

SYNTHESIS AND MAGNETIC STUDIES OF COPPER(II)- LANTHANIDE(III) COMPLEXES WITH *N,N'*-BIS (2-AMINOPROPYL)OXAMIDOCOPPER(II)

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Abstract—Seven novel μ -oxamido heterodinuclear complexes, namely $\text{Cu}(\text{oxap})\text{Ln}(\text{L})_2(\text{ClO}_4)_3$, where oxap denotes the *N,N'*-bis(2-aminopropyl)oxamido dianion, L represents 1,10-phenanthroline (phen) and Ln denotes La, Nd, Gd, Tb, Dy, Ho, Er, have been synthesized and characterized. The magnetic susceptibility measurements (4.2–300 K) of $\text{Cu}(\text{oxap})\text{Gd}(\text{phen})_2(\text{ClO}_4)_3$ indicate a weak ferromagnetic interaction between the copper(II) and gadolinium(III) ions, with the exchange integral $J_{\text{Cu-Gd}} = 2.25 \text{ cm}^{-1}$.

Binuclear metal complexes containing two different metal ions are of current interest in connection with spin-exchange and charge-transfer between metal ions and in the domain of metalloenzymes and molecular magnets.¹ Many reviews have been published on binuclear complexes containing oxamide ($\text{C}_2\text{O}_2\text{N}_2\text{H}_2^{2-}$) ligands such as *N,N'*-bis(alkylaminoalkyl)oxamides.² The effective bridging function of μ -oxamido has been revealed by X-ray analysis for some of these complexes.³⁻⁶ Recently, we first used $\text{Cu}(\text{oxae})$ as a monomeric fragment to synthesize and characterize the copper(II)-lanthanide(III) heterometal binuclear complexes $\text{Cu}(\text{oxae})\text{Ln}(\text{phen})_2(\text{ClO}_4)_3$ ⁷ [oxae denotes the *N,N'*-bis(2-aminoethyl)oxamido dianion, Ln denotes Eu, Gd, Tb, Dy, Ho, Er, phen represents 1,10-phenanthroline]. In continuation of our earlier work, in this paper seven novel heterometal binuclear complexes, $\text{Cu}(\text{oxap})\text{Ln}(\text{phen})_2(\text{ClO}_4)_3$ (Ln = La, Nd, Gd, Dy, Tb, Ho or Er), have been synthesized by using *N,N'*-bis(2-aminopropyl)oxamidocopper(II) [abbreviated as $\text{Cu}(\text{oxap})$] as starting material, and the magnetic properties of the

complex $\text{Cu}(\text{oxap})\text{Gd}(\text{phen})_2(\text{ClO}_4)_3$ have been studied.

EXPERIMENTAL

Materials

All the reagents used in the synthesis were analytical grade. The hydrated lanthanide(III) perchlorates were prepared by general methods.⁸ The starting material $\text{Cu}(\text{oxap})$ was synthesized by the literature method⁹ from 1,2-propanediamine, diethyl oxalate and copper(II) hydroxide.

Synthesis of $\text{Cu}(\text{oxap})\text{Ln}(\text{phen})_2(\text{ClO}_4)_3$ (Ln = La, Nd, Gd, Dy, Ho, Er, Tb)

The methods used to prepare the complexes are virtually identical and are exemplified by $\text{Cu}(\text{oxap})\text{Gd}(\text{phen})_2(\text{ClO}_4)_3$. To a suspension of $\text{Cu}(\text{oxap})$ (52.8 mg, 0.2 mmol) in absolute ethanol (5 cm^3) was added dropwise a solution of $\text{Gd}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (112.8 mg, 0.2 mmol) in absolute ethanol (10 cm^3) with stirring. The stirring was continued at room temperature until the mixture became a reddish solution. To this solution was added an absolute ethanol solution (10 cm^3) of phen (79.3 mg, 0.4

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mmol); the colour of the solution changed immediately and a small amount of light blue precipitate formed. After refluxing for 4 h, the blue microcrystals thus formed were filtered off, washed several times with absolute ethanol and ether and dried *in vacuo*. All analytical data, colours, yields and melting points of the complexes are collected in Table 1. The complexes are very soluble in DMF, DMSO, acetonitrile and acetone, moderately soluble in methanol and ethanol, and practically insoluble in carbon tetrachloride. They can be recrystallized from an acetonitrile-ethanol (1:1) mixture.

