

Synthesis, Characterization and Magnetic Studies of μ -Oxamido Copper(II)-Chromium(III) Heterodinuclear Complexes

LI, Yan-Tuan^{*a}(李延团) YAN, Cui-Wei^b(焉翠蔚) HU, Chun-Xia^a(胡春霞)
LIAO, Dai-Zheng^c(廖代正)

^a Department of Chemistry, Qufu Normal University, Qufu, Shandong 273165, China

^b Department of Biology, Qufu Normal University, Qufu, Shandong 273165, China

^c Department of Chemistry, Nankai University, Tianjin 300071, China

Three new μ -oxamido-bridged heterodinuclear copper(II)-chromium(III) complexes formulated $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{L})_2](\text{NO}_3)_3$, where Me_2oxpn denotes *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamido dianion and L represents 5-methyl-1,10-phenanthroline (Mephen), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen) or 2,2'-bipyridine (bpy), have been synthesized and characterized by elemental analyses, IR and electronic spectral studies, magnetic moments of room-temperature and molar conductivity measurements. It is proposed that these complexes have oxamido-bridged structures consisting of planar copper(II) and octahedral chromium(III) ions. The variable temperature magnetic susceptibilities (4.2–300 K) of complexes $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{NO}_3)_3$ (1) and $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Mephen})_2](\text{NO}_3)_3$ (2) were further measured and studied, demonstrating the ferromagnetic interaction between the adjacent chromium(III) and copper(II) ions through the oxamido-bridge in both complexes 1 and 2. Based on the spin Hamiltonian, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, the exchange integrals J were evaluated as $+21.5 \text{ cm}^{-1}$ for 1 and $+22.8 \text{ cm}^{-1}$ for 2.

Keywords μ -Oxamido-bridge, copper(II)-chromium(III), heterodinuclear complexes, magnetic properties, synthesis

Introduction

The synthesis and magnetic investigations of heterodinuclear complexes propagated by multiatom bridges are of current interest, not only for gaining insight into the pathways of electron transfer in biological systems, but also for obtaining information about designing and

synthesizing molecular-based ferromagnets and for investigating the spin-exchange mechanism between paramagnetic metal ions.¹⁻³ So far, much effort has been devoted to the design of high-spin molecules and several strategies have been proposed along this line.⁴⁻¹⁴ The strict orthogonality of magnetic orbital can be attained by choosing an appropriate combination of paramagnetic metal ions, and hence the design of ferromagnetic complexes based on the concept of strict orthogonality seems promising.^{4,10,11} It is known that a combination of chromium(III) and copper(II) ions can give rise to such strict orthogonality of magnetic orbitals.^{4,10,11} The feasibility of the strategy has been revealed by magnetic analyses for some of copper(II)-chromium(III) complexes.^{4,10,11} However, as far as we are aware, examples of such heteronuclear complexes are still few, comparatively, little attention has been given to the systems in which the chromium(III) and copper(II) ions are propagated by oxamide bridges¹⁵ although the oxamide bridge has been shown to be an excellent multiatom bridge for studying magnetic properties and many polynuclear complexes with bridging oxamide have been synthesized and magnetically characterized.^{8,9,16-21} Taking into account above facts, it is of considerable interest to synthesize and study chromium-(III)-copper(II) polynuclear complexes with bridging oxamide in order to gain some insight into the molecular magnetism of this kind of complexes. In this paper, three new heterometal dinuclear

Received March 7, 2000; accepted October 23, 2000.

Project supported by the Natural Science Foundation of Shandong Province (Q99B12) and the National Natural Science Foundation of China (29873031).

complexes, $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{L})_2](\text{NO}_3)_3$ ($\text{L} = \text{Mephen}, \text{Ph}_2\text{phen}, \text{bpy}$) have been synthesized and characterized by using *N, N'*-bis(3-amino-2,2-dimethylpropyl)oxamidocopper(II) [abbreviated as $\text{Cu}(\text{Me}_2\text{oxpn})$] as bridging ligand and the cryomagnetic properties of the complexes $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{NO}_3)_3$ (**1**) and $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Mephen})_2](\text{NO}_3)_3$ (**2**) have been measured and studied in the temperature range of 4.2–300 K to examine the effect of the oxamido bridge upon the magnetic interaction between copper(II) and chromium(III) ions. The main result of this investigation is that the copper(II) and chromium(III) ions are coupled in a ferromagnetic fashion through the oxamido bridge.

