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Synthesis, Characterization and Ferromagnetic Spin-Coupling Between Chromium(III) and Copper(II) Ions in Oxamido Bridged Cu(II)–Cr(III) Dinuclear Complexes

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Four new heterodinuclear copper(II)–chromium(III) complexes bridged by dianions of N,N′-oxamidobis(propionato)cuprate [Cu(obp)] and end-capped with 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (NO_2-phen), 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen); namely $[Cu(obp)Cr(L)_2]NO_3$ (L = phen, NO_2-phen, Cl-phen, Br-phen), have been synthesized and characterized by elemental analyses, IR and electronic spectra studies, magnetic moments at room-temperature and molar conductivity measurements. It is proposed that these complexes have extended oxamido-bridged structures consisting of a copper(II) ion and a chromium(III) ion, which have a square-planar environment and an octahedral environment, respectively. The magnetic susceptibility of $[Cu(obp)Cr(phen)_2]NO_3$ complex was measured between 4.2–300 K and the magnetic analysis was studied in detail, demonstrating the operation of a ferromagnetic interaction between the adjacent chromium(III) and copper(II) ions through the oxamido-bridge within the complex. Based on spin Hamiltonian, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, the exchange integral (J) was evaluated as $+12.8\ cm^{-1}$.

Key words: oxamido-bridge, copper(II)–chromium(III), heterodinuclear complexes, ferrromagnetic spin-coupling, synthesis

The syntheses and magnetic investigations of ferromagnetic polynuclear metal complexes are of current interest [1,2], not only for gaining some insights into the electronic and geometric structure of metalloproteins and enzymes and thus correlating structure with biological function, but also for understanding fundamental factors governing the magnetic properties of transition-metal complexes and to find appropriate systems applicable as building units for the design of molecular-based ferromagnets. So far, much effort has been devoted to the design of high-spin molecules and several strategies have been proposed along this line [3–6]. Recently, Kahn pointed out that accidental orthogonality and strict orthogonality of magnetic orbitals may give rise to a ferromagnetic spin coupling between neighbouring paramagnetic metal ions [4]. The former depends on some structural factors in a subtle manner. It appears that the accidental orthogonality of magnetic orbitals is hardly applied for the

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design of ferromagnetic complexes, because of difficulties in finding the optimum structural conditions for it to occur and, in particular, in materializing such steric conditions in designed metal complexes. The strict orthogonality of magnetic orbitals, on the other hand, can be attained by choosing an appropriate combination of paramagnetic metal ions, and hence the design of ferromagnetic complexes based on this principle seems promising [3,6]. It is known that a combination of chromium(III) and copper(II) ions can give rise to such a strict orthogonality of magnetic orbitals [3,6]. The feasibility of this strategy has been revealed by magnetic analyses of some of copper(II)–chromium(III) complexes [3,6]. However, as far as we are aware, examples of such heteronuclear complexes are still few and comparatively little attention has been given to the systems, in which the chromium(III) and copper(II) ions are propagated by oxamide bridges [7], although the oxamide bridge has been shown to be an excellent multi-atom bridge for studying magnetic properties. Many polynuclear complexes with bridging oxamide groups have been synthesized and magnetically characterized [5,7–9]. Taking into account the above facts, it is of considerable interest to synthesize and study chromium(III)-copper(II) polynuclear complexes with bridging oxamide groups in order to gain some insight into the molecular magnetism of this kind of complexes.

In this paper, four new heterodinuclear Cu(II)–Cr(III) complexes described by the overall formula $[Cu(obp)Cr(L)_2]NO_3$ (L = phen, NO_2-phen, Cl-phen, Br-phen) have been synthesized and characterized by using sodium N,N′-oxamidobis(propionato)cuprate(II), $Na_2[Cu(obp)]\cdot 3.5H_2O$, as bridging ligand and the cryomagnetic properties of the $[Cu(obp)Cr(phen)_2]NO_3$ complex has been measured between 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. $Cr(NO_3)_3\cdot 9H_2O$ and the terminal ligands 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (NO_2-phen), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen) (analytical grade) were purchased from the Beijing Chemical Company. The starting material $Na_2[Cu(obp)]\cdot 3.5H_2O$ was synthesized as previously described [9].

