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Synthesis and Magnetism of Copper(II)–Lanthanoid(III) Heterobinuclear Complexes with N,N′-Oxamidobis(propionato)cuprate(II) Ligand

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Eleven novel μ-oxamido-bridged copper(II)–lanthanoid(III) heterobinuclear complexes described by the overall formula $Cu(obp)Ln(Ph_2\text{-}phen)_2ClO_4$ (Ln = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), where obp denotes N,N′-oxamidobis(propionato) and Ph_2-phen represents 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen), have been synthesized and characterized by elemental analyses, spectroscopic (IR, UV, ESR) studies, and molar conductivity measurements. The temperature dependence of the magnetic susceptibility of complex $Cu(obp)Gd(Ph_2\text{-}phen)_2ClO_4$ has been measured over the range 4.2~300 K and the magnetic properties were studied in detail, demonstrating the presence of a very weak ferromagnetic interaction between the adjacent Gd(III) and Cu(II) ions through the oxamido-bridge. Based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, the exchange integral (J) was evaluated as $+2.98\ cm^{-1}$. A plausible mechanism for the ferromagnetic coupling between Gd(III) and Cu(II) is discussed in terms of spin-polarization.

Key words: μ-oxamido, heterobinuclear complexes, copper(II)–lanthanoid(III), magnetism

Synthesis and magnetic properties of heteropolymetallic complexes with two different paramagnetic centers have attracted considerable attention. Interest in this field is a fundamental requirement, not only for gaining some insight into the structural and electronic factors governing magnetic exchange interaction between paramagnetic centers, but also for obtaining information about designing and synthesizing molecule-based magnets and investigating the spin-exchange mechanism between paramagnetic metal ions [1–3]. Compared with the number of studies dealing with heteronuclear systems comprising d-transition metal ions [1,4–9], relatively few studies dealing with heterometal complexes containing d-transition metal ions and lanthanoid(III) ions (so-called d-f heteronuclear complexes) have been reported, due to the very weak interaction and a large anisotropic effect of lanthanoid ions [10–13]. However, since Vidali and co-workers [10] and Abid and Fenton [11] reported in 1984 d-f heteronuclear complexes, much effort has been also devoted to magnetic studies of d-f heteronuclear complexes, in particular, to the magnetic interaction between Cu(II) and Gd(III) ions. The main reason is that the d-f mixed oxides have been used in many functional materials and/or have been expected as promising

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functional materials [14]. Owing to the importance of the above mentioned problems and the necessity for a better understanding of the magnetic properties of this kind of complexes, recently, we reported the synthesis and magnetism of a trinuclear $[Cu_2^{II}Ln^{III}]$ system [10] as well as a tetranuclear $[Cu_3^{II}Ln^{III}]$ system [11]. However, in these complexes, the antiferromagnetic interaction, operating between the terminal copper(II) ions, makes it difficult to evaluate the magnetic interaction between copper(II) and lanthanide(III) ions. In order to establish the magnetic interaction between rare-earth and transition-metal ions, a research project of synthesizing heterobinuclear complexes containing rare-earth and transition-metal ions and investigating their magnetic properties is under way in our group. In this work eleven new heterometal binuclear complexes of general formula $Cu(obp)Ln(Ph_2\text{-phen})_2ClO_4$ (Ln = Y, La, Sm, Nd, Eu, Gd, Dy, Tb, Ho, Er, Yb) have been prepared by the reaction of sodium N,N′-oxamidobis(propionato)cuprate(II), $Na_2[Cu(obp)]\cdot 3.5H_2O$, with lanthanoid(III) ions and terminal ligand 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen). The ESR and magnetic properties of the $Cu(obp)Gd(Ph_2\text{-phen})_2ClO_4$ complex have also 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 ($J = +2.98\ cm^{-1}$), 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 lanthanoid perchlorates were prepared by general methods. The terminal ligand 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) was used as commercially obtained. The starting material $Na_2[Cu(obp)]\cdot 3.5H_2O$ was synthesized by the literature method [15].