Experimental

Materials

All of the reagents used in the synthesis were of analytical grade. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the terminal ligands, 2,2'-bipyridine (bpy), 5-methyl-1,10-phenanthroline (Mephen), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen) were used as commercially obtained. The starting material $[\text{Cu}(\text{Me}_2\text{oxpn})]$ was synthesized by the literature method.^{8,19}

Synthesis of $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{NO}_3)_3$ (**1**)

To a suspension of $[\text{Cu}(\text{Me}_2\text{oxpn})]$ (0.320 g, 1 mmol) stirred in absolute ethanol (5 mL) were added successively a solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.440 g, 1.1 mmol) in absolute ethanol (10 mL) and a solution of ethyl orthoformate (9 mL). The stirring was continued at room temperature until the mixture became limpid. Then this solution was filtered. To the filtrate was added a methanol solution (20 mL) of Ph_2phen (0.665 g, 2 mmol). The color of the solution turned from violet to dark-brown immediately and a small amount of precipitate formed. After stirring for 8 h, the dark-brown microcrystals were filtered off, washed several times with ethanol, water and diethyl ether and dried over P_2O_5 under reduced pressure. Recrystallization was carried out from DMF/ethanol (1:1) mixture. Yield, 1.076 g (88%), mp, 315.2 °C. Anal. $\text{CrCuC}_{60}\text{H}_{56}\text{N}_{11}\text{O}_{11}$ (M.W. 1222.71). Calcd.: C, 58.94; H, 4.62; N, 12.60; Cu, 5.20; Cr, 4.25. Found: C, 58.82; H,

4.55; N, 12.43; Cu, 5.01; Cr, 4.06.

Synthesis of $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Mephen})_2](\text{NO}_3)_3$ (**2**)

This complex was obtained as brown microcrystals by the same procedure and the same amount of reagents as above but by using Mephen (0.388 g, 2 mmol) instead of Ph_2phen . It was recrystallized from an acetonitrile solution. Yield, 0.757 g (80%), mp, 311.8 °C. Anal. $\text{CrCuC}_{38}\text{H}_{44}\text{N}_{11}\text{O}_{11}$ (M.W. 946.37). Calcd.: C, 48.23; H, 4.69; N, 16.28; Cu, 6.71; Cr, 5.49. Found: C, 48.12; H, 4.75; N, 16.39; Cu, 6.56; Cr, 5.30.

Synthesis of $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{bpy})_2](\text{NO}_3)_3$ (**3**)

This red-brown compound was prepared as described for complex **1**, except that bpy (0.312 g, 2 mmol) was used instead of Ph_2phen . Yield, 0.609 g (70%); mp, 299.1 °C. Anal. $\text{CrCuC}_{32}\text{H}_{40}\text{N}_{11}\text{O}_{11}$ (M.W. 870.27). Calcd.: C, 44.16; H, 4.63; N, 17.70; Cu, 7.30; Cr, 5.97. Found: C, 44.01; H, 4.49; N, 17.55; Cu, 7.14; Cr, 5.72.

Physical measurements

Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. IR spectra were recorded with a NICOLET FT-IR 5DX spectrometer using KBr pellets. The electronic spectra (acetonitrile solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a Shanghai DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. Variable temperature magnetic susceptibilities (4.2–300 K) were measured at the Institute of Physics, Chinese Academy of Sciences, using a vibrating magnetometer Model CF-1 (sensitivity $m = 10^{-4}$ emu.) vibrating sample magnetometer made by Neel Laboratory de CNRS, France. Diamagnetic corrections were made with Pascal's constants²² 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 χ_{M} is the molar magnetic sus-

ceptibility corrected for diamagnetisms of the constituting atoms.

