Synthesis, characterization and magnetism of copper(II)-lanthanide(III) heterobimetalic complexes with N, N'-oxamidobis-(benzoato)cuprate(II)

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Seven new μ-oxamido copper(II)-lanthanide(III) heterobimetalic complexes described by the formula Cu(obbz) Ln-(Ph-phen)$_2$NO$_3$ (Ln = La, Nd, Eu, Gd, Tb, Ho, Er), where obbz denotes the oxamidobis(benzoato) and Ph-phen represents 5-phenyl-1, 10-phenanthroline, have been synthesized and characterized by the elemental analyses, spectroscopic (IR, UV, ESR) studies, magnetic moments (at room temperature) and molar conductivity measurement. The temperature dependence of the magnetic susceptibility of Cu(obbz)Gd(Ph-phen)$_2$NO$_3$ complex has been measured over the range 4.2—300 K. The least-squares fit of the experimental susceptibilities based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, yielded $J = +1.28$ cm^{-1}, a weak ferromagnetic coupling. A plausible mechanism for a ferromagnetic coupling between Gd(III)-Cu(II) is discussed in terms of spin-polarization.

Keywords   Copper(II)-lanthanide(III), heterobimetalic complexes, ferromagnetic spin-coupling, synthesis

Introduction

Recent years have witnessed a growing interest in heterobinuclear complexes containing two different paramagnetic centers.[1-3] Interest in this field 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] There were relatively few studies dealing with heterometal complexes containing d-transition metal ions and lanthanide(III) ions (so-called d-f heteronuclear complexes), due to the very weak interaction and a large anisotropic effect of lanthanide ions.[4-7] However, since Vidali, Abid and co-workers[4,5] 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. Moreover, the fact that the d-f mixed oxides have been used in many functional materials and/or have been expected as promising functional materials,[8] stimulated us to develop d-f heteronuclear complexes, possessing new functions associated with some d-f heterometal centers. In order to provide more examples of d-f heteronuclear complexes, we have recently synthesized some d-f heteronuclear complexes and investigated their magnetic properties.[9-13] In continuation of our earlier work, seven new heterometal binuclear complexes, Cu(obbz)Ln(Ph-phen)$_2$NO$_3$ (Ln = La, Nd, Eu, Gd, Tb, Ho, Er) have been prepared by the reaction of sodium N, N'-oxamidobis(benzoato)cuprate(II) tetrahydrate, Na$_2$[Cu(obbz)]·4H$_2$O, with lanthanide(III) ions and terminal

ligand 5-phenyl-1, 10-phenanthroline (Ph-phen). The ESR and magnetic properties of the Cu(obbz)Gd(Ph-phen)₂NO₃ complex have also been studied. The main result is that the copper(II) and gadolinium(III) ions are coupled in a ferromagnetic fashion *via* isotropic coupling (J = +1.28 cm⁻¹), thus, indicating that weak coupling can be established between the transition-metal and rare-earth ions.

Experimental

Materials

All reagents used were of analytical grade. The hydrated lanthanide perchlorates were prepared by general methods. The terminal ligand 5-phenyl-1, 10-phenanthroline (Ph-phen) was of analytical grade and used as commercially obtained from Sigma Chemical Co. The starting material Na₂[Cu(obbz)]·4H₂O was synthesized as previously described.[14]

Synthesis of binuclear Cu(II)-Ln(III) (Ln = La, Nd, Eu, Gd, Tb, Ho, Er) *complexes*

The preparation methods of all copper(II)-lanthanide(III) heterobinuclear complexes were the same and are exemplified by that of Cu(obbz)Gd(Ph-

phen)₂NO₃. To a solution of Na₂[Cu(obbz)]·4H₂O (510 mg, 1 mmol) in absolute ethanol (20 mL) was added successively a solution of Gd(NO₃)₃·6H₂O (451.4 mg, 1 mmol) in absolute ethanol (10 mL), followed by a solution of ethyl orthofomate (10 mL) with stirring, continuously at room temperature until the mixture became limpid. This solution was then filtered. To the filtrate an absolute ethanol solution (20 mL) of Ph-phen (512.6 mg, 2 mmol) was added. The colour of the solution turned immediately from red-brown to violet and a small amount of precipitate was formed. After refluxing for *ca*. 12 h, the mixture was 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 P₂O₅ under reduced pressure. All analytical data, colours, yields and melting points of the binuclear 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. IR spectra were recorded with a Nicolet FT-IR 5DX spectrometer using KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-