Synthesis of $[Cu(obp)Cr(phen)_2]NO_3$ (1): To a solution of $Na_2[Cu(obp)]\cdot 3.5H_2O$ (0.369 g, 1 mmol) stirred in absolute methanol (10 mL) was added successively a solution of $Cr(NO_3)_3\cdot 9H_2O$ (0.440 g, 1.1 mmol) in absolute methanol (10 mL) and a solution of ethyl orthoformate (9 mL). To the resulting clear solution was added an absolute methanol solution (20 mL) of phen (0.364 g, 2 mmol). The color of the solution turned from violet to dark-brown immediately, and the mixture was subsequently refluxed for 8 h. After cooling to room temperature, dark-brown microcrystals thus formed were collected by suction filtration, washed several times with methanol, water and diethyl ether and dried over P_2O_5 under reduced pressure. Recrystallization was carried out from a DMF/ethanol (1:2) mixture. Yield, 0.575 g (75%), mp, 211.8°C.

Synthesis of $[Cu(obp)Cr(NO_2\text{-phen})_2]NO_3$ (2): This complex was obtained as brown microcrystals by the same procedure and the same amount of reagents as above but using NO_2-phen (0.450 g, 2 mmol) instead of phen. It was recrystallized from a MeCN solution. Yield, 0.753 g (88%), mp, 285.0°C.

Synthesis of [Cu(obp)Cr(Cl-phen)$_2$]NO$_3$ (3): This complex was obtained as a pale-red power by the same procedure and the same amounts of reagents as above but using Cl-phen (0.429 g, 2 mmol) instead of phen. Yield, 0.685 g (82%); mp, 287.9°C.

Synthesis of [Cu(obp)Cr(Br-phen)$_2$]NO$_3$ (4): This light-brown compound was prepared as described for complex **(1)**, except that Br-phen (0.518 g, 2 mmol) was used instead of phen. Yield, 0.721 g (78%); mp, 307.4°C.

Elemental analyses confirmed the compositions indicated.

Physical measurements: Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were determined 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 solutions) 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 Hg[Co(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 constants [10] 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 diamagnetism of the constituting atoms.

RESULTS AND DISCUSSION

Synthetic route and coordination environment of the dinuclear complexes: Two synthetic strategies are generally available for the preparation of discrete heterodinuclear complexes. The first is to use a heterodinucleating 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 [5–8]. In this study, our purpose was to obtain Cu(II)–Cr(III) heterodinuclear 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)]·3.5H$_2$O, which was first used to prepare alternating Cu(II)-Mn(II) bimetallic chain compound MnCu(obp)(H$_2$O)$_3$·H$_2$O [9], as a bidentate mononuclear fragment, because it can coordinate to another metal ion through the oxamido oxygens and the remarkable efficiency of the oxamidate bridge to transmit electronic effects between the metal ions. Simultaneously, 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (NO$_2$-phen), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen), respectively, were used as terminal ligands. Indeed, elemental analyses indicate that the reaction of Na$_2$[Cu(obp)]·3.5H$_2$O with Cr(NO$_3$)$_3$·9H$_2$O and L (L = phen, NO$_2$-phen, Cl-phen, Br-phen) in *ca.* 1:1:2 mole ratio yielded the heterodinuclear complexes of the general formula [Cu(obp)Cr(L)$_2$]NO$_3$, as expected. These complexes are the first examples of Cu(II)–Cr(III) heterodinuclear complexes bridged by N,N′-oxamidobis(propionato)cuprate(II). On the basis of the conductivity and room temperature magnetic measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

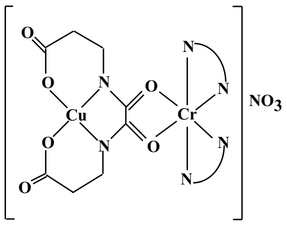

Figure 1. Plausible coordination environments of the complexes ($\widehat{N\,N}$ = phen, NO_2-phen, Cl-phen, Br-phen).

Molar conductance and general properties of the dinuclear complexes: All of the Cu(II)–Cr(III) dinuclear complexes are sparingly soluble in water, methanol, ethanol, carbon tetrachloride, chloroform and benzene; but are 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, facilitating physical measurements. For the four Cu(II)–Cr(III) dinuclear complexes, the molar conductance values (1×10^{-3} mol L^{-1} acetonitrile solutions) fall in the expected range for 1:1 electrolytes [11] (see Table 1), indicating that the nitrate anion is situated outside the metal coordination sphere. The structure of the dinuclear complexes was further supported by the spectroscopic characterization and magnetic studies.