Measurements

Elemental analyses for carbon, hydrogen and nitrogen were performed with a Perkin-Elmer elemental analyser Model 240. The metal contents were determined by EDTA titration. IR spectra were recorded with a Shimadzu IR spectrometer Model 408 using KBr pellets. Electronic spectra (in acetonitrile solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Variable-temperature magnetic susceptibilities (4.2–300 K) were performed at the Institute of Physics, Chinese Academy of Sciences, using a vibrating sample magnetometer Model CF-1. Diamagnetic corrections were made with Pascal's constants¹⁰ for all the constituent atoms. The effective magnetic moments were calculated by the equa-

tion $\mu_{\text{eff}} = 2.828 (XT)^{1/2}$, where X = susceptibility and T = temperature. ESR spectra of powder samples were recorded with a JES-FEIXG ESR apparatus using the X-band.

RESULTS AND DISCUSSION

General characterization

Elemental analyses and physical data (Table 2) for the complexes indicate that the reaction of Cu(oxap) with phen and $\text{Ln}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{La, Nd, Gd, Tb, Dy, Ho, Er}$) yielded the heterobinuclear complexes $\text{Cu}(\text{oxap})\text{Ln}(\text{phen})_2(\text{ClO}_4)_3$. The carbonyl stretching vibration at 1588 cm^{-1} for Cu(oxap) is considerably shifted towards higher frequencies (*ca* 1640 cm^{-1}) in the binuclear complexes. It is likely that the bond order of C=O (carbonyl) in the binuclear complexes is higher than that in the corresponding mononuclear complex Cu(oxap). This shift has often been used as a diagnostic for oxamido-bridged structures.² On the other hand, the C=O deformation of the ligand complex at 720 cm^{-1} 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 In addition, the $-\text{NH}_2$ vibration at 3320 cm^{-1} for Cu(oxap) and the $-\text{N}=\text{C}-$ stretching vibration at 1590 cm^{-1} for the terminal ligand (phen) were present for all the binuclear complexes and two well-resolved bands were observed at about 1130 and 1028 cm^{-1} , which are

Table 1. Elemental analyses, yield, colour and melting point of the complexes

Complex	Colour	Yield (%)	M.p. (°C)	Elemental analyses (calc.), %				
				C	H	N	Cu	Ln
1	Blue	59	304	35.7 (35.6)	3.0 (3.0)	10.5 (10.4)	5.8 (5.9)	14.7 (14.6)
2	Light blue	62	311	34.5 (34.5)	3.5 (3.4)	10.3 (10.1)	6.0 (5.7)	12.6 (12.5)
3	Light blue	66	308	34.2 (34.4)	3.2 (3.3)	10.2 (10.0)	5.8 (5.7)	14.4 (14.2)
4	Blue	68	315	35.4 (35.3)	3.0 (3.0)	10.2 (10.3)	5.6 (5.8)	15.5 (15.4)
5	Blue	57	321	35.3 (35.3)	2.8 (3.0)	10.5 (10.3)	5.8 (5.8)	15.3 (15.2)
6	Light blue	65	318	35.7 (35.4)	2.9 (3.0)	10.5 (10.3)	5.8 (5.9)	15.1 (15.0)
7	Blue	54	309	34.8 (34.9)	3.4 (3.3)	10.4 (10.2)	5.9 (5.8)	13.3 (13.1)

1, $\text{Cu}(\text{oxap})\text{Gd}(\text{phen})_2(\text{ClO}_4)_3$; 2, $\text{Cu}(\text{oxap})\text{La}(\text{phen})_2(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$; 3, $\text{Cu}(\text{oxap})\text{Tb}(\text{phen})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$; 4, $\text{Cu}(\text{oxap})\text{Er}(\text{phen})_2(\text{ClO}_4)_3$; 5, $\text{Cu}(\text{oxap})\text{Ho}(\text{phen})_2(\text{ClO}_4)_3$; 6, $\text{Cu}(\text{oxap})\text{Dy}(\text{phen})_2(\text{ClO}_4)_3$; 7, $\text{Cu}(\text{oxap})\text{Nd}(\text{phen})_2(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$.