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

Complex	Empirical formula (Formula weight)	Color	Yield (%)	Mp (°C)	C	H	N	Cu	Ln
1	CuLaC₅₂H₃₄N₇O₁₀ (1119.34)	pale-violet	89	336	55.68 (55.80)	2.95 (3.06)	8.52 (8.76)	5.57 (5.68)	12.29 (12.41)
2	CuEuC₅₂H₃₂N₇O₉ (1114.37)	violet	85	321	55.91 (56.05)	2.81 (2.89)	8.66 (8.80)	5.58 (5.70)	13.49 (13.64)
3	CuGdC₅₂H₃₂N₇O₉ (1119.66)	violet	78	329	55.85 (55.78)	2.76 (2.88)	8.58 (8.76)	5.51 (5.68)	13.89 (14.04)
4	CuNdC₅₂H₃₆N₇O₁₁ (1142.68)	pale-brown	80	338	54.52 (54.66)	3.07 (3.18)	8.36 (8.58)	5.32 (5.56)	12.43 (12.62)
5	CuTbC₅₂H₃₂N₇O₉ (1121.34)	pale-red	79	322	55.52 (55.70)	2.76 (2.88)	8.53 (8.74)	5.49 (5.67)	14.02 (14.17)
6	CuHoC₅₂H₃₄N₇O₁₀ (1145.36)	brown	73	309	54.34 (54.53)	2.86 (2.99)	8.32 (8.56)	5.38 (5.55)	14.29 (14.40)
7	CuErC₅₂H₃₂N₇O₉ (1129.67)	brown	82	315	55.17 (55.29)	2.77 (2.86)	8.47 (8.68)	5.42 (5.63)	14.68 (14.81)

1: Cu(obbz)La(Ph-phen)₂NO₃·H₂O, 2: Cu(obbz)Eu(Ph-phen)₂NO₃, 3: Cu(obbz)Gd(Ph-phen)₂NO₃, 4: Cu(obbz)Nd(Ph-phen)₂NO₃·2H₂O, 5: Cu(obbz)Tb(Ph-phen)₂NO₃, 6: Cu(obbz)Ho(Ph-phen)₂NO₃·H₂O, 7: Cu(obbz)Er(Ph-phen)₂NO₃.

Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using Hg[Co-(SCN)$_4$] as the calibrant. Variable temperature magnetic susceptibilities 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[15] for all the constituent atoms and effective magnetic moments were calculated by the equation μ_{eff} = 2.828 $(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for the diamagnetic parts of the constituting atoms. The ESR spectra were measured with a JES-FEIXG ESR-apparatus at the X-band.

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.[16,17] 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(benzoato)cuprate(II) tetrahydrate, Na$_2$[Cu(obbz)]·4H$_2$O, which was first used to prepare alternating Cu(II)-Mn(II) bimetallic chain or heterobinuclear Cu(II)-Ni(II) complexes[14] 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, 5-phenyl-1,10-phenanthroline (Ph-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(obbz)]·4H$_2$O with Ln(NO$_3$)$_3$·6H$_2$O (Ln = La, Nd, Eu, Gd, Tb, Ho, Er) and Ph-phen in 1:1:2 mole ratio yielded the heterobinuclear complexes of the general formula Cu(obbz)Ln(Ph-phen)$_2$NO$_3$, as expected. Based on the conductivity measurements, spectro-

scopic (IR, ESR and UV) characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.
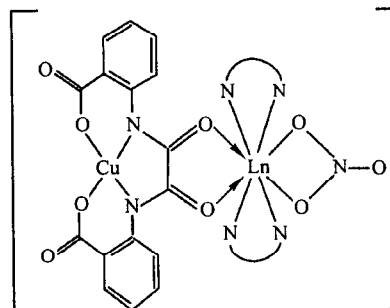

Fig. 1 Plausible coordination environments of the complexes (Ln = La, Nd, Eu, Gd, Tb, Ho, Er; N⌒N = Ph-phen).

