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Synthesis and magnetic studies of oxalato-bridged copper(II)–chromium(III)–copper(II) and copper(II)–iron(III)–copper(II) heterotrinuclear complexes

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Abstract

The strategy of "complex as ligand" allowed us to synthesize three new μ-oxalato-bridged heterotrinuclear complexes identified as $[Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ (**1**), $[Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ (**2**) and $[Cu_2Fe(ox)_3(Me_2bpy)_2]ClO_4$ (**3**), where ox represents the oxalato dianions; Mephen and Me_2bpy stand for 5-methyl-1,10-phenanthroline and 4,4′-dimethyl-2,2′-bipyridine, respectively. The three heterotrinuclear 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 spectra studies, it is proposed that these complexes have an oxalato-bridged structure consisting of two copper(II) ions and a chromium(III) or an iron (III)ion, in which the chromium(III) or iron(III) ion has an octahedral environment, and the two copper(II) ions have a square-planar environment. Variable-temperature magnetic susceptibility (4.2–300 K) measurements of the complexes **1** and **2** revealed the occurrence of an intramolecular ferromagnetic interaction between the copper(II) and chromium(III) ions for **1**. On the other hand, the spin-coupling between the copper(II) and iron(III) ions through the oxalato-bridge in complex **2** is an antiferromagnetic. The magnetic data have been also used to deduce the indicated heterotrinuclear structure. On the basis of the spin-Hamiltonian, $\hat{H} = -2J(\hat{S}_{Cu1} \cdot \hat{S}_M + \hat{S}_{Cu2} \cdot \hat{S}_M)$ ($M = Cr^{3+}$ or Fe^{3+}), the magnetic analysis was carried out for the two complexes and the spin-coupling (J) was evaluated as $+14.9\ cm^{-1}$ for **1** and $-12.7\ cm^{-1}$ for **2**.

Keywords: μ-Oxalato-bridge; Copper(II); Chromium(III); Iron(III); Heterotrinuclear complexes; Magnetism

1. Introduction

The elucidation of the structural and electronic-structural factors causing spin-exchange interaction between paramagnetic centers of heteropolynuclear complexes propagated by multiatom bridges is one of the challenges in chemistry, physics and molecular materials sciences [1–8]. Interest in this field is a fundamental requirement for gaining some insight into the pathway of electron transfer in based ferromagnets and for investigating the spin-exchange mechanism between paramagnetic metal ions.

So far, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. Among other more elaborate ligands employed in the study of magnetic interactions, the oxalato group, due to both its versatile bonding mode with metal ions and its remarkable ability to transmit electronic effects when acting as bridges between paramagnetic centers, has been shown to be an excellent multiatom bridging ligand in supporting magnetic exchange interactions. Several kinds of complexes bridged by the oxalato group have been synthesized and their magnetic properties studied [9–13]. However, to the best of our knowledge, no oxalato-bridged copper(II)–chromium(III)–copper(II) or copper(II)–iron(III)–copper(II) heterotrinuclear complexes have so far been reported. Taking into account the

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above facts, it is of considerable interest to synthesize and study copper(II)–chromium(III)–copper(II) and copper(II)–iron(III)–copper(II) heterotrinuclear complexes with bridging oxalato in order to gain some insight into the molecular magnetism of this kind of complex.

In this paper, three new μ-oxalato-bridged trinuclear complexes formulated as $[Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ (**1**), $[Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ (**2**) and $[Cu_2Fe(ox)_3(Me_2bpy)_2]ClO_4$ (**3**), where ox is the oxalato dianion; Mephen and Me_2bpy stand for 5-methyl-1,10-phenanthroline and 4,4′-dimethyl-2,2′-bipyridine, respectively, have been synthesized and characterized by using tris(oxalato)chromate(III), $[Cr(ox)_3]^{3-}$, and tris(oxalato)ferrate(III), $[Fe(ox)_3]^{3-}$, as polyatomic bridging ligands. The cryomagnetic properties of the complexes **1** and **2** were measured in the temperature range 4.2–300 K to investigate the electronic-structural variation of the metal ions effects upon the nature of spin-exchange interaction between the paramagnetic centers. At present, the three heterotrinuclear complexes have not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic susceptibility and spectral data clearly demonstrates the presence of exchange coupling between the metal ions, reveals certain electronic properties of the heterotrinuclear complexes, and allows predictions of structural features to be made.