Results and discussion

Syntheses and coordination environment of the binuclear complexes

One of the best strategies to design and synthesize heterometal polynuclear complexes is the use of mononuclear complexes as ligands, *i. e.*, "complex ligands" that contain a metal and can function as ligands to a second metal ion.⁸⁻¹⁸ It is known that complexes *N, N'*-bis-(alkylaminoalkyl)oxamidocopper(II)¹⁶ would be suitable candidates of "complex ligands" because they can coordinate to another metal ion through the oxamido oxygens to afford polynuclear species and the remarkable efficiency of the oxamido bridge to transmit electronic effects between the metal ions, and hence this family of "complex ligands" has played an important role^{8,10,12,16,23,24} in molecular magnetism. In this study, we have adopted this strategy to synthesize Cu(II)-Cr(III) heterodinuclear complexes. For this purpose, mononuclear complex *N, N'*-bis(3-amio-2,2-dimethylpropyl)oxamidocopper(II), [Cu(Me₂oxpn)], was chosen, because it can coordinate to another metal ion through the oxamido oxygens to afford di- and tri-nuclear complexes.^{21,25} Simultaneously, 5-methyl-1,10-phenanthroline (Mephen),

4,7-diphenyl-1,10-phenanthroline (Ph₂phen) and 2,2'-bipyridine (bpy) were used as the terminal ligands, respectively. Indeed, elemental analyses indicate that the reaction of [Cu(Me₂oxpn)] with Cr(NO₃)₃·9H₂O and L (L = Ph₂phen, Mephen, bpy) in ca. 1:1:2 mole ratio yielded the heterodinuclear complexes of the general formula [Cu(Me₂oxpn)Cr(L)₂](NO₃)₃, as expected. These complexes are the first examples of Cu(II)-Cr(III) heterodinuclear complexes bridged by *N, N'*-bis(3-amino-2,2-dimethylpropyl)oxamido-copper(II).

On the basis of the conductivity and room-temperature magnetic measurements, spectroscopic characterization (Table 1) and magnetic analyses (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

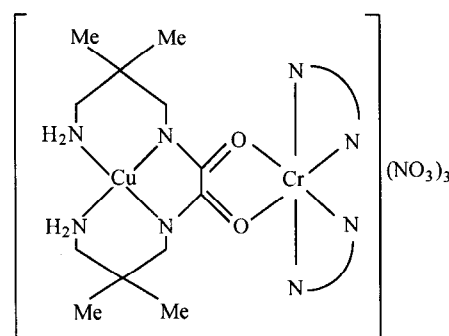


Fig. 1 Plausible coordination environments of the complexes ($\overline{N-N} = \text{Ph}_2\text{phen, Mephen, bpy}$).

Table 1 Physical data for the complexes

Complex	μ_{eff} (B.M.)	Δ_M^a ($\Omega^{-1} \cdot \text{cm}^2/\text{mol}$)	IR (cm^{-1})						UV ν (10^3 cm^{-1})/ ϵ_{max} (L/(mol·cm))			
			$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{N}=\text{C})$	$\nu(\text{Cr}-\text{N})$	$\nu(\text{Cr}-\text{O})$	$\nu(\text{NO}_3^-)$	d-d		CT	
[Cu(Me ₂ oxpn)]			3285	1605					16.5			
1	4.34	398	3285	1640	1540	490	575	1380	18.5 (215)	14.3 (22)	23.5 (18)	29.5 (23500)
2	4.35	405	3285	1658	1535	485	580	1385	18.0 (205)	14.0 (25)	23.7 (20)	29.8 (27500)
3	4.40	402	3285	1650	1532	488	578	1382	18.3 (200)	14.2 (24)	23.8 (21)	29.6 (24800)

1: [Cu(Me₂oxpn)Cr(Ph₂phen)₂](NO₃)₃, 2: [Cu(Me₂oxpn)Cr(Mephen)₂](NO₃)₃, 3: [Cu(Me₂oxpn)Cr(bpy)₂](NO₃)₃.