General properties of the binuclear complexes

The binuclear 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 Cu(obbz)Gd(Ph-phen)$_2$NO$_3$ complex can be recrystallized from a DMF/ethanol (1:1) mixture. The solid Cu(II)-Ln(III) binuclear complexes are fairly stable in air. For the seven Cu(II)-Ln(III) binuclear complexes, the observed molar conductance values in DMF solution (in the range 5.0—8.0 (Ω^{-1}·cm^2·mol^{-1}) are given in Table 2. These values are indicative of the non-electrolytic nature,[18] suggesting a weak coordination of the nitrate anion. This is consistent with the measured IR data.

Infrared spectra

The most relevant IR absorption bands of the binuclear complexes and the mononuclear fragment Na$_2$[Cu-(obbz)]·4H$_2$O, along with their assignments are shown in Table 2. We will only discuss some selected infrared bands. The carbonyl stretching vibration at 1600 cm^{-1} for Na$_2$[Cu(obbz)]·4H$_2$O is considerably shifted towards higher frequencies (*ca.* 30—50 cm^{-1}) in the binuclear 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 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 $\nu(C = O)$, it is likely that the bond order of $C = O$ (carbonyl) in the binuclear complexes is higher than that in the corresponding mononuclear complex $Na_2[Cu(obbz)]\cdot4H_2O$. 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 800 cm^{-1} of the ligand complex, $Na_2[Cu(obbz)]\cdot4H_2O$, disappeared in the spectra of the binuclear complexes. This may be attributed to the coordination of the carbonyl oxygens to the Ln(III) ion.[11] This coordination mode of the complex ligand, $Na_2[Cu(obbz)]\cdot4H_2O$, has been revealed by X-ray diffraction analysis of an analogous complex.[14] In addition, the $- N = C -$ stretching vibration for the terminal ligand (Ph-phen) was shifted to higher frequences (1530 cm^{-1}) 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 370—380 cm^{-1} due to $\nu(Ln—N)$, further supports this view. On the other hand, the antisymmetric stretching vibration of the carboxylate group for $Na_2[Cu(obbz)]\cdot4H_2O$ remains at 1580 cm^{-1} in the binuclear complexes, indicating that the carboxylate group is not coordinated. However, the spectra of the binuclear 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 ν_4 and ν_1 vibrations of the nitrate group of C_{2v} symmetry.[19] The medium band at 1030 cm^{-1} due to the ν_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 cm^{-1} indicating that the coordinated nitrate ions is bidentate.[20] Thus, the above spectral observations, together with the molar conductance data, confirm that the nitrate ion is coordinated to the Ln(III) ions in a bidentate fashion in these binuclear complexes (see Fig. 1).

Table 2 Physical data for the complexes

Complex	Λ_M*	IR (cm^{-1})						UV (nm)			
					$\nu(NO_3^-)$						
		$\nu_{as}(CO_2^-)$	$\nu(C=O)$	$\nu(Ln\text{-}N)$	ν_4	ν_1	ν_2	$d\text{-}d$	$f\text{-}f$	Assignment	CT
$Na_2[Cu(obbz)]\cdot4H_2O$		1580	1600					513			
1	5.5	1580	1630	380	1490	1310	1030	532			320
2	6.5	1580	1650	375	1490	1305	1030	545			326
3	5.0	1580	1650	385	1492	1315	1032	540			328
4	6.0	1580	1640	380	1490	1310	1030	545	735	$(^4I_{9/2}\to^7F_{7/2})$	325
5	7.0	1580	1645	387	1491	1308	1032	542	450	$(^7F_6\to^5F_4)$	319
6	8.0	1580	1655	382	1490	1310	1031	537	642	$(^5I_8\to^4F_5)$	317
7	6.8	1580	1650	370	1490	1306	1032	536	655	$(^4I_{15/2}\to^7F_{9/2})$	325