2. Experimental

2.1. Materials

All the reagents used in the synthesis were of analytical grade. Potassium tris(oxalato)chromium(III) trihydrate ($K_3[Cr(ox)_3]\cdot 3H_2O$), potassium tris(oxalato) iron(III) trihydrate ($K_3[Fe(ox)_3]\cdot 3H_2O$) and $Cu(ClO_4)_2\cdot 6H_2O$ were synthesized according to the literature [14–16] methods. The terminal ligands 5-methyl-1,10-phenanthroline (Mephen) and 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) were used as commercially obtained.

2.2. Synthesis of the heterotrinuclear complexes

2.2.1. $[Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ (1)

A methanol solution (15 ml) of $K_3[Cr(ox)_3]\cdot 3H_2O$ (1.0 mmol, 0.491 g) was added successively dropwise to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (2.1 mmol, 0.778 g) stirred in methanol (20 ml). The vigorous stirring was continued at room temperature until the mixture became limpid (about 10 min). It was then filtered to eliminate impurities. A methanol solution (15 ml) of Mephen (2.0 mmol, 0.389 g) was added to the filtrate. The solution changed color immediately and a small amount of red-violet precipitate was formed. After stirring the mixture for ca. 6 h the red-violet microcrystals thus formed were filtered, washed with methanol, water and diethyl ether several times and dried over P_2O_5 under reduced pressure. It was recrystallized from a hot acetonitrile solution and red-violet needle crystals were obtained. Yield: 0.764 g (82%); m.p. 272 °C. *Anal.* Found: C, 41.2; H, 2.1; N, 5.8; Cr, 5.4; Cu, 13.5. Calc. for $CrCu_2C_{32}H_{20}$ $N_4O_{16}Cl$ (M.W. 931.07): C, 41.3; H,2.2; N, 6.0; Cr, 5.6; Cu, 13.7%.

2.2.2. $[Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ (2)

A methanol solution (10 ml) of Mephen (2.0 mmol, 0.389 g) was added successively dropwise to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (2.1 mmol, 0.778 g) stirred in methanol (20 ml). The solution obtained was stirred for ca. 20 min at room temperature. The resulting solution was then filtered to eliminate impurities. An aqueous solution (15 ml) of $K_3[Fe(ox)_3]\cdot 3H_2O$ (1.0 mmol, 0.491 mg) was added to the filtrate with vigorous stirring at room temperature. After stirring the mixture for ca. 8 h in darkness, the purple microcrystals thus formed were filtered, washed with methanol, water and diethyl ether several times and dried over P_2O_5 under reduced pressure. It was recrystallized from an acetonitrile/ethanol (1:3) mixture and purple needle crystals were collected. Yield: 0748 g (80%); m.p. 232 °C. *Anal.* Found: C, 40.9; H, 2.3; N, 5.7; Fe, 5.7; Cu, 13.4. Calc. for $FeCu_2C_{32}H_{20}N_4O_{16}Cl$ (M.W.934.92): C, 41.1; H, 2.2; N, 6.0; Fe, 6.0; Cu, 13.6%.

2.2.3. $[Cu_2Fe(ox)_3(Me_2bpy)_2]ClO_4$ (3)

This complex was obtained as a brown powder by the same procedure as described for complex **2**, except that Me_2bpy was used instead of Mephen. Yield: 0.705 g (77%); m.p. 199 °C. *Anal.* Found: C, 39.2; H, 2.3; N, 6.4; Fe, 6.4; Cu, 13.6. Calc. for $FeCu_2C_{30}H_{24}N_4O_{16}Cl$ (M.W. 914.93): C, 39.4; H, 2.6; N, 6.1; Fe, 6.1; Cu, 13.9%.