Table 2. Physical data for the complexes

Complex	Λ_M^a ($\Omega^{-1} \text{ cm}^2$ mol^{-1})	IR (cm^{-1})				UV ($\times 10^3 \text{ cm}^{-1}$)		
		—NH ₂	C=O	—N=C—	ClO ₄ ⁻	<i>d-d</i>	<i>f-f</i>	Assignment
Cu(oxap)		3320	1588			19.3		
Cu(oxap)La(phen) ₂ (ClO ₄) ₃ ·3H ₂ O	245	3320	1640	1592	1130	18.7		
					1028			
Cu(oxap)Tb(phen) ₂ (ClO ₄) ₃ ·2H ₂ O	238	3320	1650	1585	1130	18.7	22.3	(⁷ F ₆ → ⁵ D ₄)
					1028			
Cu(oxap)Nd(phen) ₂ (ClO ₄) ₃ ·2H ₂ O	280	3320	1650	1590	1130	18.6	13.6	(⁴ I _{9/2} → ⁴ F _{7/2})
					1028			
Cu(oxap)Gd(phen) ₂ (ClO ₄) ₃	256	3320	1645	1590	1130	18.6		
					1028			
Cu(oxap)Dy(phen) ₂ (ClO ₄) ₃	260	3320	1645	1592	1130	18.8	22.1	(⁶ H _{15/2} → ⁴ I _{15/2})
					1028			
Cu(oxap)Er(phen) ₂ (ClO ₄) ₃	273	3320	1648	1590	1130	18.8	15.3	(⁴ I _{15/2} → ⁴ F _{9/2})
					1028			
Cu(oxap)Ho(phen) ₂ (ClO ₄) ₃	245	3320	1650	1585	1130	18.6	15.6	(⁵ I ₈ → ⁵ F ₅)
					1028			

^a Values for $1 \times 10^{-3} \text{ mol dm}^{-3}$ acetonitrile solutions.

typical for monodentate perchlorate groups.¹² For the seven complexes, the molar conductance values are in the range expected for 1 : 2 electrolytes,¹³ indicating that two perchlorate anions are outside and only one perchlorate anion is inside the coordination sphere. This is consistent with the measured IR data. The absorption maxima of the ligand field band due to copper(II) ions are summarized in Table 2. The electronic spectra show a band at $(18.6\text{--}18.8) \times 10^3 \text{ cm}^{-1}$ for all binuclear complexes. The frequency is lower than that for the mononuclear copper(II) complex ($19.3 \times 10^3 \text{ cm}^{-1}$). Such a red shift of the *d-d* band may be attributed to the decreased planarity of the [CuN₄] chromophore on forming a binuclear complex with a lanthanide(III) ion.¹⁴ In addition, in the electronic spectra of Cu(oxap)Ln(phen)₂(ClO₄)₃ (Ln = Tb, Dy, Ho, Er,

Nd), *f-f* transitions of Ln^{III} were obtained from solutions in acetonitrile. These data are listed in Table 2 along with their assignments.¹⁵ Other *f-f* transitions which are expected to appear may be concealed by *d-d*, charge-transfer or intraligand transitions.¹⁶

Based on the composition of these complexes, IR, electronic spectra, conductivity measurements, ESR, magnetic data (see below) and the crystal structure of an analogous complex,⁶ the presumed coordination environments of the complexes are shown in Fig. 1.

Spin-exchange interaction of Cu(oxap)Gd(phen)₂(ClO₄)₃

Since we were interested in the study of magnetic properties, variable-temperature (4.2–300 K) magnetic susceptibility and magnetic moments for the binuclear complex Cu(oxap)Gd(phen)₂(ClO₄)₃ were measured and are shown in Fig. 2. The reason for the choice of gadolinium is the relative simplicity of its magnetic properties, which do not show large anisotropy effects as for other lanthanides. Gadolinium(III) is an *f*⁷ ion, since its ground state (⁸S_{7/2}) is orbitally non-degenerate and well-separated from the excited state, giving simple single ion magnetic properties.¹⁷ As a consequence, the complex Cu(oxap)Gd(phen)₂(ClO₄)₃ is an ideal model for studying magnetic interaction between Cu^{II} and Ln^{III} ions among the seven complexes. As shown in Fig. 2, the effective magnetic moment at room

