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Synthesis and Magnetic Properties of μ-Oxalato-Bridged Cu(II)–Fe(III)–Cu(II) Heterotrinuclear Complexes

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Three new μ-oxalato-bridged copper(II)–iron(III)–copper(II) heterotrinuclear complexes described by the overall formula $[Cu_2Fe(ox)_3L_2]ClO_4$, where ox represents the oxalato dianions and L stands for 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) or 5-chloro-1,10-phenanthroline (Cl-phen), have been synthesized and characterized by elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR and electronic spectral studies. It is proposed that these complexes have extended ox-bridged structures, consisting of two copper(II) and an iron(III) ions, in which the central iron(III) ion has an octahedral environment and the end capped two copper(II) ions have a square-planar environment. The variable-temperature susceptibilities of $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$ complex were measured and studied in the 4.2~300 K range. The least-squares fit of the experimental susceptibility based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, yielded $J = -9.89\ cm^{-1}$. The magnetic coupling parameter is consistent with an antiferromagnetic exchange interaction between the copper(II) and iron(III) ions through the oxalato-bridge in the complex.

Key words: oxalato-bridge, Cu(II)–Fe(III)–Cu(II), heterotrinuclear complexes, magnetic properties

Interest in syntheses and magnetic properties of heteropolymetallic systems with different paramagnetic centers is a fundamental requirement, not only for elucidation of the structural and electronic factors governing magnetic interaction between paramagnetic centers, but also for gaining some insight into the electronic and geometric structure of metalloproteins and enzymes and, thus, correlating structure with biological function, and for obtaining useful information about designing and synthesizing molecule-based magnets and investigating the spin-exchange mechanism between paramagnetic metal ions [1–8]. So far much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. Amongst 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 [9–12].

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Therefore, with the aim of providing some answers to questions regarding the effectiveness of bridging ligands, like oxalates, in propagating exchange interactions, it is of considerable interest to synthesize and to study polynuclear complexes with bridging oxalato in order to gain some insight into the molecular magnetism of this kind of complexes.

In this paper, we describe the synthesis and characterization of three new copper(II)–iron(III)–copper(II) heterotrinuclear complexes, $[Cu_2Fe(ox)_3L_2]ClO_4$, using potassium tris(oxalato)iron(III) as a polyatomic bridging ligand [L = 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) or 5-chloro-1,10-phenanthroline (Cl-phen), ox stands for oxalate dianions]. The magnetic properties of the complex $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$ were studied in detail.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. 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 [13,14]. The terminal ligands, 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) or 5-chloro-1,10-phenanthroline (Cl-phen), were used as commercially obtained.

Synthesis of $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$ (1): To a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (2.1 mmol, 778.1 mg) stirred in methanol (20 mL) was added successively dropwise a methanol solution (15 mL) of $K_3[Fe(ox)_3]\cdot 3H_2O$ (1.0 mmol, 491.3 mg). The vigorous stirring was continued at room temperature (about 30 minutes). Then, to the resulting mixture was added a methanol solution (20 mL) of Ph-phen (2.0 mmol, 512.6 mg). After stirring the mixture for *ca* 12 h in a darkness, the blue 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 (1:2) mixture. Yield, 762.5 mg (72%); m.p. 301.2°C.

Synthesis of $[Cu_2Fe(ox)_3(Ph_2\text{-}phen)_2]ClO_4$ (2): This complex was obtained as dark blue microcrystals by the same procedure, using the same amounts of reagents as above, but with Ph_2-phen instead of Ph-phen. Recrystallization was carried out from a hot acetonitrile solution. Yield, 1029.6 mg (85%); m.p. 299.7°C.

Synthesis of $[Cu_2Fe(ox)_3(Cl\text{-}phen)_2]ClO_4$ (3): This complex was obtained as violet-blue powder by the same procedure using the same amounts of reagents as above, but with Cl-phen instead of Ph-phen. Yield, 605.1 mg (62%); m.p. 248.9°C.