2.3. Physical measurements

Analysis 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 (in acetonitrile 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 the 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 [17] for all the constituent atoms and effective magnetic moments were calculated using the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

3. Results and discussion

3.1. Synthetic route and coordination environment of the trinuclear complexes

Two synthetic strategies are generally available for the preparation of heterometal complexes. The first is to use a designed polynucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions [18]. The second uses a complex as a "ligand" that contains a potential donor group capable of coordinating to another metal ion [19]. In this study, our aim was to obtain copper(II)–chromium(III)–copper(II) and copper(II)–iron(III)–copper(II) heterotrinuclear complexes, therefore, the latter method was adopted. As the "ligand complexes" we have selected potassium tris(oxalato)chromium(III) trihydrate ($K_3[Cr(ox)_3]\cdot 3H_2O$) and potassium tris(oxalato)iron(III) trihydrate, $K_3[Fe(ox)_3]\cdot 3H_2O$, respectively, as mononuclear fragments, because: (i) they can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes, (ii) $K_3[Cr(ox)_3]\cdot 3H_2O$ and $K_3[Fe(ox)_3]\cdot 3H_2O$ play the key role in producing oxalato-bridged copper(II)–chromium(III)–copper(II) and copper(II)–iron(III)–copper(II) heterotrinuclear complexes, since iron(III) and chromium(III) ions generally lead to ill characterized materials contaminated by the precipitation of $Fe(OH)_3$ and $Cr(OH)_3$ rather than the corresponding complexes. In order to avoid this, in our synthetic approach to oxalato-bridged copper(II)–chromium(III)–copper(II) and copper(II)–iron(III)–copper(II) heterotrinuclear complexes, the two mononuclear fragments $K_3[Cr(ox)_3]\cdot 3H_2O$ and $K_3[Fe(ox)_3]\cdot 3H_2O$ were used as the chromium(III)-site component and iron(III)-site component, respectively. Simultaneously, 5-methyl-1,10-phenanthroline (Mephen) and 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) were used as the terminal ligands. Indeed, the elemental analyses and physical data (see Table 1) for the newly prepared complexes indicate that the reaction of $K_3[Cr(ox)_3]\cdot 3H_2O$ or $K_3[Fe(ox)_3]\cdot 3H_2O$ with $Cu(ClO_4)_2\cdot 6H_2O$ and the terminal ligand L (L = Mephen, Me_2bpy) in ca. 1:2:2 mole ratio readily yielded the heterotrinuclear complexes of the general formula $[Cu_2M(ox)_3L_2]ClO_4$ ($M = Cr^{3+}$ and Fe^{3+}), as expected. These compounds are the first examples of heterotrinuclear copper(II)–chromium(III)–copper(II) and copper(II)–iron(III)–copper(II) complexes bridged

Table 1
Molar conductances, effective magnetic moments and IR data (cm^{-1}) for the trinuclear complexes

Complexes	Λ_M ($S\ cm^2 mol^{-1}$)	μ_{eff} (μ_B)	ν(ox) (bidentate)		ν(ox) (bridging)		ν(Cu–O)	ν(Cu–N)	$\nu(ClO_4^-)$	δ(C–H)
			ν_{as}(CO)	δ(CO)	ν_{as}(CO)	ν_s(CO)				
1	140	4.72	1710, 1680, 1645	785	1620	1375, 1335	465	420	1100, 630	853, 720
2	150	6.27	1715, 1682, 1650	790	1628	1380, 1340	463	429	1098, 630	850, 725
3	148	6.15	1718, 1685, 1650	790	1624	1378, 1339	462	427	1099, 629	856, 730

1, $[Cu_2Cr(ox)_3(Mephen)_2]ClO_4$; **2**, $[Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ and **3**, $[Cu_2Fe(ox)_3(Me_2bpy)_2]ClO_4$.

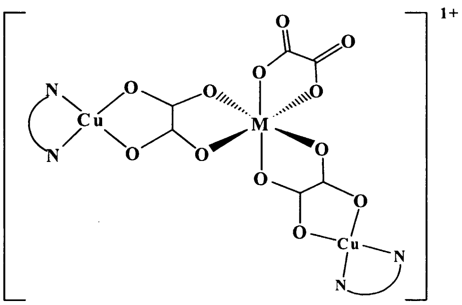

Fig. 1. Suggested coordination environment of the complexes (N N = Mephen, Me_2bpy; M = Cr^{3+}, Fe^{3+}).

by oxalato groups. Although crystal structures of the three heterotrinuclear complexes are not known, the magnetic and spectroscopic data are sufficient to deduce the occurrence of a magnetically coupled heterotrinuclear unit containing two copper(II) and one chromium(III) or one iron(III) ions. On the basis of the physical and chemical evidence, the three heterotrinuclear complexes may be presumed to have the coordination environment as shown in Fig. 1.

