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Synthesis of Ferromagnetic $Cu_3^{II}Cr^{III}$-Type Heterotetranuclear Complexes with Oxalato Bridges

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Three new μ-oxalato-bridged$Cu_3^{II}Cr^{III}$-type heterotetranuclear complexes have been synthesized and identified as: $[Cu_3Cr(ox)_3(phen)_3](ClO_4)_3$ **(1)**, $[Cu_3Cr(ox)_3(Me_2phen)_3](ClO_4)_3$ **(2)** and $[Cu_3Cr(ox)_3(NO_2phen)_3](ClO_4)_3$ **(3)**, where ox represents the oxalato dianions; phen, Me_2phen and NO_2phen represent 1,10-phenanthroline; 2,9-dimethyl-1,10-phenanthroline or 5-nitro-1,10-phenanthroline respectively. These complexes are the first examples of $[Cu_3^{II}Cr^{III}]$ species bridged by oxalato groups. The three complexes have not yet been isolated in crystalline form suitable for X-ray structure analysis, but based on elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR, ESR and electronic spectral studies, these complexes are proposed to have oxalato-bridged structure consisting of three copper(II) ions and a chromium(III) ion, in which the chromium(III) ion has an octahedral environment, and the three copper(II) ions have a square-planar environment. Variable temperature magnetic susceptibility (4.2~300 K) measurements and studies of the complexes **(1)** and **(2)** revealed the occurrence of an intramolecular ferromagnetic interaction between the copper(II) and chromium(III) ions through the oxalato-bridge within each molecule. The magnetic data have been also used to deduce the indicated μ-oxalato-bridged $[Cu_3^{II}Cr^{III}]$ tetranuclear structure. On the basis of the spin Hamiltonian operator, $\hat{H} = -2J(\hat{S}_{Cu1}\cdot\hat{S}_{Cr} + \hat{S}_{Cu2}\cdot\hat{S}_{Cr} + \hat{S}_{Cu3}\cdot\hat{S}_{Cr})$, the magnetic analyses were carried out for the two Cu^{II}–Cr^{III} heterotetranuclear complexes and the spin-coupling constants (J) were evaluated as $+10.97\ cm^{-1}$ for **(1)** and $+9.28\ cm^{-1}$ for **(2)**, indicating that the bridging oxalato would be able to transmit ferromagnetic interaction in the strict orthogonality $[Cu_3^{II}Cr^{III}]$ tetranuclear system.

Key words: oxalato-bridge, copper(II), chromium(III), heterotetranuclear complexes, ferromagnetism

The studies on synthesis and magnetic investigations of ferromagnetic heteropolynuclear complexes containing different paramagnetic centers have been an active field of research. Interest in this area is fundamental requirement, 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 [1–4].

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Owing to their fundamental importance in the synthesizing molecular-based ferromagnets, so far, much effort has been devoted to the design and synthesis of high-spin molecules and several strategies have been proposed along this line [5–14]. Among other more elaborate strategies employed in the design of high-spin molecules, based on the concept of strict orthogonality of magnetic orbitals, which can be attained by choosing an appropriate combination of paramagnetic metal ions, seems promising in the design of ferromagnetic polynuclear complexes [8]. It is known that a combination of copper(II) and chromium(III) ions can give rise to such a strict orthogonality of magnetic orbitals [9,10]. The feasibility of this strategy has been revealed by magnetic analyses of some copper(II)–chromium(III) complexes [9,10,14]. However, as far as we are aware, examples of such heteronuclear complexes are still few, and to the best of our knowledge no $Cu_3^{II}Cr^{III}$-type heterotetranuclear complex with oxalato-bridge has been reported. Taking into account the above facts, it is of considerable interest to synthesize $Cu_3^{II}Cr^{III}$-type complexes with bridging oxalato in order to know whether the bridging oxalato would be able to transmit ferromagnetic interaction in a system showing strict orthogonality like the $[Cu_3^{II}Cr^{III}]$ one.