^a Values for 1×10^{-3} mol/L acetonitrile solution.

Molar conductance and general properties of the dinuclear complexes

All the Cu(II)-Cr(III) dinuclear complexes are

sparingly soluble in water, ethanol, carbon tetrachloride, chloroform and benzene, but soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature. In the solid state all of the complexes are

fairly stable in air so as to facilitate physical measurements. For the three Cu(II)-Cr(III) dinuclear complexes, the molar conductance values (1×10^{-3} mol/L acetonitrile solution) fall in the expected range for 1:3 electrolytes²⁶ (see Table 1), indicating that the three nitrate anions are situated outside the metal coordination sphere. The structure of the dinuclear complexes were further supported on the basis of the spectroscopic characterization and magnetic studies.

Infrared spectra

In order to clarify the mode of bonding, the IR spectra of the mononuclear fragment [Cu(Me₂oxpn)] and the Cu(II)-Cr(III) heterodinuclear complexes were studied and assigned on the basis of a careful comparison of the latter with the former. The most relevant IR absorption bands from the IR spectra of the complexes along with their assignments are shown in Table 1. We will only discuss here selected infrared bands. In the IR spectra of the three dinuclear complexes the carbonyl stretching vibration at 1605 cm⁻¹ for mononuclear fragment [Cu(Me₂oxpn)] is significantly shifted towards higher frequencies (ca. 30–50 cm⁻¹). Therefore, in general, 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 ligands, the amide I band reverts to near its original position (in the protonated species).^{9,16} Although the amide I band is the result of 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 dinuclear complexes is higher than that in the corresponding mononuclear complex, [Cu(Me₂oxpn)]. This shift has often been used as a diagnostic indicator for oxamido-bridged structures.^{9,16} On the other hand, the C=O deformation at 715 cm⁻¹ of the ligand complex, [Cu(Me₂oxpn)], disappeared but the -NH₂ vibration at 3285 cm⁻¹ for mononuclear complex [Cu(Me₂oxpn)] is still present in the spectra of all the dinuclear complexes. These facts may be attributed to the coordination of the carbonyl oxygens in mononuclear fragment [Cu(Me₂oxpn)] to the Cr(III) ion.^{9,23} The coordination mode of the oxamido group has been supported by the crystal structures of analogous complexes.^{17,20} The appearance of a new band at 580–575 cm⁻¹ due to $\nu(\text{Cr}-$

O) further confirms the coordinated nature of the carbonyl oxygens in these dinuclear complexes. Furthermore, the -N=C- stretching vibration for the terminal ligands (bpy, Ph₂phen, Mephen) was found in the corresponding dinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands be coordinated with the Cr(III) ion. The additional band observed at around 485–498 cm⁻¹ due to $\nu(\text{Cr}-\text{N})$ further supports this view. In addition, a strong sharp band centered at 1380 cm⁻¹, typical for a non-coordinated nitrate group²⁷ was observed for all the dinuclear complexes. This is consistent with the conductance data of the dinuclear complexes.

Electronic spectra

The electronic absorption spectral data for these complexes (acetonitrile solutions) are given in Table 1. As shown in Table 1, the electronic spectra of the complexes are similar to each other. For all three dinuclear complexes, three d-d bands in the visible and infrared range are observed (see Table 1). The two weak bands observed in the $(23.5\text{--}23.8) \times 10^3$ cm⁻¹ and $(14.0\text{--}14.3) \times 10^3$ cm⁻¹ regions are due to the ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4A_2 \rightarrow {}^2T_2 + {}^2E$ transitions of Cr(III) and are characteristic of an octahedral configuration around chromium(III),⁷ whilst the strong band at $(18.0\text{--}18.5) \times 10^3$ cm⁻¹ 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 [Cu(Me₂oxpn)] (16.5×10^3 cm⁻¹). Such a blue shift of copper(II) ion in the d-d band may be attributed to the increased ligand field strength for the [CuN₄] chromophore on forming a dinuclear complex with a chromium(III) ion.^{9,28} In addition, a stronger absorption in the short wavelength range (see Table 1) may be attributable to the charge-transfer absorption bands, which may be due to the spin-exchange interaction between the copper(II) and chromium(III) ions through the π -path orbital set up by an oxamido bridge.¹⁶ Further investigation of these and similar systems is required in order to obtain more detailed assignment for charge transfer.