3.2. Molar conductances and general properties of the trinuclear complexes

These heterotrinuclear 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 three complexes are fairly stable in air so as to allow physical measurements. For the three heterotrinuclear complexes, the observed molar conductance values (140–150 Ω^{-1} cm^2 mol^{-1}) in acetonitrile solution at 25 °C are given in Table 1. These values are indicative of 1:1 electrolytic nature [20], in accord with the presumed structure of the heterotrinuclear complexes shown in Fig. 1. The trinuclear structure was further characterized by the following results.

3.3. Infrared spectra

In order to clarify the mode of bonding, the IR spectra of the mononuclear fragments $K_3[Cr(ox)_3]\cdot 3H_2O$ and $K_3[Fe(ox)_3]\cdot 3H_2O$ were compared with the spectra of the three heterotrinuclear complexes. Since the IR spectra of all the three trinuclear complexes are similar, discussion is confined to the most important vibration in the 400–4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands of the heterotrinuclear complexes and the mononuclear fragments $K_3[Cr(ox)_3]\cdot 3H_2O$ or $K_3[Fe(ox)_3]\cdot 3H_2O$, together with their assignments are given in Table 1. It is noteworthy that the spectra of the mononuclear complexes $K_3[Cr(ox)_3]\cdot 3H_2O$ and $K_3[Fe(ox)_3]\cdot 3H_2O$ only show the typical bidentate coordination mode of the oxalato groups. However, the IR spectra of the three heterotrinuclear complexes exhibit bands corresponding to the bidentate oxalato ligand (ca. 1700, 1680, 1650 cm^{-1} [$\nu_{as}(CO)$]; 780 cm^{-1} [$\delta(CO)$]) and also the bridging oxalato ligand (ca. 1620 cm^{-1} [$\nu_{as}(CO)$]; 1380, 1340 cm^{-1} [$\nu_s(CO)$]) [12,13], suggesting that the oxalato groups of the mononuclear fragments coordinate with copper(II) ions to form heterotrinuclear complexes. The appearance of a new band at ca. 460 cm^{-1}, due to ν(Cu–O) has further proved the coordination mode of oxalato groups. On the other hand, the C–H deformation bands [δ(C–H)] of the aromatic ring of the end-capping ligands (Mephen, Me_2bpy) are found in corresponding trinuclear 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 430 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 band at ca. 630 cm^{-1}, typical for a non-coordinated perchlorate group [21], were present for all trinuclear complexes, which coincides with the conductance data of these trinuclear complexes.

3.4. Electronic spectra

In order to obtain further structural information of these heterotrinuclear complexes, the electronic spectra (in DMF solutions) of the mononuclear fragments $K_3[Cr(ox)_3]\cdot 3H_2O$, $K_3[Fe(ox)_3]\cdot 3H_2O$ and the trinuclear complexes were studied and assigned on the basis of a careful comparison of the latter with the former. For all three trinuclear complexes, a strong band at $(16.2\text{–}16.5) \times 10^3$ cm^{-1} ($\varepsilon = 290\text{–}293$ mol^{-1} dm^3 cm^{-1}) may be attributed to the $^2B_{1g} \rightarrow {}^2E_g$ transition of copper(II) in a square-planar environment [22], while the stronger band at $(31.5\text{–}32.2) \times 10^3$ cm^{-1} ($\varepsilon = 3450\text{–}3500$ mol^{-1} dm^3 cm^{-1}) observed in the electronic spectra of the three trinuclear complexes may be attributable to a charge-transfer band. In addition, in the spectrum of the copper(II)–chromium(III)–copper(II) trinuclear complex, two absorption bands centered at 23.2×10^3 cm^{-1} ($\varepsilon = 210$ mol^{-1} dm^3 cm^{-1}) and 14.1×10^3 cm^{-1} ($\varepsilon = 160$ mol^{-1} dm^3 cm^{-1}) are due to the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^2T_2 + {}^2E$ transitions of chromium(III) and are characteristic of an octahedral configuration around chromium(III) [22]. On the other hand, the electronic spectra of the two copper(II)–iron(III)–copper(II) heterotrinuclear complexes are similar. The electronic absorption spectrum of complex **3** in DMF solution is shown, by way of example, in Fig. 2. As shown (Fig. 2) for the two copper(II)–iron(III)–copper(II) heterotrinuclear complexes, three d–d bands appearing in the $(11.8\text{–}11.7) \times 10^3$ cm^{-1} ($\varepsilon = 145\text{–}150$ mol^{-1} dm^3 cm^{-1}), $(18.5\text{–}18.3) \times 10^3$ cm^{-1} ($\varepsilon = 135\text{–}138$ mol^{-1} dm^3 cm^{-1}) and $(25.3\text{–}25.4) \times 10^3$ cm^{-1} ($\varepsilon = 320\text{–}332$ mol^{-1} dm^3