In this work detailed here three new μ-oxalato-bridged $Cu_3^{II}Cr^{III}$-type heterotetranuclear complexes formulated $[Cu_3Cr(ox)_3L_3](ClO_4)_3$ (ox = oxalate dianions, L = phen, Me_2phen, NO_2phen) have been synthesized and characterized by using potassium tris(oxalato)chromium(III) trihydrate ($K_3[Cr(ox)_3]\cdot 3H_2O$), as a polyatomic bridging ligand and the cryomagnetic properties of the $[Cu_3Cr(ox)_3(phen)_3](ClO_4)_3$ **(1)** and $[Cu_3Cr(ox)_3(Me_2phen)_3](ClO_4)_3$ **(2)** complexes were studied in detail. The main result of this investigation is that the copper(II) and chromium(III) ions are coupled in a ferromagnetic fashion *via* isotropic coupling ($J = +10.97$ cm^{-1} for **(1)** and $J = +9.28$ cm^{-1} for **(2)**) through the oxalato bridge. At present, the three $[Cu_3^{II}Cr^{III}]$ tetranuclear complexes have not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic studies and spectral data clearly demonstrates the presence of exchange coupling between the metal ions, reveals certain electronic properties of these $[Cu_3^{II}Cr^{III}]$ tetranuclear complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Potassium tris(oxalato)-chromium(III) trihydrate ($K_3[Cr(ox)_3]\cdot 3H_2O$) and $Cu(ClO_4)_2\cdot 6H_2O$ were synthesized according to the literature [15] method. The terminal ligands: 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (Me_2phen) or 5-nitro-1,10-phenanthroline (NO_2phen) were used as commercially obtained.

Synthesis of $[Cu_3Cr(ox)_3(phen)_3](ClO_4)_3$ (1): To a 20 mL solution stirred water of $Cu(ClO_4)_2\cdot 6H_2O$ (3.1 mmol, 1149 mg) was added successively dropwise a methanol solution (20 mL) of phen (3.0 mmol, 541 mg). The vigorous stirring was continued at room temperature until the mixture became limpid (about 30 minutes). It was then filtered to eliminate impurities. To the filtrate (containing the $[Cu(phen)(H_2O)_2](ClO_4)_2$ precursor) was slowly added a water solution (15 mL) of $K_3[Cr(ox)_3]\cdot 3H_2O$ (1.0 mmol, 491.3 mg) with a rapid stirring. The colour of the solution turned from blue to violet-red immediately and a small amount of precipitate formed. After refluxing for *ca.* 3 h, the mixture was then allowed to cool to room temperature and the violet-red microcrystals thus obtained were removed by filtration, washed several times with methanol, water and diethyl ether and dried over P_2O_5 under reduced pressure. It was recrystallized from a hot acetonitrile/ethanol (1:2) mixture. Yield, 955.4 mg (71%); m.p. 335.6°C. Anal. calc. for $Cu_3CrC_{42}H_{24}N_6O_{24}Cl_3$ (M.W. 1345.67): C, 37.49; H, 1.80; N, 6.25; Cr, 3.86; Cu, 14.17%. Found: C, 37.26; H, 1.72; N, 6.01; Cr, 3.63; Cu, 13.89%.

Synthesis of $[Cu_3Cr(ox)_3(Me_2phen)_3](ClO_4)_3$ (2): This complex was obtained as red-brown microcrystals by the same procedure as above, but by using Me_2phen instead of phen. Recrystallization was carried out from DMF/ethanol (1:3) mixture. Yield, 1072.4 mg (75%); m.p. 319.3°C. Anal. calc. for $Cu_3CrC_{48}H_{36}N_6O_{24}Cl_3$ (M.W. 1429.83): C, 40.32; H, 2.54; N, 5.88; Cr, 3.64; Cu, 13.33%. Found: C, 40.10; H, 2.75; N, 5.64; Cr, 3.42; Cu, 13.16%.

Synthesis of $[Cu_3Cr(ox)_3(NO_2phen)_3](ClO_4)_3$ (3): This complex was prepared as orange-red powder in a manner similar to the synthesis of the complex **(1)** except that NO_2phen instead of phen was used. Yield, 962.4 mg (65%); m.p. 290.2°C. Anal. calc. for $Cu_3CrC_{42}H21N_9O_{30}Cl_3$ (M.W. 1480.66): C, 34.07; H, 1.43; N, 8.51; Cr, 3.51; Cu, 12.88%. Found: C, 34.23; H, 1.21; N, 8.27; Cr, 3.29; Cu, 12.65%.