All our efforts to grow crystals of these copper(II)-chromium(III) dinuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, based on the composition of these complexes,

their IR and electronic spectra, conductivity measurements, magnetic studies (*vide infra*) and the crystal structure of analogous complexes,^{17,20} these complexes are proposed to have an oxamido-bridged structure and to contain a chromium(III) ion and a copper(II) ion, which have an octahedral environment and a square-planar environment, respectively, as shown in Fig. 1. The plausible structure is further characterized by the following magnetic study.

Magnetic studies

The observed magnetic moment per dinuclear complex at room temperature, shown in Table 1, is slightly higher than the spin-only value (4.24 B. M.) for the magnetically noninteracting of Cu(II)-Cr(III) ($S_{\text{Cu}} = 1/2$; $S_{\text{Cr}} = 3/2$) heterodinuclear complexes. This suggests a ferromagnetic spin-exchange interaction in these complexes.²⁹ In order to obtain further information on the structure of the complexes, the magnetic data have been used to deduce the indicated binuclear structure. Thus, variable-temperature molar susceptibility (4.2–300 K) data were collected for complexes [Cu(Me₂oxpn)Cr(Ph₂phen)₂](NO₃)₃ (**1**) and [Cu(Me₂oxpn)Cr(Mephen)₂](NO₃)₃ (**2**) and the results are shown in Fig. 2 in the form of plots of χ_{M} vs. T and μ_{eff} vs. T , where χ_{M} , μ_{eff} and T denote molar susceptibility, effective magnetic moment and absolute temperature, respectively. From Fig. 2 it is evident that the magnetic behaviors of the two complexes are similar. As the temperature is lowered, the effective magnetic moments increasing gradually from 4.34 B. M. for **1** and 4.35 B. M. for **2** at 300 K, reach a maximum value of 4.85 B. M. at 14.6 K for **1** and 4.87 B. M. at 15.1 K for **2**, and then sharply decrease to 4.35 B. M. (**1**) and 4.37 B. M. (**2**) at 4.5 K. The maximum values (4.85 and 4.87 B. M.) are comparable to the spin-only value 4.90 B. M. for the spin-state $S = 2$, which should arise from a ferromagnetic spin-coupling of the spin system Cr(III)-Cu(II) ($S_{\text{Cr}} = 3/2$, $S_{\text{Cu}} = 1/2$). Thus, the observed magnetic behavior clearly demonstrates a ferromagnetic spin-exchange interaction between copper(II) and chromium(III) ions through the oxamido-bridge within the each dinuclear unit.¹¹ This is consistent with

the room-temperature magnetic moment data of the complexes. The rapid decrease of the magnetic moments at very low temperature may be attributed to an intermolecular antiferromagnetic interaction. In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic analysis for the complexes was carried out with the susceptibility Eq. (1) which includes a parameter θ to correct for the contribution from an intermolecular magnetic interaction based on the Heisenberg spin-exchange operator $\hat{H} = -2\hat{J}\hat{S}_1 \cdot \hat{S}_2$.