Measurements: Analyses for C, H and N were carried out on a Perkin-Elmer elemental analyzer model 240 confirming the compositions given. Metal contents were determined on an ICP-9000 isoionic emission spectrophotometer. The infrared spectra were measured on a Shimadzu infrared spectrophotometer model 810 in KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. 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 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 [15] 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 trinuclear complexes: Two synthetic strategies are generally available for the preparation of discrete heterotrinuclaear complexes. The first one uses the heterobinucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions. The second strategy uses the complex ligand that contains a potential donor group capable of coordinating to another metal ion. In this study, our aim was to obtain copper(II)–iron(III)–copper(II) heterotrinuclear complexes, therefore, the latter method was adopted. As the ligand complex we have selected potassium tris(oxalato)iron(III) trihydrate, $K_3[Fe(ox)_3]\cdot 3H_2O$, as a mononuclear fragment, because it can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes. Simultaneously, 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) or 5-chloro-1,10-phenanthroline (Cl-phen) were used as the terminal ligands. Indeed, the elemental analytical data for the newly prepared complexes indicate that the reaction of $K_3[Fe(ox)_3]\cdot 3H_2O$ with $Cu(ClO_4)_2\cdot 6H_2O$ and the terminal ligand L (L = Ph-phen, Ph_2-phen, Cl-phen) in *ca* 1:2:2 mole ratio yielded the trinuclear complexes of the general formula $[Cu_2Fe(ox)_3L_2]ClO_4$, as expected. These complexes are the first examples Cu(II)–Fe(III)–Cu(II) bridged by potassium tris(oxalato)iron(III). On the basis of the molar conductivity, room-temperature magnetic moment measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

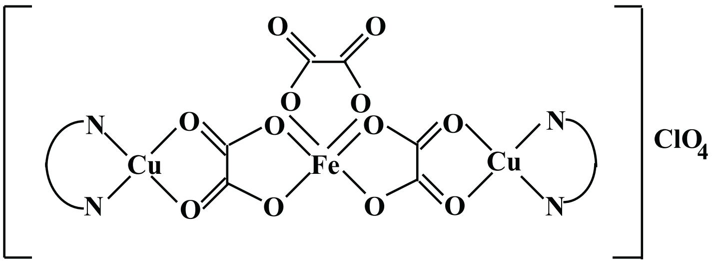

Figure 1. Suggested coordination environment of the complexes ($\widehat{N\,N}$ = Ph-phen, Ph_2-phen, Cl-phen).

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 complexes are fairly stable in air so as to allow physical measurements. For the three trinuclear complexes, the observed molar conductance values in acetonitrile solution at 25°C (in the 140~148 $\Omega^{-1}cm^2mol^{-1}$ range) are given in Table 1. These values are indicative of 1:1 electrolytic nature [16], in accord with the presumed structure of the trinuclear complexes shown in Fig. 1. The trinuclear structure was further proved by the following results.

Infrared spectra: Since the IR spectra of all the three trinuclear complexes are similar, discussion is confined to the most important vibrations in 400~4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands of the trinuclear complexes and the mononuclear fragment $K_3[Fe(ox)_3]\cdot 3H_2O$, together with their assignments, are given in Table 1. We here discuss selected infrared bands. It is noteworthy that the spectrum of the mononuclear complex $K_3[Fe(ox)_3]\cdot 3H_2O$ only shows typical of a bidentate coordination mode of the oxalato group. However, the IR spectra of the three trinuclear complexes exhibit bands corresponding to the bidentate oxalato ligand (*ca* 1720, 1685, 1645 cm^{-1} [$\nu_{as}(CO)$]; 780 cm^{-1} [$\delta(CO)$]) and also the bridging oxalato ligand (*ca* 1630 cm^{-1} [$\nu_{as}(CO)$]; 1370, 1320 cm^{-1} [$\nu_s(CO)$]) [11,12], suggesting that the oxalato group of the mononuclear fragment coordinate with copper(II) ions to form trinuclear complexes. The appearance of a new band at 470 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 of aromatic ring of the end-capping ligands (Ph-phen, Ph_2-phen, Cl-phen) 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 420 cm^{-1} due to ν(Cu–N) further supports this view. In addition, the bands centered at 1100 cm^{-1} and 630 cm^{-1}, typical for ν(Cl–O) stretching of the perchlorate group [17,18], was found for the three trinuclear complexes, which coincides with the conductance data of these trinuclear complexes.

Electronic spectra: In order to obtain further structural information of these trinuclear complexes, the electronic spectra of the mononuclear fragment $K_3[Fe(ox)_3]\cdot 3H_2O$ and the trinuclear copper(II)-iron(III)-copper(II) complexes were studied and assigned on the basis of a careful comparison of the latter with the former. As shown in Table 2, the electronic spectra of three trinuclear complexes in DMF solutions are similar. For all three trinuclear complexes, four d-d bands centered at 850~853, 532~540, 392~398 and 625~630 nm were observed. The very weak absorptions of the three d-d bands (850~853, 532~540 and 392~398 nm) are commensurate with a six-coordinated octahedral configuration around iron(III) [19], whilst the strong band (625~630 nm) may be attributed to the d-d transition of copper(II) in a square-planar environment. In addition, a stronger band at 318~325 nm was also observed in the electronic spectra of the trinuclear complexes, which may be attributed to charge-transfer bands. Further investigation of these and similar systems is still required in order to obtain a detailed assignment for charge transfer.