Synthesis of Cu(II)–Ln(III) binuclear complexes: All the copper(II)–lanthanoid(III) heterobinuclear complexes were prepared in a similar fashion and therefore, the synthesis of one of them, namely, $Cu(obp)Gd(Ph_2\text{-phen})_2ClO_4$, is detailed herein. To a solution of $Na_2[Cu(obp)]\cdot 3.5H_2O$ (369 mg, 1 mmol) in absolute ethanol (20 cm^3) was added successively a solution of $Gd(ClO_4)_3\cdot 6H_2O$ (564 mg, 1 mmol) in absolute ethanol (10 cm^3), followed by a solution of ethyl orthofomate (10 cm^3) with stirring, being continued at room temperature until the mixture became limpid. The solution was then filtered. To the filtrate was added an absolute ethanol solution (20 cm^3) of Ph_2-phen (665 mg, 2 mmol). The colour of the solution changed immediately and a small amount of blue precipitate was formed. After refluxing for *ca*. 12 h, the blue microcrystals thus formed were allowed to cool to room temperature and the blue microcrystals thus obtained were removed by filtration, washed several times with ethanol, water and diethyl ether and dried over P_2O_5 under reduced pressure. It was recrystallized from an acetonitrile/ethanol (1:4) mixture. Colours, yields and melting points of the complexes are collected in Table 1.

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. Elemental analyses confirm the compositions indicated. IR spectra were recorded with a Nicolet FT-IR 5DX spectrometer using KBr pellets. The electronic spectra (DMF solution) were measured on a Cary 300 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Variable temperature magnetic susceptibilities (4.2~300 K) were measured using a Quantum Design MPMS-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [16] for all the constituent atoms and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms. ESR spectra were measured with a JES-FEIXG ESR-apparatus using the X-band.

Table 1. Colors, yields and melting points (m.p.) of the binuclear complexes.

Complex	Empirical Formula (Formula Weight)	Color	Yield (%)	M.p. (°C)
(1)	$CuYC_{56}H_{40}N_6O_{10}Cl$ (1144.87)	light-blue	88	322
(2)	$CuLaC_{56}H_{42}N_6O_{11}Cl$ (1212.87)	blue	84	316
(3)	$CuNdC_{56}H_{40}N_6O_{10}Cl$ (1200.16)	pale-red	83	328
(4)	$CuSmC_{56}H_{44}N_6O_{12}Cl$ (1242.39)	pale-brown	82	299
(5)	$CuEuC_{56}H_{40}N_6O_{10}Cl$ (1207.96)	blue	87	320
(6)	$CuGdC_{56}H_{40}N_6O_{10}Cl$ (1213.26)	blue	62	331
(7)	$CuTbC_{56}H_{40}N_6O_{10}Cl$ (1214.86)	brown	65	297
(8)	$CuDyC_{56}H_{42}N_6O_{11}Cl$ (1236.47)	pale-brown	74	319
(9)	$CuHoC_{56}H_{40}N_6O_{10}Cl$ (1220.86)	pale-red	66	338
(10)	$CuErC_{56}H_{40}N_6O_{10}Cl$ (1223.26)	pale-red	78	307
(11)	$CuYbC_{56}H_{44}N_6O_{12}Cl$ (1264.99)	blue	65	325

(1) = $Cu(obp)Y(Ph_2\text{-}phen)_2ClO_4$, **(2)** = $Cu(obp)La(Ph_2\text{-}phen)_2ClO_4{\cdot}H_2O$,
(3) = $Cu(obp)Nd(Ph_2\text{-}phen)_2ClO_4$, **(4)** = $Cu(obp)Sm(Ph_2\text{-}phen)_2ClO_4{\cdot}2H_2O$,
(5) = $Cu(obp)Eu(Ph_2\text{-}phen)_2ClO_4$, **(6)** = $Cu(obp)Gd(Ph_2\text{-}phen)_2ClO_4$,
(7) = $Cu(obp)Tb(Ph_2\text{-}phen)_2ClO_4$, **(8)** = $Cu(obp)Dy(Ph_2\text{-}phen)_2ClO_4{\cdot}H_2O$,
(9) = $Cu(obp)Ho(Ph_2\text{-}phen)_2ClO_4$, **(10)** = $Cu(obp)Er(Ph_2\text{-}phen)_2ClO_4$,
(11) = $Cu(obp)Yb(Ph_2\text{-}phen)_2ClO_4{\cdot}2H_2O$.