$$\chi_{\text{M}} = \frac{N\beta^2 g^2}{k(T - \theta)} \left[\frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT)} \right] + N\alpha \quad (1)$$

where each symbol has its usual meaning. As shown in Fig. 2, good least-square fits to the experimental data were attained with Eq. (1). The magnetic parameters thus determined are $J = +21.5 \text{ cm}^{-1}$, $g = 2.01$, $\theta = -0.71 \text{ K}$, $N\alpha = 100 \times 10^{-6} \text{ cm}^3/\text{mol}$ for **1**, and $J = +22.8 \text{ cm}^{-1}$, $g = 2.00$, $\theta = -0.75 \text{ K}$, $N\alpha = 100 \times 10^{-6} \text{ cm}^3/\text{mol}$ for **2**. The agreement factors F , defined here as $F = \sum [(\chi_{\text{M}})_{\text{obs.}} - (\chi_{\text{M}})_{\text{calcd.}}]^2 / (\chi_{\text{M}})_{\text{obs.}}$, are then equal to 1.7×10^{-5} (**1**), 2.8×10^{-5} (**2**), respectively. The results have confirmed that the spin coupling between chromium(III) and copper(II) ions through an oxamido-bridge is ferromagnetic. The ferromagnetic spin-exchange interaction between chromium(III) and copper(II) ions within the each complex may be explained by several models which have so far been proposed.³⁰⁻³² According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise antiferromagnetic coupling ($J < 0$) should be involved in the system. For the present complexes, if the whole molecular symmetry is considered to be C_{2v} , the 3d metallic orbitals of copper(II) and chromium(III) ions transform³³ as $a_1(d_x^2 \text{ and } d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{zx})$. Around the copper(II) ion, there is just one unpaired electron which occupies the b_1 orbital, and around chromium(III) there are three unpaired electrons which populate the a_1 , a_2 and b_2 orbitals. According to group theory, because there is no orbital interaction to be feasible between the magnetic orbitals of the metal centers, namely $\langle b_1 | a_1 \rangle = 0$, $\langle b_1 | a_2 \rangle = 0$, $\langle b_1 | b_2 \rangle = 0$, hence, the ferromagnetic exchange interactions should be observed in the complexes.

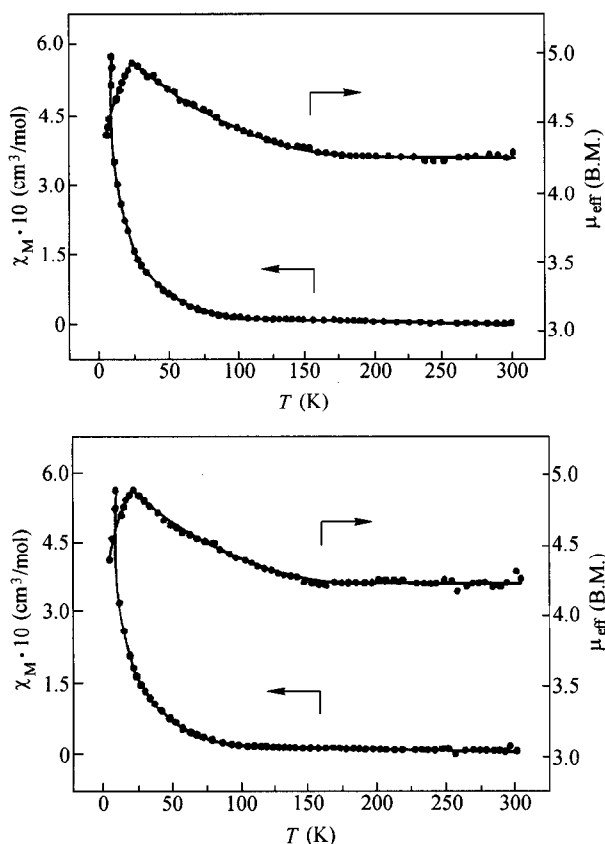


Fig. 2 Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complexes $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{NO}_3)_3$ (**1**) and $[\text{Cu}(\text{Me}_2\text{oxpn})\text{Cr}(\text{Mephen})_2](\text{NO}_3)_3$ (**2**). The curves are based on Eq. (1) using the parameters given in the text. (●), experimental data; (—) (calculation curves as described in the text.