Measurements: Analyses for C, H and N were carried out on a Perkin-Elmer elemental analyzer model 240. Metal contents were determined on an ICP-4300 isoionic emission spectrophotometer. The infrared spectra were recorded with a Nicolet FT-IR spectrophotometer model 470 in KBr pellets. The electronic spectra (DMF solution) were measured on a Cary 300 spectrophotometer. ESR spectra were recorded with a JES-FEIXG ESR apparatus using an X-band and Mn-reference. Molar conductances were measured (DMF solution) with a DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using $Hg[Co(SCN)_4]$ as a calibrant. 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 using 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.

RESULTS AND DISCUSSION

Synthetic route and coordination environment of the $[Cu_3^{II}Cr^{III}]$ complexes: The design and synthesis of heteropolymetallic complexes has for a long time been a challenging field for coordination chemists owing to the relative difficulty of synthesizing new compounds. In general, two synthetic strategies are available for the preparation of heterometallic complexes. The first is to use designed polynucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions [17]. The second uses a complex as a "ligand" that contains a potential donor group capable of coordinating to another metal ion [18]. In this study, our aim was to obtain oxalato-bridged $[Cu_3^{II}Cr^{III}]$ heterotetranuclear complexes; therefore, this synthetic method was adopted. For this purpose, mononuclear fragment potassium tris(oxalato)chromium(III) trihydrate, $K_3[Cr(ox)_3]\cdot 3H_2O$, was selected as "ligand complex", because (i) it can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes, (ii) $K_3[Cr(ox)_3]\cdot 3H_2O$ plays the key role in producing oxalato-bridged $[Cu_3^{II}Cr^{III}]$ heterotetranuclear complexes, since chromium(III) ion generally leads to ill characterized materials contaminated by the precipitation of $Cr(OH)_3$ rather than the corresponding complexes. In order to avoid this, in our synthetic approach to oxalato-bridged $[Cu_3^{II}Cr^{III}]$ heterotetranuclear complexes, the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$ was used as the chromium(III)-site component. Simultaneously, 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (Me_2phen) or 5-nitro-1,10-phenanthroline (NO_2phen) were used as the terminal ligands. Indeed, the elemental analyses and physical data (see Tables 1 and 2) for the newly prepared complexes indicate that the reaction of $K_3[Cr(ox)_3]\cdot 3H_2O$ with $Cu(ClO_4)_2\cdot 6H_2O$ and the terminal ligand L (L = phen, Me_2phen, NO_2phen) in *ca*. 1:3:3 mole ratio yielded the heterotetranuclear complexes of the general formula $[Cu_3Cr(ox)_3L_3](ClO_4)_3$, as expected. These complexes are the first examples of $[Cu^{II}_3Cr^{III}]$ species bridged by potassium tris(oxalato)chromium(III). On the basis of the molar conductivity, room-temperature magnetic moment measurements, spectroscopic (IR, UV and ESR) characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

General properties of the tetranuclear complexes: These heterotetranuclear complexes are more soluble in acetonitrile, DMF and DMSO giving stable solutions at room temperature, whereas they are moderately soluble in methanol and acetone, and practically insoluble in carbon tetrachloride, chloroform and benzene. In the solid state all the complexes are fairly stable in air so as to allow physical measurements. For the three tetranuclear complexes, the observed molar conductance values (212~235 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) in DMF solution at 25°C are given in Table 1. These values are indicative of 1:3 electrolytic nature [19], in accord with the presumed structure of the tetranuclear complexes shown in Fig. 1. The $[Cu^{II}_3Cr^{III}]$ heterotetranuclear structure was further characterized by the following results.