RESULTS AND DISCUSSION

Synthetic route and coordination environment of the binuclear complexes: Two synthetic strategies are generally available for the preparation of discrete heterobinuclear complexes. The first is to use heterobinucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions. The second is to use "complex ligand" that contains a potential donor group capable of coordinating to another metal ion [4,10,11,17]. In this study, our purpose was to obtain Cu(II)–Ln(III) heterobinuclear complexes, therefore, the latter synthetic method was adopted. As "ligand complex" we have chosen sodium N,N′-oxamidobis(propionato)cuprate(II), $Na_2[Cu(obp)]{\cdot}3.5H_2O$, which was first used to prepare alternating Cu(II)-Mn(II) bimetallic chain complexes [15] by Kahn *et al.*, as a bidentate mononuclear fragment, because it can coordinate to another metal ion through the carbonyl oxygens of oxamido group. Simultaneously, 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) was used as terminal ligand. Indeed, elemental analyses and physical data (see Tables 1 and 2) indicate that the reaction of $Na_2[Cu(obp)]{\cdot}3.5H_2O$ with $Ln(ClO_4)_3{\cdot}6H_2O$ (Ln = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) and Ph_2-phen in 1:1:2 mole ratio yielded the heterobinuclear complexes of the general formula $Cu(obp)Ln(Ph_2\text{-}phen)_2ClO_4$, as expected. These complexes are the first examples of Cu(II)–Ln(III) heterobinuclear complexes bridged by N,N′-oxamidobis(propionato)cuprate(II). Based on the conductivity measurements, spectroscopic (IR, UV, ESR) characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

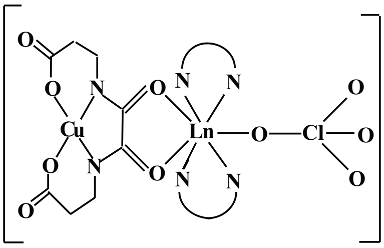

Figure 1. Plausible coordination environments of the complexes (Ln = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb; N͡N = Ph_2-phen).

Molar conductances and general properties of the new complexes: The complexes are well 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 solid Cu(II)–Ln(III) binuclear complexes are fairly stable in air, allowing physical measurements. For the eleven Cu(II)–Ln(III) binuclear complexes, the observed molar conductance values in DMF solution (in the range 2.0~6.5 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) are given in Table 2. These values are indicative of the non-electrolytic nature [18], suggesting a weak coordination of the perchlorate anion. This is consistent with the measured IR data.

Infrared spectra: Since the IR spectra of all the eleven binuclear complexes are quite similar, the discussion is confined to the most important vibration of the 200~4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands of the binuclear complexes and the mononuclear fragment $Na_2[Cu(obp)]\cdot 3.5H_2O$, 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 1610 cm^{-1} for $Na_2[Cu(obp)]\cdot 3.5H_2O$ is considerably shifted towards higher frequencies (*ca.* 20~50 cm^{-1}) in the binuclear complexes. This fact may be due to the following reason. It is generally believed that the deprotonated amide nitrogen is coordinated to the metal ion, its amide I band shifts considerably towards lower wavenumbers. However, in the case of an oxamide dianion coordinated to two metal ions as a bridging ligand, the amide I band reverts to near its original position (in the protonated species) [17]. Although the amide I is due to a composite N–C=O vibration, it can essentially be seen as ν(C=O). It is likely that the bond order of C=O (carbonyl) in the binuclear complexes is higher than that in the corresponding mononuclear complex $Na_2[Cu(obp)]\cdot 3.5H_2O$. This shift has often been used as a diagnostic indicator for oxamido-bridged structures [17]. On the other hand, the C=O deformation vibration at 728 cm^{-1} of the ligand complex, $Na_2[Cu(obp)]\cdot 3.5H_2O$, disappeared in the spectra of the binuclear complexes. This fact may be attributed to the coordination of the carbonyl oxygens to the Ln(III) ion [11]. This coordination mode of the complex ligand, $Na_2[Cu(obp)]\cdot3.5H_2O$, has been revealed by X-ray diffraction analysis of an analogous complex [15]. Furthermore, the appearance of a new band at 560~572 cm^{-1} due to ν(Ln–O) further confirms the coordinated nature of the complex ligand in these binuclear complexes. In addition, the –N=C– stretching vibration for the terminal ligand (Ph_2-phen) was shifted to higher frequencies (see Table 2) in these binuclear complexes, suggesting that the N atoms of the terminal ligand is coordinated with the Ln(III) ion. The additional band observed at around 420~428 cm^{-1} due to ν(Ln–N) further supports this view. On the other hand, the antisymmetric stretching vibration of the carboxylate group for $Na_2[Cu(obp)]\cdot3.5H_2O$ remains at 1575 cm^{-1} in the binuclear complexes, indicating that the carboxylate group is not coordinated with the Ln(III) ion. However, the spectra of the binuclear complexes exhibit characteristic vibrational frequencies of monodentate coordinated perchlorate group, which is suggested by two well-resolved bands observed at around 1130 and 1020 cm^{-1} [19]. Thus, on the basis of the above spectral observations, together with the molar conductance data, confirm that the perchlorate ion is coordinated to the Ln(III) ions in a monodentate fashion in these binuclear complexes (see Figure 1).