References

- Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F., *Molecular Magnetic Materials*, Ed. NATO ASI Series, Kluwer, Dordrecht, **1991**.
- Kahn, O., *Molecular Magnetism*, **1993**, New York, Verlag-Chemie.
- Iwamura, H.; Miller, J. S. *Proceedings of the Symposium on Chemistry and Physics of Molecular Based Magnetic Materials: Molecular Crystals and Liquid Crystals*, **1993**, p. 232.
- Journaux, Y.; Kahn, O.; Zarembowitch, J.; Galy, J.; Jaud, J. *J. Am. Chem. Soc.* **1983**, *105*, 7585.
- Kahn, O. *Struct. Bond.* (Berlin), **1987**, *68*, 89.
- Lloret, F.; Nakatani, K.; Journaux, Y.; Kahn, O.; Yu, P.; Renard, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 642.
- Yu, P.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100.
- Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 4063.
- Li, Y. T.; Liao, D. Z.; Jiang, Z. H.; Wang, G. L. *Polyhedron*, **1995**, *14*, 2209.
- Yu, P.; Kahn, O.; Nakatani, K.; Codjovi, E.; Mathoniere, C.; Sletten, J. *J. Am. Chem. Soc.* **1991**, *113*, 6558.
- Zhuong, J. Z.; Okawa, H.; Matsumoto, N.; Sakiyama, H.; Kida, S. *J. Chem. Soc. Dalton Trans.*, **1991**, 479.
- Lloret, F.; Julve, M.; Ruiz, R.; Journaux, Y.; Nakatani, K.; Kahn, O.; Sletten, J. *Inorg. Chem.* **1993**, *32*, 27.
- Ohba, M.; Tamaki, H.; Matsumoto, N.; Okawa, H. *Inorg. Chem.* **1993**, *32*, 5383.
- Cortes, R.; Urriaga, M. K.; Lezama, L.; Isabel, M.; Rojo, T. *Inorg. Chem.* **1994**, *33*, 829.
- Li, Y. T.; Yan, C. W.; Miao, S. H.; Liao, D. Z. *Polyhedron* **1998**, *15*, 2491.
- Ojima, H.; Nonoyama, K. *Coord. Chem. Rev.* **1988**, *92*, 85.
- Zhang, Z. Y.; Liao, D. Z.; Jiang, Z. H.; Hao, S. Q.; Yao, X. K.; Wang, H. G.; Wang, G. L. *Inorg. Chim. Acta*, **1990**, *173*, 201.
- Liao, D. Z.; Li, L. C.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Trans. Met. Chem.* **1992**, *17*, 356.
- Ma, S. L.; Jiang, Z. H.; Liao, D. Z.; Yan, S. P.; Wang, G. L. *Polyhedron*, **1993**, *12*, 1523.
- Mathoniere, C.; Kahn, O.; Daran, J.-C.; Hilbig, H.; Kohler, H. *Inorg. Chem.* **1993**, *32*, 4057.
- Benelli, C.; Fabretti, A. C.; Giusti, A. *J. Chem. Soc., Dalton Trans.* **1993**, 409.
- Selwood, P. W. *Magnetochemistry*, Intersciences, New York, **1956**, pp. 78—79.
- Lloret, F.; Journaux, Y.; Julve, M. *Inorg. Chem.* **1990**, *29*, 3967.
- Ribas, J.; Costa, R.; Journaux, Y.; Mathoniere, C.; Kahn, O.; Gleizes, A. *Inorg. Chem.* **1990**, *29*, 2042.
- Ribas, J.; Garcia, A.; Monfort, M. *Polyhedron* **1991**, *11*, 103.
- Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley, New York, **1986**.
- Sakamoto, M.; Takagi, M.; Ishimori, T.; Okawa, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1613.
- Lambert, S. L.; Spiro, C. L.; Gagne, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1982**, *21*, 68.
- Dance, I. G. *Inorg. Chim. Acta* **1974**, *9*, 77.
- Hay, P. J.; Thibeault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
- Kahn, O.; Charlot, M. F. *Nouv. J. Chem.* **1980**, *4*, 567.
- Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.

(E200003049 JIANG, X.H.; DONG, L.J.)