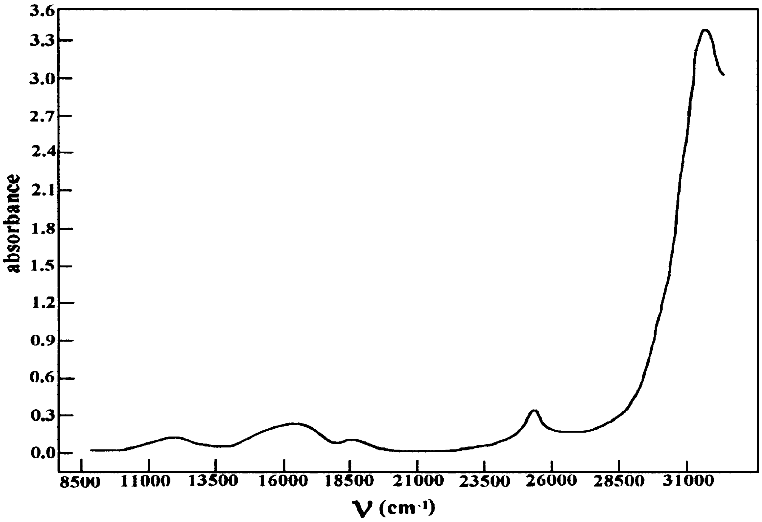

Fig. 2. Electronic absorption spectrum of complex **3** in DMF solution.

cm^{-1}) regions are also observed, which may be tentatively assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g(G)$ transitions in the order of increasing energy, consistent with the presence of a six-coordinated octahedral configuration around the iron(III) ion [22]. These formally spin-forbidden bands for iron(III) ion may be activated by an exchange mechanism [23]. It should be pointed out that such assignments are speculative in the absence of crystal structure determinations and polarized single crystal spectra. Indeed, further investigation of these and similar systems is still required in order to obtain a reasonable interpretation for the very high values of ε in the spin-forbidden transitions of the iron(III) ion.

3.5. ESR spectra

The X-band powder ESR spectra of the three trinuclear complexes have been recorded at room temperature. It is noted that the ESR spectrum of the copper(II)–chromium(III)–copper(II) trinuclear complex exhibits a dissymmetric broad band around $g \approx 2.0$. Since there is a lack of structural data for the complex, it is difficult to interpret quantitatively this broad band. In addition, to the best of our knowledge, no detailed assignment of ESR spectra for a copper(II)–chromium(III)–copper(II) trinuclear system has so far been reported. Thus, at this stage, the dissymmetric broad band appearing for the complex may be rationalized by the following reasons. According to Kambe's approach [24], in the copper(II)–chromium(III)–copper(II) trinuclear system, first the spins of the two copper(II)ions couple ($S_{\mathrm{Cu1}} = S_{\mathrm{Cu2}} = 1/2$) to give two spin states of $S' = 1$ and 0. Then S' couple to the chromium(III) ion ($S_{\mathrm{Cr}} = 3/2$) to yield four total spin states of $S_{\mathrm{T}} = 5/2$, 3/2, 1/2, 3/2. On the Boltzmann distribution, these states are a thermal population at room temperature owing to a weak interaction ($J = +14.9$ cm^{-1}, vide infra). Thus, the dissymmetric broad signals may be ascribed to the complex in these spin states [25]. On the other hand, for the two copper(II)–iron(III)–copper(II) trinuclear complexes the ESR spectra showed no signals [26], indicating that the ground state of the two heterotrinuclear complexes is $S = 2$, in accord with the following magnetically deduced conclusion. Further ESR spectral investigations for solutions at low temperatures (frozen solutions) of these and similar systems are still required in order to obtain some insight into the structure of this kind of complex.