Electronic spectra: In order to clarify the mode of bonding, the electronic spectra of the mononuclear fragment $Na_2[Cu(obp)]\cdot3.5H_2O$ and Cu(II)–Ln(III) heterobinuclear complexes were studied and assigned on the basis of a careful comparison of the latter with the former. As shown in Table 2, the electronic spectra of all the complexes exhibit a band at 530~545 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 (595 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 $[CuN_2O_2]$ chromophore on forming a binuclear 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 bands, which may be due to the spin-exchange interaction between the copper(II) and lanthanoid(III) ions through the π-path orbital set up by an oxamido bridge [17]. 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 $Cu(obp)Ln(Ph_2\text{-phen})_2ClO_4$ (Ln = Nd, Sm, Tb, Dy, Ho, Er), f-f transitions of Ln(III) were also observed. These data are listed in Table 2 along with their assignments [20]. Other f-f transitions which are expected to appear may be concealed by d-d, charge-transfer, or intraligand transitions.

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 [15], these complexes are proposed to have an extended oxamido-bridged binuclear structure and to contain a lanthanoid(III) ion and a copper(II) ion, which have the presumed coordination environment as shown in Figure 1. It should be pointed out that lanthanide(III) ions have generally different geometries from each other, especially light and the heavy ones. Thus, the most direct and forceful evidence for the above assumption made might come from X-ray crystal-

Table 2. Physical data for the complexes.

Complex	Λ_M^*	IR (cm^{-1})						UV (nm)			
		$\nu_{as}(CO_2^-)$	ν(C=O)	ν(Ln–O)	$\nu(ClO_4^-)$	ν(N=C)	ν(Ln–N)	d-d	f-f	Assignment	CT
Na_2[Cu(obbz)]		1575	1610					595			
(1)	4.0	1575	1630	560	1130, 1025	1540	420	535			328
(2)	3.8	1575	1650	565	1130, 1025	1538	423	541			330
(3)	2.0	1575	1640	562	1130, 1026	1535	425	545	736	$(^4I_{9/2} \rightarrow {}^7F_{7/2})$	325
(4)	4.2	1575	1645	570	1130, 1025	1540	421	543	410	$(^4H_{5/2} \rightarrow {}^4I_{9/2})$	312
(5)	5.0	1575	1660	568	1130, 1028	1540	426	538			317
(6)	6.5	1575	1650	572	1130, 1020	1540	422	540			315
(7)	6.0	1575	1655	566	1130, 1028	1540	428	530	452	$(^7F_6 \rightarrow {}^5F_4)$	320
(8)	5.5	1575	1658	570	1130, 1028	1535	427	545	450	$(^6H_{5/2} \rightarrow {}^4I_{15/2})$	322
(9)	5.0	1575	1650	563	1130, 1020	1534	421	535	642	$(^5I_8 \rightarrow {}^4F_5)$	320
(10)	5.2	1575	1660	568	1130, 1020	1540	420	540	650	$(^4I_{15/2} \rightarrow {}^7F_{9/2})$	324
(11)	5.5	1575	1654	564	1130, 1028	1540	424	532			316

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

lographic studies. Unfortunately, all our efforts to grow crystals of these binuclear complexes suitable for X-ray structure determination so far have been unsuccessful. Thus, at this stage, on the basis of the reactant metal complex unit and the physical and chemical evidence, the new binuclear species may be described as an oxamido-bridged binuclear structure, as shown in Figure 1. The plausible structure is further characterized by the following ESR and magnetic studies.