IR spectra: In order to clarify the mode of bonding, the IR spectra of the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$ and the Cu^{II}–Cr^{III} heterotetranuclear complexes were studied and assigned on the basis of a careful comparison of the latter with the former. Since the IR spectra of all the three heterotetranuclear complexes are similar, discussion is confined to the most important vibration in 400~4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands of the tetranuclear complexes and the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$, together with their assignments are given in Table 1. It is noteworthy that the spectrum of the mononuclear complex $K_3[Cr(ox)_3]\cdot 3H_2O$ shows a broad band at *ca*. 1720 cm^{-1} and a medium band at 805 cm^{-1}, which are attributed to ν(CO) and δ(CO) of a bidentate coordination mode of the oxalato groups, respectively. However, the IR spectra of the three Cu^{II}–Cr^{III} tetranuclear complexes only exhibit bands corresponding to the typical bridging coordination mode of oxalato groups (*ca*. 1640 cm^{-1} [ν_{as}(CO)]; 1340, 1320 cm^{-1} [ν_s(CO)]) [13,20]), suggesting that the oxalato groups of the mononuclear fragment ($K_3[Cr(ox)_3]\cdot 3H_2O$) have coordinated with three copper(II) ions to form tetranuclear complexes. The appearance of a new band at *ca*. 560 cm^{-1}, due to ν(Cu–O) has further proved the coordination mode of oxalato groups. On the other hand, the δ(C–H) deformation bands of aromatic ring of the end-capping ligands (phen, Me_2phen, NO_2phen) are found in corresponding tetranuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinate with the copper(II) ions. The additional band observed at around 580 cm^{-1} due to ν(Cu–N) further supports this view. In addition, a broad intense band centered at *ca*. 1100 cm^{-1} and a strong sharp

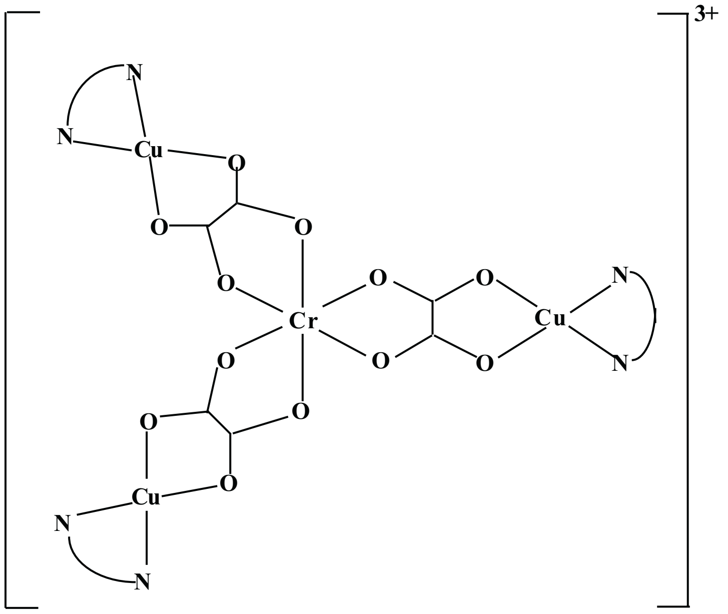

Figure 1. Suggested coordination environment of the tetranuclear complexes ($\overset{\frown}{N\ N}$ = phen, Me_2phen, NO_2phen).

band at *ca.* 630 cm^{-1}, typical for a non-coordinated perchlorate group [21], were present for all the tetranuclear complexes, which coincides with the conductance data of these tetranuclear complexes.

Electronic spectra: The electronic spectral data of these complexes (in DMF solutions) are given in Table 2. As shown in this table, the electronic spectra of the three tetranuclear complexes are similar to each other. For all three tetranuclear complexes, three d-d bands in the visible and infrared range are observed (see Table 2). The two weak bands centred at $(23.0\sim23.3)\times10^3$ cm^{-1} and $(14.0\sim14.3)\times10^3$ cm^{-1} are commensurate with a six-coordinated octahedral configuration around chromium(III) ion [22], whilst the strong band at $(16.3\sim16.6)\times10^3$ cm^{-1} may be attributed to the d-d transition of copper(II) in a square-planar environment [22]. In addition, a stronger band at $(33.2\sim34.1)\times10^3$ cm^{-1} was also observed in the electronic spectra of the tetranuclear complexes, which may be attributed to charge-transfer band. Further investigation of these and similar systems is still required in order to obtain a detailed assignment for charge transfer.