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

Electronic spectra

In order to clarify the mode of bonding, the electronic spectra of the mononuclear fragment $Na_2[Cu(obbz)]\cdot4H_2O$ 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 532—545 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 the d-d band may be attributed to the decreased planarity of 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 lanthanide(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 electron-
ic spectra of Cu(obbz)Ln(Me$_2$-phen)$_2$NO$_3$(Ln = Tb,
Nd, Ho, Er), f-f transitions of Ln(III) were obtained.
These data are listed in Table 2 along with their assign-
ments.[21] Other f-f transitions which are expected to ap-
pear may be concealed by d-d, charge-transfer, or in-
traligand 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,
IR, ESR, electronic spectra, conductivity measure-
ments, magnetic characterization (vide infra) and also
the crystal structure of the analogous complex,[14] these
complexes are proposed to have an extended oxamido-
bridged binuclear structure and to contain a lanthanide
(III) ion and a copper(II)ion, whichhave the presumed
coordination environment as shown in Fig. 1. The plau-
sible structure is further characterized by the following
ESR and magnetic studies.

ESR and magnetic studies of Cu(obbz)Gd(Ph-phen)$_2$NO$_3$

The X-band powder ESR spectra of the Cu(obbz)-
Gd(Ph-phen)$_2$NO$_3$ and Na$_2$[Cu(obbz)] · 4H$_2$O 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 $g = 2.1$,
which also indicates a magnetic spin-exchange interac-
tion between Gd(III) and Cu(II) ions.[7] 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 ex-
change coupling between gadolinium(III) and Cu(II).
According to Kambe's approach,[22] 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 in-
fra). Thus, the dissymmetric broad signals may be as-
cribed to the complex in these spin states.[7]

In order to obtain further information on the struc-
ture of the binuclear complexes, variable-temperature
(4.2—300 K) magnetic susceptibility data were collect-
ed for complex Cu(obbz)Gd(Ph-phen)$_2$NO$_3$, as an ex-
ample, and the results are shown in Fig. 2 in the form
of 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 tempera-
ture, respectively. 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 in-
terpreted without considering the contribution of the or-
bital angular momentum and the anisotropic effect.[7,10]
Therefore, we chose Gd(III) complex for the detail
study of magnetic properties. Based on the inherent na-
ture of the Gd(III), the Cu(obbz)Gd(Ph-phen)$_2$NO$_3$
complex is an ideal model for the magnetic interaction
between Cu(II) and Ln(III) ions among the seven binu-
clear complexes. As shown in Fig. 2, the effective mag-
netic moment at room temperature is 8.21 ± 0.01
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 in-
creases gradually from 8.21 B.M. at 300 K, reaches a
maximum of 8.89 B.M. at 12.5 K, and sharply de-
creases to 8.30 B.M. at 4.2 K. The maximum value
(8.89 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 be-
tween the Cu(II) and Gd(III) ions within this complex.
A decrease in the magnetic moment below 12.5 K may
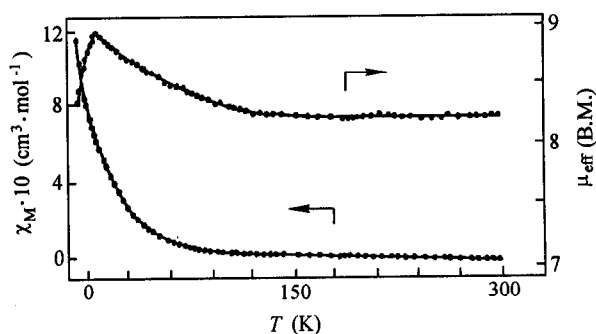be attributed to an intermolecular antiferromagnetic inter-
action.

Fig. 2   Magnetic susceptibility (χ_M) and effective magnetic
moment(μ_{eff}) vs. T for Cu(obbz)Gd(Ph-phen)$_2$NO$_3$
complex. The solid line denotes the least-squares fit
the data to equation (1) given in the text.

In order to understand the spin-exchange interac-

tion, 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:[10]

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

where χ_M denotes the molecular susceptibility per binuclear complex and the other symbols have their usual meanings. As shown in Fig. 2, good least-square fits to the experimental data were attained with (1). The magnetic parameters thus determined are $J = +1.28$ cm^{-1} and $g = 2.08$. 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. One plausible mechanism, that causeed a ferromagnetic coupling between Gd(III) and Cu(II) as proposed by Benelli[23] and Kahn[24] *et al*., is the spin-polarization, that occurs when the magnetic orbital of Cu (II) overlaps with the empty $5d$ orbital[24] 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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