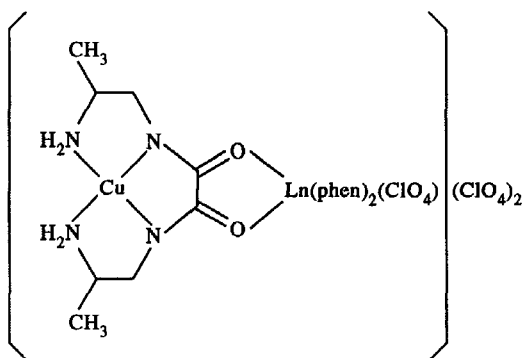


Fig. 1. Coordination environments of the complexes.

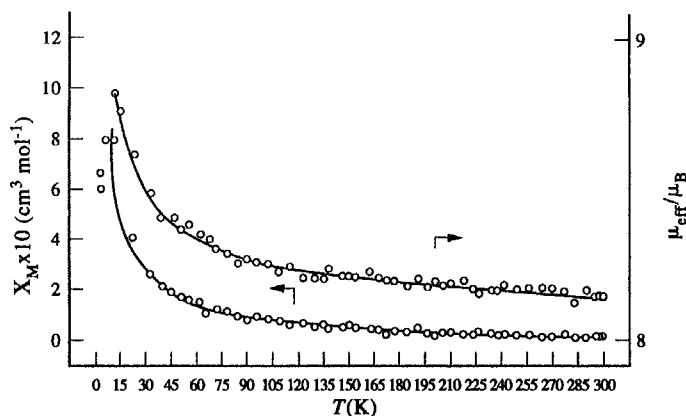


Fig. 2. Variable-temperature magnetic susceptibility and magnetic moment for Cu(oxap)Gd(phen)₂(ClO₄)₃. The curve is drawn based on eq. (2) using the magnetic parameters given in the text.

temperature is $8.15\mu_B$, which is slightly larger than the spin-only value ($8.12\mu_B$) in the absence of the magnetic interaction of this spin-system ($S_{\text{Cu}} = 1/2$, $S_{\text{Gd}} = 7/2$). As the temperature is lowered, the magnetic moment increases from $8.15\mu_B$ at 300 K to $8.79\mu_B$ at 12 K. This is typical of a ferromagnetic coupling between the Cu^{II} and Gd^{III} ions. The expected value of $\mu_{\text{eff}} = 8.94\mu_B$ for a spin $S = 4$ ground state is not reached, which is indicative of intermolecular antiferromagnetic interactions and/or zero-field splitting effects in the ground state.

In order to understand quantitatively the magnitudes of spin-exchange interaction between Gd^{III} and Cu^{II} ions, a magnetic analysis was performed with the susceptibility equation based on the Heisenberg spin-exchange operator:

$$\hat{H} = -2JS_1 \cdot S_2, \quad (1)$$

where J is the magnetic exchange integral between Gd^{III} and Cu^{II} ions. For the Cu^{II}-Gd^{III} ($S_{\text{Cu}} = 1/2$, $S_{\text{Gd}} = 7/2$) system, the theoretical expression of magnetic susceptibility is easily derived from operator (1):

$$\chi_M = \frac{4Ng^2\beta^2}{KT} \left[\frac{15 + 7\exp(-8J/KT)}{9 + 7\exp(-8J/KT)} \right], \quad (2)$$

where χ_M denotes the molecular susceptibility per binuclear complex and the other symbols have their usual meanings. We estimated J by taking data points above $T = 12$ K and using the ESR g value of 2.0. Least-squares fitting of the data yielded $J = 2.25 \text{ cm}^{-1}$. The agreement factor F , defined here as $F = \Sigma[(\chi_M)_{\text{obs.}} - (\chi_M)_{\text{calc.}}]^2 / \Sigma(\chi_M)_{\text{obs.}}$, is then equal to 3.4×10^{-3} . The results ($J > 0$ and J value is small) indicate the existence of a weak ferro-

magnetic spin interaction between Gd^{III} and Cu^{II} ions.