Infrared spectra: Since the IR spectra of the four binuclear complexes are similar, the discussion is confined to the most important vibrations of 200~4000 cm^{-1} region to the structure. 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. The carbonyl stretching vibration at 1610 cm^{-1} for $Na_2[Cu(obp)]\cdot3.5H_2O$ is considerably shifted towards higher frequencies (*ca*. 30~50 cm^{-1}) in the dinuclear complexes. Therefore, when the deprotonated amide nitrogen is coordinated to the metal ion, its amide I band shifts considerably towards lower wave numbers. In the case of an oxamide dianion coordinated to two metal ions as bridging ligands, the amide I band reverts to near its original position (in the protonated species) [8]. Although the amide I is due to a composite N–C=O vibration, it can essentially be seen as υ(C=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 $Na_2[Cu(obp)]\cdot3.5H_2O$. This shift has often been used as a diagnostic indicator for oxamido-bridged structures [8]. On the other hand, the C=O deformation at 728 cm^{-1} of the ligand complex, $Na_2[Cu(obp)]\cdot3.5H_2O$, disappeared in the spectra of the dinuclear complexes. This may be attributed to the coordination of the carbonyl oxygens to the Cr(III) ion [7,9]. The coordination mode of the oxamido group has been supported by the crystal structure of an analogous complex [9]. The appearance of a new band at 580–590 cm^{-1}, due to ν(Cr–O), further confirms the coordinated nature of the carbonyl oxygens in these dinuclear complexes. In addition, 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 in the mononuclear complex is not coordinated with the chromium(III) ion.

Table 1. Physical data for the complexes.

Complex	μ_{eff}	Λ_M^a	IR (cm^{-1})						UV $\nu(10^3\ cm^{-1})/\varepsilon_{max}(mol^{-1}\ cm^{-1}L)$			
	(B.M.)	($\Omega^{-1}\ cm^2\ mol^{-1}$)	$\nu(CO_2^-)$	ν(C=O)	ν(N=C)	ν(Cr-N)	ν(Cr-O)	$\nu(NO_3^-)$	d-d			CT
$Na_2[Cu(obp)]$			1575(s)	1610(vs)					16.8			
(1)	4.37	150	1575(s)	1640(vs)	1528(s)	492(w)	590(w)	1380(s)	18.4 (218)	14.0 (18)	23.2 (12)	30.1 (21700)
(2)	4.45	152	1575(s)	1658(vs)	1530(s)	480(w)	586(w)	1385(s)	18.2 (215)	14.1 (12)	24.0 (23)	29.0 (24500)
(3)	4.40	145	1575(s)	1650(vs)	1535(s)	488(w)	580(w)	1382(s)	18.0 (220)	14.2 (25)	23.0 (15)	30.5 (24800)
(4)	4.42	148	1575(s)	1660(vs)	1520(s)	485(w)	582(w)	1380(s)	18.3 (210)	14.0 (30)	23.5 (28)	30.0 (21500)

(1): $[Cu(obp)Cr(phen)_2]NO_3$, **(2):** $[Cu(obp)Cr(NO_2\text{-}phen)_2]NO_3$, **(3):** $[Cu(obp)Cr(Cl\text{-}phen)_2]NO_3$,
(4): $[Cu(obp)Cr(Br\text{-}phen)_2]NO_3$.

[a] Values for 1×10^{-3} mol dm^{-3} acetonitrile solution, s = strong, vs = very strong, w = weak.

Furthermore, the –N=C– stretching vibration for the terminal ligands (phen, NO_2-phen, Cl-phen, Br-phen) were found in the corresponding dinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands are coordinated with the Cr(III) ion. The additional band, observed at around 480–492 cm^{-1} due to ν(Cr–N), further supports this view. Besides these observations, a strong sharp band centered at 1380 cm^{-1}, typical for a non-coordinated nitrate group [12] was observed for all the dinuclear complexes. This is consistent with the conductance data of the dinuclear complexes.