ESR spectra: In order to obtain further information on the structure of the tetranuclear complexes, the X-band powder ESR spectra of the three tetranuclear complexes and the mononuclear fragment $K_3[Cr(ox)_3]\cdot 3H_2O$ have been recorded at room temperature. It is noted that the ESR spectra of the three tetranuclear complexes are similar and exhibit a dissymmetric broad band around g = 2.000 (see Table 2), which is different from the spectrum of $K_3[Cr(ox)_3]\cdot 3H_2O$. This fact indicates a magnetic spin-exchange interaction between Cr(III) and Cu(II) ions. Since there is a lack of structural data for these heterotetranuclear complexes, it is difficult to interpret quan-

Table 1. Molar conductances, effective magnetic moments and IR data for the tetranuclear complexes.

Complex	Λ_M	μ_{eff}	IR (cm^{-1})					
	(S·cm^2·mol^{-1})	(B.M.)	ν_{as}(CO)	ν_s(CO)	ν(Cu–N)	ν(Cu–O)	ν(ClO_4^-)	δ(C–H)
[$Cu_3Cr(ox)_3(phen)_3$](ClO_4)$_3$	220	5.15	1650	1370, 1342	586	560	1100, 625	850, 725
[$Cu_3Cr(ox)_3(Me_2phen)_3$](ClO_4)$_3$	228	5.18	1655	1372, 1343	583	561	1098, 630	852, 720
[$Cu_3Cr(ox)_3(NO_2phen)_3$](ClO_4)$_3$	212	5.21	1640	1375, 1340	585	566	1099, 629	855, 718

Table 2. Electronic spectral bands, assignments and ESR data of the tetranuclear complexes.

Complex	UV-Vis ν(10^3 cm^{-1})/ε_{max} (L·mol^{-1}·cm^{-1})				ESR
	CT	$^2A_2 \rightarrow {}^4T_1$	$^4A_2 \rightarrow {}^4T_2 + {}^2E$	$^2B_{1g} \rightarrow {}^2E_g$	g values
[$Cu_3Cr(ox)_3(phen)_3$](ClO_4)$_3$	33.8(23980)	23.2(20)	14.3(27)	16.6(232)	2.001
[$Cu_3Cr(ox)_3(Me_2phen)_3$](ClO_4)$_3$	34.1(25370)	23.3(25)	14.0(23)	16.5(196)	1.998
[$Cu_3Cr(ox)_3NO_2(phen)_3$](ClO_4)$_3$	33.2(21890)	23.0(18)	14.1(15)	16.3(183)	2.000

titatively this broad band. In addition, to the best of our knowledge, no a detailed assignment of ESR spectra for $[Cu_3^{II}Cr^{III}]$ tetranuclear systems have so far been reported. Thus, at this stage, the dissymmetric broad band appeared for these complexes may be rationalized by the following reasons. According to Kambe's approach [23], in $[Cu_3^{II}Cr^{III}]$ heterotetranuclear systems, the four spins $S_{Cr}=3/2$ and $S_{Cu1}=S_{Cu2}=S_{Cu3}=1/2$ coupled to yield the total spin of one S = 3, three S = 1, three S = 2 and one S = 0. On the basis of Boltzmann's distribution all these states are in a thermal population at room temperature owing to a weak interaction (*vide infra*). Thus, the dissymmetric broad signals may be ascribed to the complexes in these spin states [24].

Based on the composition of these complexes, their electronic spectra, IR, ESR spectra, conductivity measurements and magnetic studies (*vide infra*), these complexes are proposed to have an extended ox-bridged structure and to contain three copper(II) and a chromium(III) ions, in which the chromium(III) ion has an octahedral environment and the three copper(II) ions have a square-planar environment, as shown in Fig. 1. It should be pointed out that the most direct and forceful evidence for the above assumption might come from X-ray crystallographic studies. Unfortunately, all our efforts to grow crystals of the tetranuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, the plausible tetranuclear structure is supported by the following magnetic studies.