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

Com-	Λ_M	μ_{eff}	ν(ox) (bidentate)		ν(ox) (bridging)					
plex	$S\cdot cm^2\cdot mol^{-1}$	(B.M.)	$\nu_{as}(CO)$	$\delta(CO)$	$\nu_{as}(CO)$	$\nu_s(CO)$	ν(Cu–O)	ν(Cu–N)	$\nu(ClO_4^-)$	ν(C–H)
(**1**)	142	6.28	1720,1683,1665	780	1632	1370,1330	470	415	1100, 630	856,725
(**2**)	140	6.15	1715,1688,1660	785	1630	1366,1320	472	421	1098, 630	850,722
(**3**)	148	6.20	1712,1685,1668	782	1635	1372,1328	465	420	1100, 628	852,719

(**1**) = $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$, (**2**) = $[Cu_2Fe(ox)_3(Ph_2\text{-}phen)_2]ClO_4$, (**3**) = $[Cu_2Fe(ox)_3(Cl\text{-}phen)_2]ClO_4$.

Table 2. Electronic spectral bands and assignments of the trinuclear complexes.

Complex	UV (nm)/ε_{max} (mol^{-1}·cm^{-1}·L)				
	CT	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	$^6A_{1g} \rightarrow {}^4E_g(G)$	$^2B_{1g} \rightarrow {}^2E_g$
[$Cu_2Fe(ox)_3$(Ph-phen)$_2$]ClO_4	318(29670)	845(10)	540(9)	392(18)	628(17)
[$Cu_2Fe(ox)_3$(Ph_2-phen)$_2$]ClO_4	325(31780)	853(8)	535(14)	395(11)	625(20)
[$Cu_2Fe(ox)_3$(Cl-phen)$_2$]ClO_4	320(28465)	850(12)	532(16)	398(15)	630(14)

In spite of our many attempts, single crystals suitable for X-ray crystallography have not yet been obtained for these complexes. However, based on the composition of these complexes, their infrared spectra, electronic spectra, conductivity measurements and magnetic characterization (*vide infra*), these complexes are proposed to have an extended ox-bridged structure and to contain two copper(II) and an iron(III) ions, in which the central iron(III) ion has an octahedral environment and the end capped two copper(II) ions have a square-planar environment, as shown in Figure 1. The plausible trinuclear structure of these complexes is further characterized by the following magnetic studies.

Magnetic properties of [$Cu_2Fe(ox)_3$(Ph-phen)$_2$]ClO_4: The observed magnetic moment per trinuclear complex at room temperature, shown in Table 1, is less than the spin-only value (6.40 B.M) for a copper(II)–iron(III)–copper(II) trinuclear complex with three spin-system (S_1, S_2, S_3) = (1/2, 5/2, 1/2) in the absence of an exchange interaction. This result suggests the presence of a weak antiferromagnetic spin-exchange interaction in these complexes [20]. In order to obtain further information on the structure of the complexes, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for complex [$Cu_2Fe(ox)_3$(Ph-phen)$_2$]ClO_4, and the results are shown in Figure 2 in the form of the μ_{eff} *versus* T plot, μ_{eff} being the effective magnetic moment and T the absolute temperature. From Figure 2 it is evident that the curve of the effective magnetic moment (μ_{eff}) decrease steadily when the temperature

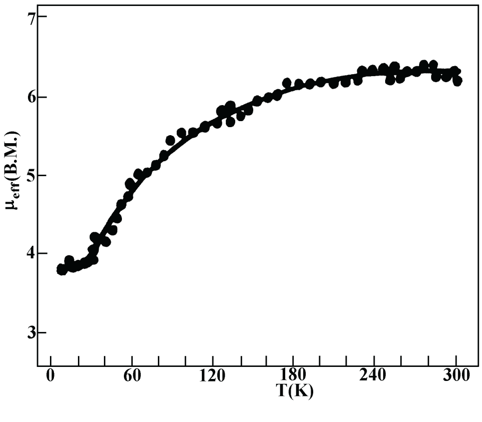

Figure 2. Temperature variation of μ_{eff} for the complex [$Cu_2Fe(ox)_3$(Ph-phen)$_2$]ClO_4. The curve is based on equation (1) using the magnetic parameters given in the text. (•), experimental data; (-), calculated curve as described in the text.

is lowered, indicating the operation of intramolecular antiferromagnetic interaction through the ox-bridge within each trinuclear complex. Thus, as noted above, the observed magnetic behavior both at room-temperature and variable-temperature clearly demonstrates the operation of a weak intramolecular antiferromagnetic spin-exchange interactions between iron(III) and copper(II) ions through the ox-bridge within each trinuclear unit [21].