Electronic spectra: In order to clarify the mode of bonding, the electronic spectra of the mononuclear fragment $Na_2[Cu(obp)]\cdot 3.5H_2O$ and the Cu(II)–Cr(III) heterodinuclear complexes were studied and assignment were made on the basis of a careful comparison of the latter with the former. The electronic absorption spectral data for these complexes (acetonitrile solutions) are given in Table 1. As shown in this table, the electronic spectra of the four complexes are similar to each other. For all four dinuclear complexes, three d-d bands in the visible and infrared range are observed (see Table 1). The two weak bands observed in the $(23.0\sim24.0) \times 10^3$ cm^{-1} and $(14.0\sim14.2) \times 10^3$ 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) [13], whilst the strong band at $(18.0\sim18.4)\times10^3$ 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 (16.8×10^3 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 $[CuN_2O_2]$ chromophore on forming a dinuclear complex with a chromium(III) ion [14]. In addition, a stronger absorption in the short wave length range (see Table 1) may be attributed 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 [8]. Further investigations of these and similar systems are 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 an analogous complex [9], these complexes are proposed to have an extended 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 Figure 1. The plausible structure is further illustrated by the following magnetic study.

Magnetic properties of $[Cu(obp)Cr(phen)_2]NO_3$: 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 non-interacting of Cu(II)–Cr(III) ($S_{Cu} = 1/2$, $S_{Cr} = 3/2$) heterodinuclear complexes. This suggests the operation of ferromagnetic spin-exchange interaction in these complexes [7,15]. 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 the complex $[Cu(obp)Cr(phen)_2]NO_3$, by way of example, and the results are shown in Figure 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 Figure 2 it is evident that the magnetic moments are increasing gradually from 4.37 B.M. at 300 K, reach a maximum value of 4.86 B.M. at *ca.* 18.5 K, and then sharply decrease to 4.39 B.M. at 4.3 K. The maximum value (4.86 B.M.) is comparable to the spin-only value 4.90 B.M., for the spin-state S = 2, which should arise from ferromagnetic spin-coupling of the spin system Cr(III)–Cu(II) ($S_{Cr} = 3/2$, $S_{Cu} = 1/2$). Thus, the observed magnetic behavior clearly demonstrates the operation of a ferromagnetic spin-exchange interaction between copper(II) and chromium(III) ions through the oxamido-bridge within the dinuclear unit [7]. This is consistent with the room-temperature magnetic moment data of the complex. 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, a magnetic analysis of the complex was carried out with the susceptibility equation (1), which includes a parameter θ to correct for the contribution from an intermolecular magnetic interaction based on the Heisenberg spin-exchange operator ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$),

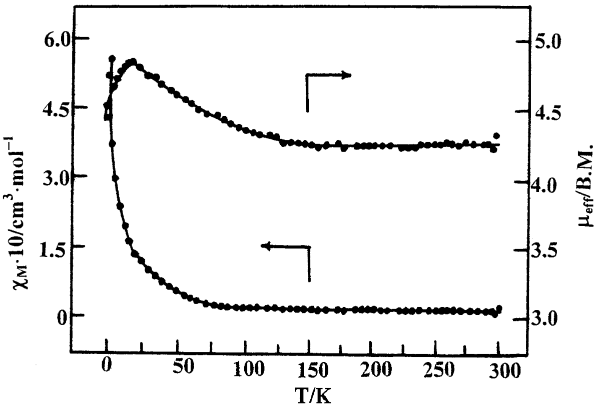

Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complex $[Cu(obp)Cr(phen)_2]NO_3$. The curves are based on equation (1) using the parameters given in the text. (•), experimental data; (–), calculation curves as described in the text.

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

where each symbol has its usual meaning. As indicated by the traces in Figure 2, a good least-square fitting to the experimental data is attained with (1) using the magnetic parameters $J = +12.8\ cm^{-1}$, $g = 2.00$, $\theta = -0.15$ K, and $N\alpha = 100 \times 10^{-6}\ cm^3\ mol^{-1}$. The agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$, is then equal to 1.98×10^{-5}. This result has 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 molecule may be explained by several models, which have so far been proposed [16,17]. According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise antiferromagnetic coupling ($J < 0$) should be involved in the system. On the basis of the crystal structure of complex [9], that is analogous to 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 transform [18] as $a_1(d_{z^2}$ 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 point group theory, because there is no orbital interaction 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, ferromagnetic exchange interactions should be observed in the complex.

Acknowledgments

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