Magnetic properties: The observed magnetic moment per tetranuclear complex at room temperature, shown in Table 1, is slightly higher than the spin-only value (4.90 B.M) for a $[Cu_3^{II}Cr^{III}]$ tetranuclear complex with four spin-system (S_{Cu1}, S_{Cu2}, S_{Cu3}, S_{Cr}) = (1/2, 1/2, 1/2, 3/2) in the absence of an exchange interaction. This result suggests the presence of a weak ferromagnetic spin-exchange interaction in these complexes. Being interested in the magnetic behavior of these complexes, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for the complexes $[Cu_3Cr(ox)_3(phen)_3](ClO_4)_3$ **(1)** and $[Cu_3Cr(ox)_3(Me_2phen)_3](ClO_4)_3$ **(2)**, and the results are shown in Fig. 2 in the form of plot of $\chi_M T$ *vs*. T, where χ_M and T denote molar susceptibility and absolute temperature. From Fig. 2 it is evident that the curve of $\chi_M T \sim T$ increases steadily when the temperature is lowered, indicating the operation of intramolecular ferromagnetic interaction through the ox-bridge within the complexes. The rapid decrease of the magnetic moment at low temperature may be attributed to secondary effects such as zero-field splitting and/or to an intermolecular antiferromagnetic interaction. Thus, as noted above, the observed magnetic behavior both at room-temperature and variable-temperature clearly demonstrates the operation of a weak intramolecular ferromagnetic spin-exchange interactions between chromium(III) and copper(II) ions through the ox-bridge within the $[Cu_3^{II}Cr^{III}]$ tetranuclear unit [14]. In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic susceptibility data were analyzed on the basis of equation (1), which includes a parameter θ to correct for the contribution from the secondary effects based on the isotropic spin-Hamiltonian operator, $\hat{H} = -2J(\hat{S}_{Cu1}\cdot\hat{S}_{Cr} + \hat{S}_{Cu2}\cdot\hat{S}_{Cr} + \hat{S}_{Cu3}\cdot\hat{S}_{Cr})$ ($S_{Cu1} = S_{Cu2} = S_{Cu3} = 1/2$, $S_{Cr} = 3/2$).

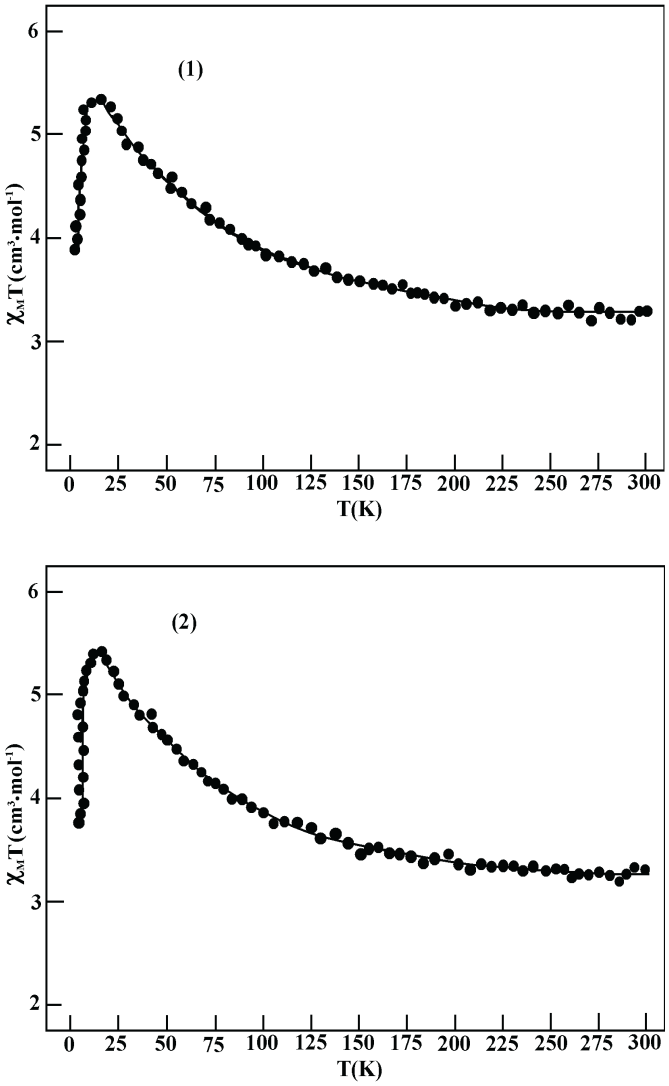

Figure 2. Temperature variation of χ_MT for the complexes $[Cu_3Cr(ox)_3(phen)_3](ClO_4)_3$ **(1)** and $[Cu_3Cr(ox)_3(Me_2phen)_3](ClO_4)_3$ **(2)**. The curves are based on equation (1) using the magnetic parameters given in the text. (•), experimental data; (-), calculated curve as described in the text.