Based on the composition of these complexes, their infrared spectra, electronic spectra, ESR spectra, conductivity measurements and magnetic studies (vide infra), these heterotrinuclear complexes are proposed to have an extended ox-bridged structure and to contain two copper(II) ions and a chromium(III) or an iron(III) ion, in which the chromium(III) or iron(III) ion has an octahedral environment and the two 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 may come from X-ray crystallographic studies. Unfortunately, all our efforts to grow crystals of these heterotrinuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, the plausible heterotrinuclear structure is supported by the following magnetic studies.

3.6. Magnetic studies

The observed effective magnetic moment (μ_{eff}) per trinuclear complex at room temperature is given in Table 1. As shown in this table, the μ_{eff} value of complex **1** is 4.72 μ_{B} at room temperature, which is slightly higher than the spin-only value (4.58 μ_B) for a copper(II)–chromium(III)–copper(II) heterotrinuclear complex with a three spin-system (S_{Cu1}, S_{Cu2}, S_{Cr}) = (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 the complex. On the other hand, the μ_{eff} values of complexes **2** and **3** at room temperature (see Table 1) are less than the spin-only value (6.40 μ_B) of the magnetically non-interacting copper(II)–iron(III)–copper(II) heterotrinuclear system, indicating the presence of a weak antiferromagnetic spin-exchange interaction in the two copper(II)–iron(III)–copper(II) trinuclear complexes.

Being interested in the magnetic behavior of these trinuclear complexes, variable-temperature (4.2–300 K) magnetic susceptibility data were further collected for complexes [$Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ (**1**) and [$Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ (**2**) in order to investigate the electronic-structural variation of the metal ions effect upon the nature of the spin-exchange interaction between the paramagnetic centers of this kind of complex, and the results are shown in Figs. 3 and 4, respectively, in the form of plots of μ_{eff} versus T. From Fig. 3 it is evident that the curve of the effective magnetic moment (μ_{eff}) increases steadily when the temperature is lowered, indicating the operation of an intramolecular ferromagnetic interaction through the ox-bridge within the complex [27]. The rapid decrease of the magnetic moment at low temperature may be attributed to an intermolecular antiferromagnetic interaction. On the other hand, as shown in Fig. 4, the variation of μ_{eff} with temperature for complex **2** is a slight decrease on lowering the temperature. This result suggested that the operation of an antiferromagnetic spin-exchange occurred in the complex. Thus, as noted above, the observed magnetic behavior for complex **1** both at room temperature and at variable temperatures clearly demonstrates the operation of an intramolecular ferromagnetic spin-exchange interaction between chromium(III) and copper(II) ions through the ox-bridge within the heterotrinuclear unit, while the spin-coupling between the copper(II) and iron(III) ions within complex **2** is antiferromagnetic.

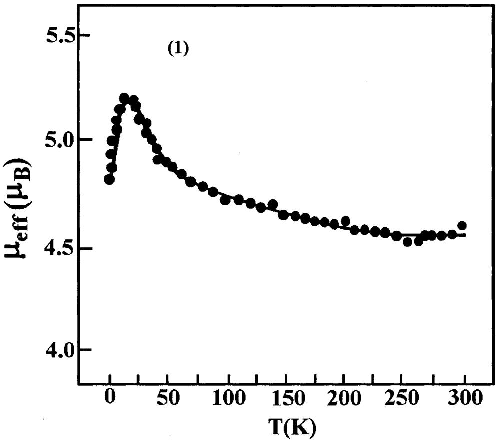

Fig. 3. Temperature variation of μ_{eff} for the [$Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ (**1**) complex. The curve is based on Eq. (1) using the magnetic parameters given in the text. (●), experimental data; (——), calculated curve as described in the text.