ESR spectra: In order to obtain further information on the structure of the binuclear complexes, the X-band powder ESR spectra of the Cu(obp)Gd(Ph_2-phen)$_2$$ClO_4$ and Na_2[Cu(obp)]·3.5H_2O complexes 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 (see Figure 2), which also indicates a magnetic spin-exchange interaction between Gd(III) and Cu(II) ions [13]. Since there is 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 [21], two spins, $S_{Cu(II)} = 1/2$ and $S_{Gd(III)} = 7/2$, are coupled to yield the total spin states of S = 3 and S = 4. Due to the Boltzmann distribution, the two states are both populated at room temperature, owing to a very weak interaction (*vide infra)*. Thus, the dissymmetric broad signals may be ascribed to the complex in these spin states [13].

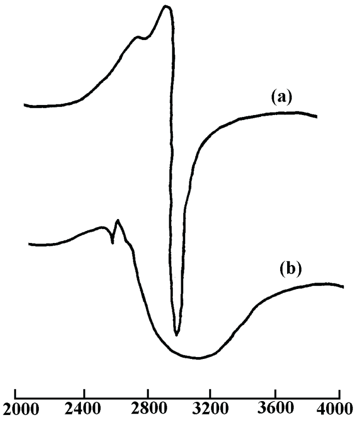

Figure 2. X-band powder ESR spectra of Na_2[Cu(obp)]·3.5H_2O (a) and Cu(obp)Gd(Ph_2-phen)$_2$$ClO_4$ (b) at room temperature.

Magnetic studies of Cu(obp)Gd(Ph_2-phen)$_2$$ClO_4$: On the basis of the above discussion of ESR spectra of the complexes, it has shown that a spin-coupled interaction exists between copper(II) and gadolinium(III) ions. In order to determine the nature and magnitude of the spin-exchange interaction, variable-temperature (4.2~300 K) magnetic susceptibility data were collected for Cu(obp)Gd(Ph_2-phen)$_2$$ClO_4$ complex, as an example, and the results are shown in Figure 3 as plots χ_M *vs*. T and μ_{eff} *vs*. T, where χ_M, μ_{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 property, which do not show large anisotropy effects as other lanthanides do. Since the ground state of Gd(III) is $^8S_{7/2}$ and the energy level of the lowest excited state is very high, the magnetic data usually can be interpreted without considering the contribution of the orbital angular momentum and the anisotropic effect [13]. However, for the other Cu(II)–Ln(III) heterobinuclear systems (Ln = Y, La, Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb), the theoretical expression has never been derived, due to a very weak interaction and a large anisotropic effect of lanthanoid ions. Thus, a complete interpretation of their magnetic data is not yet feasible. On the basis of the above facts, the $Cu(obp)Gd(Ph_2\text{-}phen)_2ClO_4$ complex is an ideal model for studying the magnetic interaction between Cu(II) and Ln(III) ions among the eleven binuclear complexes, and the magnetic data may be used to deduce the indicated structure. As shown in Figure 3, the effective magnetic moment at room temperature is 8.22 B.M., which is slightly larger than the spin-only value (8.12 B.M.) in the absence of the magnetic interaction of this spin-system ($S_{Cu(II)} = 1/2$, $S_{Gd(III)} = 7/2$). As the temperature is lowered, the magnetic moment increases gradually from 8.22 B.M. at 300 K, to a maximum of 8.91 B.M. at 12.8 K, and sharply decreases to 8.29 B.M. at 4.5 K. The maximum value (8.91 B.M.) is comparable to the expected value of $\mu_{eff} = 8.94$ B.M. for a spin S = 4 ground state, which should arise from ferromagnetic spin-coupling of the spin-system Gd(III)–Cu(II) ($S_{Cu(II)} = 1/2$, $S_{Gd(III)} = 7/2$). This is typical of a ferromagnetic coupling between the Cu(II) and Gd(III) ions within this complex. A decrease in the magnetic moment below 12.8 K may be attributed to an intermolecular antiferromagnetic interaction and /or the zero-field splitting effects.