$$\chi_M = \frac{N\beta^2}{k(T-\theta)}\left[\frac{A}{C}\right] + N\alpha \tag{1}$$

$$A = [2 + 10\exp(4J/kT) + 28\exp(10J/kT)]g_1^2 + 4g_2^2\exp(8J/kT) + 20g_3\exp(7J/kT)$$

$$B = 3 + \exp(-2J/kT) + 5\exp(4J/kT) + 7\exp(8J/kT) + 6\exp(3J/kT) + 20\exp(7J/kT)$$

Where $g_1 = (g_{Cr} + g_{Cu})/2$, $g_2 = (5g_{Cr} - g_{Cu})/4$, $g_3 = (3g_{Cr} + g_{Cu})/4$, χ_M denotes the molecular susceptibility per tetranuclear complex, and the remaining symbols have their usual meanings. As shown in Fig. 2, good least-square fits to the experimental data were obtained with equation (1) for the complexes $[Cu_3Cr(ox)_3(phen)_3](ClO_4)_3$ **(1)** and $[Cu_3Cr(ox)_3(Me_2phen)_3](ClO_4)_3$ **(2)**. The magnetic parameters thus determined and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{calc.} - (\chi_M)_{obs}]^2/\Sigma(\chi_M)_{obs}$ are $J = +10.97\ cm^{-1}$, $g_{Cr} = 1.998$, $g_{Cu} = 2.045$, $\theta = -0.16$ K, $N_\alpha = 300\times10^{-6}\ cm^3\cdot mol^{-1}$, $F = 2.9\times10^{-4}$ for **(1)** and $J = +9.28\ cm^{-1}$, $g_{Cr} = 1.995$, $g_{Cu} = 2.058$, $\theta = -0.12$ K, $N_\alpha = 300\times10^{-6}\ cm^3\cdot mol^{-1}$, $F = 3.2\times10^{-4}$ for **(2)**. The results indicate that the complex undergo weak ferromagnetic spin-exchange interaction between the copper(II) and chromium(III) ions through an oxalato-bridge within each tetranuclear molecule.

To describe the mechanism of the exchange interaction, several models have been proposed [6,25–27]. According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise an antiferromagnetic coupling ($J < 0$) should be involved in the system. Thus, the magnetic behavior for the two tetranuclear complexes can be rationalized on the basis of these models. Considering the symmetry of the [Cr(ox)Cu] skeleton of the oxalate bridging network close to C_{2V} (for the definition of X and Y coordinates, see Fig. 3), in $[Cu_3^{II}Cr^{III}]$ heterotetranuclear system, the 3d metallic orbitals of copper(II) and chromium(III) ions transform as $a_1(d_{z^2}$ and $d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{xz})$ [28]. Around the copper(II) ion, there is just one unpaired electron which occupies the b_1 orbital, and around the chromium(III) ion there are three unpaired electrons which populate the a_1, a_2, b_1 and b_2 orbitals. According to the point group theory, because there is no orbital interaction to be feasible between the magnetic orbitals of the metal centers, namely, $<b_1(Cu)|a_1(Cr)> = 0$, $<b_1(Cu)|a_2(Cr)> = 0$, $<b_1(Cu)|b_2(Cr)> = 0$, therefore, the ferromagnetic interaction between the copper(II) and chromium(III) ions within the $[Cu_3^{II}Cr^{III}]$ heterotetranuclear complexes should be observed. This may be the reason for a ferromagnetic spin-exchange interaction observed in these $[Cu_3^{II}Cr^{III}]$ tetranuclear complexes.