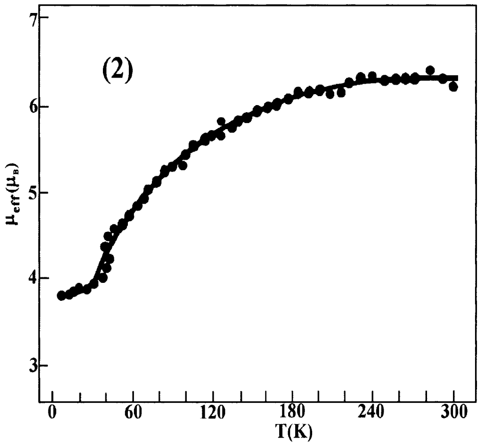

Fig. 4. Temperature variation of μ_{eff} for the [$Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ (**2**) complex. The curve is based on Eq. (2) using the magnetic parameters given in the text. (●), experimental data; (——), calculated curve as described in the text.

In order to understand quantitatively the nature and magnitude of the spin-exchange interaction, the magnetic susceptibility data were analyzed for complex **1** on the basis of Eq. (1) [28] which includes a parameter θ to correct for the contribution from an intermolecular magnetic interaction based on the spin-Hamiltonian $\hat{H} = -2J \times (\hat{S}_{Cu1} \cdot \hat{S}_{Cr} + \hat{S}_{Cu2} \cdot \hat{S}_{Cr})$ ($S_{Cu1} = S_{Cu2} = 1/2, S_{Cr} = 3/2$):

$$\begin{aligned} \chi_M &= \frac{N\beta^2 g^2}{4k(T-\theta)}\left[\frac{A}{B}\right], \\ A &= 10 + \exp(-5J/kT) + 10\exp(-2J/kT) \\ &\quad + 35\exp(3J/kT), \\ B &= 2 + 2\exp(-5J/kT) \\ &\quad + 2\exp(-2J/kT) + 3\exp(3J/kT), \end{aligned} \tag{1}$$

where, χ_M denotes the molecular susceptibility per trinuclear complex, and the remaining symbols have their usual meanings. As shown in Fig. 3, good least-square fits to the experimental data were obtained with Eq. (1) for complex **1**. The magnetic parameters thus determined and the agreement factor F, defined here as $F = \sum[(\chi_M)_{calc} - (\chi_M)_{obs}]^2/\sum(\chi_M)_{obs}$ are $J = +14.9$ cm^{-1}, $g = 2.00$, $\theta = -0.23$ K, $F = 3.6 \times 10^{-4}$. The results indicate that the complex undergoes weak ferromagnetic spin-exchange interaction between the copper(II) and chromium(III) ions.

The cryomagnetic property of complex **2** is showed in Fig. 4. The magnetic analysis was carried out with the susceptibility equation based on a symmetrical three-spin system derived from the spin-Hamiltonian operator, $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) - 2J'\hat{S}_1 \cdot \hat{S}_3$, where $\hat{S}_1$, $\hat{S}_2$ and $\hat{S}_3$ are the spin operators of copper(II), iron(III) and copper(II), respectively. The meaning of J and J' is indicated in Fig. 5, which represents the simplest scheme consistent with the available data.

Because the two copper(II) ions in the copper(II)–iron(III)–copper(II) heterotrinuclear clusters are far apart, the quality of the fit does not depend on J' and hence the fit with $J' = 0$ has been accepted to be more plausible [29–31]. Assuming that the exchange integral between the terminal copper(II) ions is zero ($J' = 0$), the molar susceptibility of the copper(II)–iron(III)–copper(II) ($S_1 = S_3 = 1/2$, $S_2 = 5/2$) system is given by

$$\begin{aligned} \chi_M &= \frac{N\beta^2 g^2}{4kT}\left[\frac{A}{B}\right], \\ A &= 35 + 10\exp(-7J/kT) \\ &\quad + 35\exp(-2J/kT) + 84\exp(5J/kT), \\ B &= 3 + 2\exp(-7/kT) + 3\exp(-2J/kT) \\ &\quad + 4\exp(5J/kT), \end{aligned} \tag{2}$$

where χ_M denotes the molecular susceptibility per trinuclear complex, and the remaining symbols have their usual meanings. As shown by the trace in Fig. 4, good fitting to the experimental data is attained with Eq. (2) for complex **2** using magnetic parameters $J = -12.7$ cm^{-1}, $g = 2.02$, $F = 7.8 \times 10^{-4}$. The results (negative and small J value) have confirmed that the spin-coupling between iron(III) and copper(II) ions through an oxalato group is antiferromagnetic.