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 ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$), where the exchange integral J is negative for an antiferromagnetic interaction and positive for a ferromagnetic one. For the Cu(II)–Gd(III) binuclear system ($S_{Cu(II)} = 1/2$, $S_{Gd(III)} = 7/2$), the theoretical expression of magnetic susceptibility is given as:

$$\chi_M = \frac{4N\beta^2 g^2}{kT}\left[\frac{15 + 7\exp(-8J/kT)}{9 + 7\exp(-8J/kT)}\right] \qquad (1)$$

where χ_M denotes the molecular susceptibility per binuclear complex and the other symbols have their usual meanings. As shown in Figure 3, good least-squares fits to the experimental data were attained with (1). The magnetic parameters thus determined are $J = +2.98\ cm^{-1}$ 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 2.7×10^{-5}. The results confirmed that the spin coupling between gadolinium(III) and copper(II) ions through an oxamido group represents a ferromagnetic spin-exchange interaction. Moreover, the very good agreement factor (F) also indicates that the contribution of the intermolecular antiferromagnetic interactions and the zero-field splitting effects in the ground state is evidently weaker than the intramolecular spin-exchange and can be neglected.

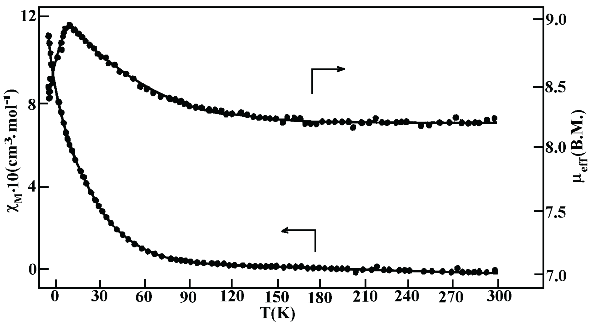

Figure 3. Magnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) *vs* T for Cu(obp)Gd(Ph_2-phen)$_2ClO_4$ complex. The solid lines denote the least-squares fit of the data to equation (1).

The small J value of the complex may account for the fact that the 4f-electrons are shielded by the outer shell electrons [22]. However, the ferromagnetic coupling between Gd(III) and Cu(II) is interesting because the Gd(III) ion has unpaired electrons in all seven f orbitals and at least one of them or one linear combination can given a zero overlap with the magnetic orbitals of Cu(II). Thus, this gives an antiferromagnetic coupling [23]. However, the observed Cu(II)–Gd(III) coupling in many Cu(II)–Gd(III) clusters is always ferromagnetic, in spite of the difference among these units in coordination numbers, geometries, and bridging groups [24–26]. One plausible mechanism that cause a ferromagnetic coupling between Gd(III) and Cu(II), as proposed by Kahn [25] and Benelli [26] *et al.*, is the spin-polarization, that occurs when the magnetic orbital of Cu(II) overlaps with the empty 5d orbital [25] 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 fact that the 4f orbital is shielded by the outer filled 5s and 5p orbitals, and lanthanoid ions generally form complexes using 6s, 6p, and/or 5d orbitals, further supports the spin-polarization mechanism. Further investigations are still required involving other lanthanides and different stoichiometries in order to get a reasonable explanation and deeper insight into this exciting field of magnetic interactions.

Conclusions: The strategy of "complex as ligand" allowed us to synthesize and characterize eleven new μ-oxamido-bridged Cu(II)–Ln(III) (Ln = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) heterobinuclear complexes. At present, though the crystal structure of these heterobinuclear complexes is not known, the combination of magnetic susceptibility and ESR spectra (*vide infra*) clearly demonstrates the presence of exchange coupling between the metal atoms, reveals certain electronic properties of these complex molecules, and allows predictions of structural features to be made. Based on the inherent nature of these lanthanide(III) ions, variable-temperature (4.2~300 K) magnetic susceptibility data were collected for Cu(II)–Gd(III) binuclear complex, as an example, and the magnetic interaction between Cu(II) and Gd(III) ions was studied detaily in order to deduce the indicated binuclear structure. The main result is that the copper(II) and gadolinium(III) ions are coupled in a ferromagnetic fashion *via* isotropic coupling ($J = +2.98\ \text{cm}^{-1}$), indicating that weak coupling can be established between transition-metal and rare-earth ions. A plausible mechanism for the ferromagnetic coupling between Gd(III) and Cu(II) is discussed in terms of spin-polarization.

Acknowledgments

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