If we compare this $J_{\text{Gd-Cu}}$ value with those reported previously^{7,16,18} for CuGd clusters, we find that the present coupling constant is similar to most of them, i.e. the coupling between Gd^{III} and Cu^{II} ions is ferromagnetic. This is surprising because the Gd^{III} ion has unpaired electrons in all seven f orbitals and at least one of them or one linear combination can give a non-zero overlap with the magnetic orbitals of Cu^{II}. Thus, this gives an antiferromagnetic coupling.¹⁹ The fact that the coupling between Gd^{III} and Cu^{II} in many CuGd clusters is ferromagnetic may be due to the spin polarization^{19,20} that occurs when the magnetic orbital on Cu^{II} overlaps the empty $6s$ orbital of Gd^{III}. The fraction of unpaired electrons that is so transferred from Cu^{II} to Gd^{III} keeps the f electrons parallel due to Hund's rule, determining a ferromagnetic coupling between the two metal ions.²⁰ The facts that 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, support the spin-polarization mechanism.¹⁶ Indeed, ferromagnetic coupling between Gd^{III} and Cu^{II} is possible only through a superexchange interaction mediated by the bridging oxygen ligands. In other words, the magnetic orbitals centred on Gd^{III} and Cu^{II} must have a fairly large overlap density on the oxygen atom, which can be obtained only through a fairly substantial covalency of the Gd—O bond.¹⁷

We also previously investigated the magnetic behaviour of Cu(oxae)Gd(phen)₂(ClO₄)₃⁷ [oxae = N,N' -bis(2-aminoethyl)oxamido dianion] and observed antiferromagnetic coupling between the Gd^{III} and Cu^{II} ions in this complex. The two complexes Cu(oxap)Gd(phen)₂(ClO₄)₃ and

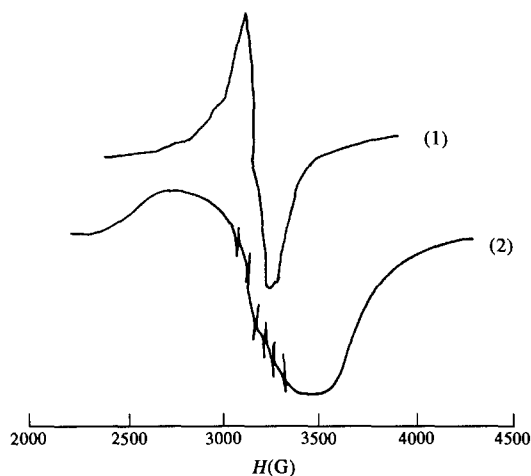


Fig. 3. X-Band powder ESR spectra of Cu(oxap) (1) and Cu(oxap)Gd(phen)₂(ClO₄)₃ (2).

Cu(oxae)Gd(phen)₂(ClO₄)₃ have essentially the same skeletal structure and their IR and electronic spectra are also similar. The only difference between Cu(oxap)Gd(phen)₂(ClO₄)₃ and Cu(oxae)Gd(phen)₂(ClO₄)₃ is that there is a methyl substituent in the former. However, its presence led to an essential difference between the sign of the exchange parameter J in the two complexes. We have no reasonable explanation for this behaviour so far. Further studies are in progress involving other lanthanides and different stoichiometries in order to get a reasonable explanation and deeper insight into this exciting field of magnetic interactions.

ESR spectra

The X-band powder ESR spectra of Cu(oxap)Gd(phen)₂(ClO₄)₃ and Cu(oxap) at room temperature are shown in Fig. 3. The spectrum of the former is obviously different from that of the latter and exhibits a broad band around $g = 2.0$, which also indicates a magnetic spin-exchange interaction between Gd^{III} and Cu^{II} ions.¹⁷ Due to lack of structural data of complexes of this kind, it is difficult to quantitatively interpret this broad band. Qualitatively, however, it is clear that these features reflect the exchange coupling between Gd^{III} and Cu^{II} ions. According to Kambé's approach,²¹ two spins $S_{\text{Cu}^{\text{II}}} = 1/2$ and $S_{\text{Gd}^{\text{III}}} = 7/2$ couple to yield the total spin states of $S = 3$ and $S = 4$. On the basis of Boltzmann's distribution, two states are both populated at room temperature owing to very

weak interactions ($J = 2.25 \text{ cm}^{-1}$). Thus, the asymmetric broad signal may be ascribed to a complex in these spin states.¹⁷

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