temperature for $[Cu_3(Me_2oxpn)_3Gd(NO_3)](NO_3)_2$ complex is higher than the spin-only value (8.49 B.M.) in the absence of the magnetic interaction of $Cu^{II}{}_3Gd^{III}$ spin-system ($S_{Cu1} = S_{Cu2} = S_{Cu3} = 1/2$, $S_{Gd} = 7/2$) and increased steadily upon cooling down. This is typical of a ferromagnetic coupling between the Cu(II) and Gd(III) ions within this complex.

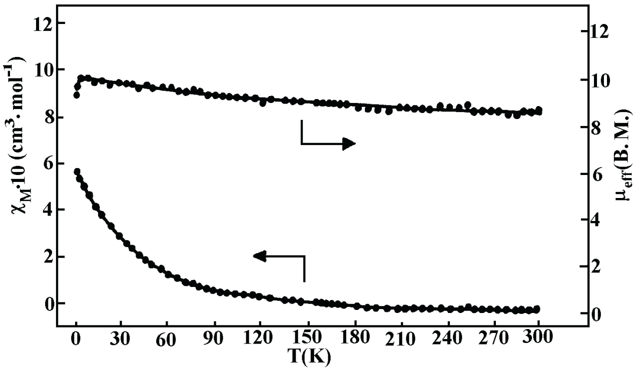

**Figure 2.** Magnetic susceptibility ($\chi_M$) and effective magnetic moment ($\mu_{eff}$) *vs* T for $[Cu_3(Me_2\text{-}oxpn)_3Gd(NO_3)](NO_3)_2$ complex. The solid line denotes the least-squares fit the data to equation (2) given in the text.

The magnetic susceptibility expression for the $Cu_3^{II}Gd^{III}$ tetranuclear system with Gd(III) ion at the center and copper(II) ions at the corners of a triangle was derived by extention of Kambe's approach [27]. The Hamiltonian for this system is given by:

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_0 + \hat{S}_2 \cdot \hat{S}_0 + \hat{S}_3 \cdot \hat{S}_0) \qquad (1)$$

where J is the exchange integral between Cu(II) and Gd(III). For the $Cu_3^{II}Gd^{III}$ tetranuclear system ($S_{Cu1} = S_{Cu2} = S_{Cu3} = 1/2$, $S_{Gd} = 7/2$), the theoretical expression of magnetic susceptibility is given in equation (2):

$$\chi_M = \frac{N\beta^2 g^2}{kT}\left[\frac{A}{B}\right] \qquad (2)$$

$A = 10 + 110\exp(24J/kT) + 60\exp(14J/kT) + 28\exp(6J/kT) + 120\exp(17J/kT) + 56\exp(9J/kT)$
$B = 5 + 11\exp(24J/kT) + 9\exp(14J/kT) + 7\exp(6J/kT) + 18\exp(17J/kT) + 14\exp(9J/kT)$

where $\chi_M$ denotes the molecular susceptibility per tetranuclear complex and the other symbols have their usual meanings. As shown in Figure 2, good least-square fits to the experimental data were attained with equation (2). The best fit yielded $J = +3.88$ cm$^{-1}$ and $g = 2.01$. The agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$, equals $8.5\times10^{-5}$. The positive sign of J corresponds to a ferromagnetic Gd(III)–Cu(II) interaction. The small J value may account for the fact that 4f-electrons are shielded by the outershell electrons [28]. However, the ferromagnetic interaction existing in the present complex between Gd(III) and Cu(II) 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 nonzero overlap with the magnetic orbitals on copper(II). Thus, this gives an antiferromagnetic coupling. One plausible mechanism, that causes a ferromagnetic coupling between Gd(III) and Cu(II) as proposed by Gatteschi [29] and Kahn [30] *et al.*, is the spin-polarization, that occurs when the magnetic orbital of Cu(II) overlaps with the empty 5d orbital [30] 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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