On the basis of the above discussion of magnetic properties of complexes **1** and **2**, it has been shown that the two complexes **1** and **2** differ in magnetic properties from each other. That is, ferromagnetic spin-coupling occurs in **1**, whereas antiferromagnetic spin-coupling occurs in **2**. In fact, the present complexes $[Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ (**1**) and $[Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ (**2**) have the same skeleton of the oxalate bridging structure and the same terminal ligand (Mephen), thus, their IR and coordination environment are also similar. The only difference between $[Cu_2Cr(ox)_3(Mephen)_2]ClO_4$ and $[Cu_2Fe(ox)_3(Mephen)_2]ClO_4$ is that the central metal ion is chromium(III) in the former case and iron(III) in the latter. The essential difference between the sign of the exchange parameter J in the two complexes indicates that the kind of metal ion may affect the nature of the exchange interaction. The magnetic behavior for the two heterotrinuclear complexes can be rationalized on the basis of the method of magnetic orbital interaction between the metal ions, as proposed by Kahn et al. [5,10]. Considering the symmetry of the [M(ox)Cu] (M = Fe^{3+}and Cr^{3+}) skeleton of the oxalate bridging network is close to C_{2v} (for the definition of X and Y coordinates, see Fig. 6), if M = Fe(III) ion, the 3d metallic orbitals of copper(II) and iron(III) ions transform [5] as $a_1(d_{z^2}, d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{xz})$. Around the copper(II) ion, there is just one unpaired electron which occupies the b_1 orbital, and around the iron(III) ion there are five unpaired electrons which populate the a_1, a_2, b_1 and b_2 orbitals. According to point group theory, because no strict orthogonality of the magnetic orbitals between copper(II) and iron(III) ions can be realized, namely, $S = \langle b_1(\mathrm{Cu})|b_1(\mathrm{Fe})\rangle \neq 0$, an antiferromagnetic interaction between the copper(II) and iron(III) ions within complex **2** should be observed. On the other hand, when M = Cr(III) ion, the 3d metallic orbitals of copper(II) and chromium(III) ions transform as $a_1(d_{z^2}, d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{xz})$. Around the chromium(III) ion there are three unpaired electrons which populate the a_1, a_2 and b_2 orbitals [32–34], since no orbital interaction is feasible between the magnetic orbitals of the metal centers, that is $\langle b_1(\mathrm{Cu})|a_1(\mathrm{Cr})\rangle = 0$, $\langle b_1(\mathrm{Cu})|a_2(\mathrm{Cr})\rangle = 0$, $\langle b_1(\mathrm{Cu})|b_2(\mathrm{Cr})\rangle = 0$. This may be the reason for a ferromagnetic spin-exchange interaction observed in the copper(II)–chromium(III)–copper(II) complex.

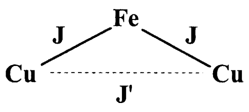

Fig. 5. Magnetic exchange parameters of the copper(II)–iron(III)–copper(II) trinuclear complexes.

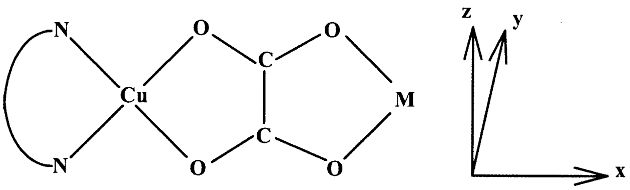

Fig. 6. The structure of the [M(ox)Cu] (M = Fe^{3+} and Cr^{3+}) skeleton.

It is clear from the above discussion that in this system the nature of spin-exchange interactions may be tunable by choosing an appropriate combination of paramagnetic metal ions, and this strategy opens vast perspectives [5,35]. Indeed, further investigations on this and similar systems are still required in order to get a deeper insight into this exciting field of magnetic interactions and are in progress in our laboratory.

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