In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic susceptibility data were analyzed on the basis of a symmetrical three-spin system derived from a spin-Hamiltonian operator:

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) - 2J'\hat{S}_1 \cdot \hat{S}_3$$

$\hat{S}_1, \hat{S}_2$ and $\hat{S}_3$ being the spin operators of copper(II), iron(III) and copper(II), respectively. The meaning of J and J′ is indicated by the following diagram, which respresents the simplest scheme consistent with the available data:

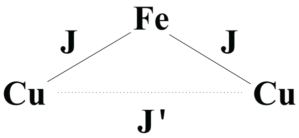

Figure 3. Magnetic exchange parameters of the trinuclear complexes.

Because the two copper(II) ions in the Cu_2Fe 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. Assuming that the exchange integral between the terminal copper(II) ions is zero (J′ = 0), the molar susceptibility of copper(II)–iron(III)–copper(II) ($S_1 = S_3 = 1/2$, $S_2 = 5/2$) system is given by

$$\chi_M = \frac{N\beta^2 g^2}{4kT}\left[\frac{A}{B}\right] \tag{1}$$

A = 35 + 10exp(−7J/kT) + 35exp(−2J/kT) + 84exp(5J/kT), B = 3 + 2exp(−7/kT) + 3exp(−2J/kT) + 4exp(5J/kT),

where χ_M denotes the molecular susceptibility per trinuclear complex, and the remaining symbols have their usual meanings. As shown in Figure 2, good least-square fits to the experimental data were obtained with equation (1) for complex $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$. 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: $J = -9.89\ cm^{-1}$, $g = 2.04$, $F = 2.8\times10^{-5}$. The results (negative and small J value) indicate that the complex undergoes weak antiferromagnetic spin-exchange interaction between the copper(II) and iron(III) ions. The small and negative J value observed for the complex can be rationalized on the basis of the method of magnetic orbital interaction between the iron(III) and copper(II) ions, as proposed by Kahn [9,22].

Considering the symmetry of the [Fe(ox)Cu] skeleton of the oxalate bridging network close to C_{2V} (for the definition of X and Y coordinates, see Figure 4), the 3d metallic orbitals of copper(II) and iron(III) ions transform [22] as $a_1(d_{z^2}$ and $d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{xz})$. 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 the point group theory, because there is no orthogonality between b_1(Cu) and b_1(Fe), namely $S = \langle b_1(Cu)|b_1(Fe)\rangle \neq 0$, therefore, the antiferromagnetic interaction between the Cu(II) and Fe(III) ions should be observed. In addition, because the distance between the Cu(II) and Fe(III) ions in these trinuclear complexes is long, the small J value is reasonable.

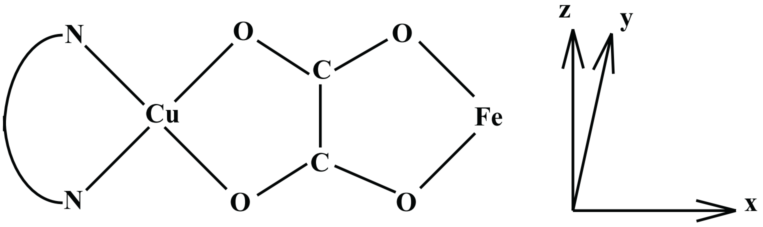

Figure 4. The structure of the [Fe(ox)Cu] skeleton.

Conclusions: One area of current interest involves Cu(II)–Fe(III) heteropolynuclear complexes, which are potential analogue compounds for a redox center of the cytochrome oxidase molecule. These systems also raise important magnetochemical questions, in which the focus is more upon the fundamental electronic properties of the compound. In order to gain insight into the molecular magnetism of this kind of complexes, in this paper, we describe the synthesis and characterization of three new copper(II)–iron(III)–copper(II) heterotrinuclear complexes, $[Cu_2Fe(ox)_3L_2]ClO_4$, using potassium tris(oxalato)iron(III) as a polyatomic bridging ligand [L = 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen) or 5-chloro-1,10-phenanthroline (Cl-phen), ox stands for oxalate dianions]. Although the crystal structure of the $Cu_2^{II}Fe^{III}$ complexes is not known, the magnetic and spectroscopic data are sufficient to deduce the occurrence of a magnetically coupled heterotrinuclear unit containing one Fe(III) and two Cu(II) ions. The heterotrinuclear cluster described above has been shown to contain antiferromagnetically coupled Cu(II) and Fe(III) ions. The lowest multiplet has total spin S = 3/2 and is consistent with the expected ionic spins of 1/2 and 5/2 for Fe(III). The magnetic data can be understood in terms of a weak coupling between the copper atoms and a much stronger coupling between iron and copper atoms. This is consistent with the structure shown in Figure 3, where the copper atoms are not bridged directly, but where iron and copper atoms are directly connected by the bridge. These descriptions are currently being sought in order to arrive at a more detailed understanding of the magnetism of these interesting complexes.

Acknowledgments

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