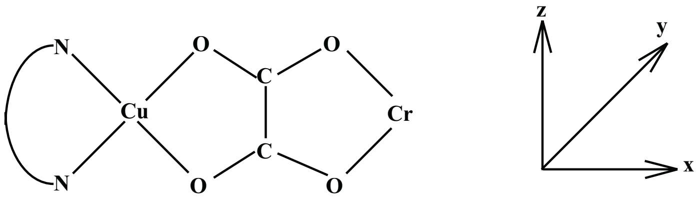

Figure 3. The structure of the [Cr(ox)Cu] skeleton.

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REFERENCES

1. Kahn O., *Molecular Magnetism*, NY, Verlag-chemie (1993).
2. Winpenny R.E.P., *Chem. Soc. Rev.*, **27**, 447 (1998).
3. Benelli C. and Gatteschi D., *Chem. Rev*., **102**, 2369 (2002).
4. Kahn M.L., Mathoniere C. and Kahn O., *Inorg. Chem*., **30**, 3692 (1999).
5. Kahn O., *Struct. Bond. (Berlin)*, **68**, 89 (1987).
6. Kahn O. and Charlot M.F., *Nouv. J. Chim*., **4**, 567 (1980).
7. Journaux Y., Kahn O., Zarembowitch J., Galy J. and Jaud J., *J. Am.Chem. Soc*., **105**, 7585 (1983).
8. Zhuong J.Z., Matsumoto N., Okawa H. and Kida S., *Inorg. Chem*., **30**, 436 (1991).
9. Yu P., Kahn O., Nakatani K., Codjovi E., Mathoniere C. and Sletten J., *J. Am. Chem. Soc.*, **113**, 6558 (1991).
10. Zhuong J.Z., Okawa H., Matsumoto N., Sakiyama H. and Kidda S., *J. Chem. Soc., Dalton Trans.*, 479 (1991).
11. Lloret F., Julve M., Ruiz R., Journaux Y., Nakatani K., Kahn O. and Sletten J., *Inorg. Chem*., **32**, 27 (1993).
12. Ohba M., Tamaki H., Matsumoto N. and Kawa H., *Inorg. Chem*., **32**, 5383 (1993).
13. Cortes R., Urtiaga M.K., Lezama L., Arriortua M.I. and Rojo T., *Inorg. Chem*., **33**, 829 (1994).
14. Li Y.T., Yan C.W., Miao S.H. and Liao D.Z., *Polyhedron*, **15**, 2491 (1998).
15. Brauer G. (Ed.), *Handbook of Preparative Inorganic Chemistry*, Academic Press, N.Y., 1372 (1965).
16. Selwood P.W., "*Magnetochemistry*", Interscience, N.Y., 78 (1956).
17. Gunter M.J., Berry K.J. and Murray K.S., *J. Am. Chem. Soc*., **106**, 4227 (1984).
18. Sinn E., in "*Biological and Inorganic Copper(II) Chemistry*", K.D. Karlin and J. Zubieta (Eds.), Adenine Press, Guilderland, N.Y. (1986).
19. Geary W.J., *Coord. Chem. Rev*., **7**, 81 (1971).
20. Curtis N.F., *J. Chem. Soc*., 1584 (1968).
21. Nakamoto, K., "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", 3rd. edn., Wiley Interscience, N.Y., 1978.
22. Lever A.B.P., "*Inorganic Electronic Spectroscopy*", Elsevier Publishing Co., Amsterdam (1984).
23. Kambe K., *J. Phys. Soc. Jpn*., **5**, 48 (1950).
24. Suzuki M., Oshio H., Uenara A., Endo K., Yanaga M., Kida S. and Saito K., *Bull. Chem. Soc. Jpn*., **61**, 3907 (1988).
25. Yu P., Journaux Y. and Kahn O., *Inorg. Chem*., **28**, 100 (1989).
26. Hay P.J., Thibeault J.C. and Hoffman R., *J. Am. Chem. Soc*., **97**, 4884 (1975).
27. Dance I.G., *Inorg. Chim. Acta*, **9**, 77 (1974).
28. Morgenstern-Badarau I., Rerat M., Kahn O., Jaud J. and Galy J., *Inorg. Chem*., **21**, 3050 (1982).