

## Synthesis, Characterization and Magnetic Properties of Copper(II)–Iron(III) Heterotetranuclear Complexes Bridged by Tris(oxalato)ferrate(III)

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The strategy of “complex as ligand” allowed us to synthesize three new  $\mu$ -oxalato-bridged heterotetranuclear complexes identified as  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$  (**1**),  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$  (**2**) and  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{phen})_3](\text{ClO}_4)_3$  (**3**), where ox represents the oxalato dianions;  $\text{Me}_2\text{bpy}$ ,  $\text{Me}_2\text{phen}$  and phen stand for 4,4'-dimethyl-2,2'-bipyridine, 2,9-dimethyl-1,10-phenanthroline or 1,10-phenanthroline, respectively. These complexes are the first examples of  $[\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}]$  species bridged by oxalato groups. 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 an iron(III) ion, in which the iron(III) ion has an octahedral environment, and the three copper(II) ions have a square-planar environment. The complexes (**1**) and (**2**) were further characterized by variable-temperature magnetic susceptibility (4.2–300 K) measurements and the observed data were simulated by the equation based on the spin Hamiltonian operator,  $\hat{H} = -2J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Fe}} + \hat{S}_{\text{Cu2}} \cdot \hat{S}_{\text{Fe}} + \hat{S}_{\text{Cu3}} \cdot \hat{S}_{\text{Fe}})$ , giving the exchange integrals  $J = -9.15 \text{ cm}^{-1}$  for (**1**) and  $J = -8.79 \text{ cm}^{-1}$  for (**2**). The results indicate the presence of an antiferromagnetic spin-exchange interaction between the copper(II) and iron(III) ions through the oxalato-bridge in both complexes (**1**) and (**2**).

**Key words:**  $\mu$ -oxalato-bridge, copper(II), iron(III), heterotetranuclear complexes, magnetism, synthesis

Recent years have witnessed a growing interest involving copper(II)–iron(III) heteropolynuclear complexes, which are potential analogue complexes for a redox center of the cytochrome oxidase molecule. Interest in this area is a 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 [1–6].

It is known, that 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

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bridging ligand in supporting magnetic exchange interactions. Several kinds of complexes, bridged by the oxalato group, have been synthesized and their magnetic properties studied [7–11]. However, to the best of our knowledge, no oxalato-bridged  $[\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}]$ -type heterotetranuclear complexes have so far been reported. Therefore, we considered it of interest to synthesize and to study  $[\text{Cu}^{\text{II}}\text{Fe}^{\text{III}}]$  species, with bridging oxalato, in order to gain some insight into the molecular magnetism of this kind of complexes.

In this work, detailed here three new  $\mu$ -oxalato-bridged heterotetranuclear complexes, formulated as  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$  (**1**),  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$  (**2**) and  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{phen})_3](\text{ClO}_4)_3$  (**3**), where ox is the oxalato dianions;  $\text{Me}_2\text{bpy}$ ,  $\text{Me}_2\text{phen}$  and phen stand for 4,4'-dimethyl-2,2'-bipyridine, 2,9-dimethyl-1,10-phenanthroline and 1,10-phenanthroline, respectively, have been synthesized and characterized by using tris(oxalato)ferrate(III),  $[\text{Fe}(\text{ox})_3]^{3-}$ , as a polyatomic bridging ligand. The cryomagnetic properties of the complexes (**1**) and (**2**) were measured and studied in detail between range 4.2–300 K. At present, the three heterotetranuclear 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 heterotetranuclear 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)iron(III) trihydrate ( $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ ) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  were synthesized according to [12,13]. The terminal ligands 4,4'-dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{bpy}$ ); 2,9-dimethyl-1,10-phenanthroline ( $\text{Me}_2\text{phen}$ ) or 1,10-phenanthroline (phen) were used as commercially obtained.

**Synthesis of  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$  (**1**):** To a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (3.1 mmol, 1149 mg) stirred in water (15 mL) was added successively dropwise a methanol solution (15 mL) of  $\text{Me}_2\text{bpy}$  (3.0 mmol, 553 mg). The vigorous stirring was continued at room temperature until the mixture became limpid (about 25 minutes). It was then filtered to eliminate impurities. To the filtrate (containing the  $[\text{Cu}(\text{Me}_2\text{bpy})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  precursor) was slowly added a water solution (20 mL) of  $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  (1.0 mmol, 491.3 mg) with a rapidly stirring at room temperature. The colour of the solution turned from dark-blue to light-brown immediately and a small amount of precipitate formed. After refluxing for ca. 2 h in a darkness, the mixture was then allowed to cool to room temperature and the brown microcrystals thus obtained were removed by filtration, washed several times with methanol, water and diethyl ether and dried over  $\text{P}_2\text{O}_5$  under reduced pressure. It was recrystallized from a hot acetonitrile solution. Yield, 980 mg (72%); m.p. 312.5°C. Anal. calc. for  $\text{Cu}_3\text{FeC}_{42}\text{H}_{36}\text{N}_6\text{O}_{24}\text{Cl}_3$  (M.W. 1361.62): C, 37.05; H, 2.66; N, 6.17; Fe, 4.10; Cu, 14.00%. Found: C, 37.18; H, 2.49; N, 6.29; Fe, 3.82; Cu, 13.84%.

**Synthesis of  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$  (**2**):** This complex was obtained as red-violet microcrystals by the same procedure as above, but by using  $\text{Me}_2\text{phen}$  instead of  $\text{Me}_2\text{bpy}$ . Recrystallization was carried out from DMF/ethanol (1:1) mixture. Yield, 1147 mg (80%); m.p. 327.9°C. Anal. calc. for  $\text{Cu}_3\text{FeC}_{48}\text{H}_{36}\text{N}_6\text{O}_{24}\text{Cl}_3$  (M.W. 1433.68): C, 40.21; H, 2.53; N, 5.86; Fe, 3.90; Cu, 13.30%. Found: C, 40.09; H, 2.71; N, 5.72; Fe, 3.74; Cu, 13.18%.

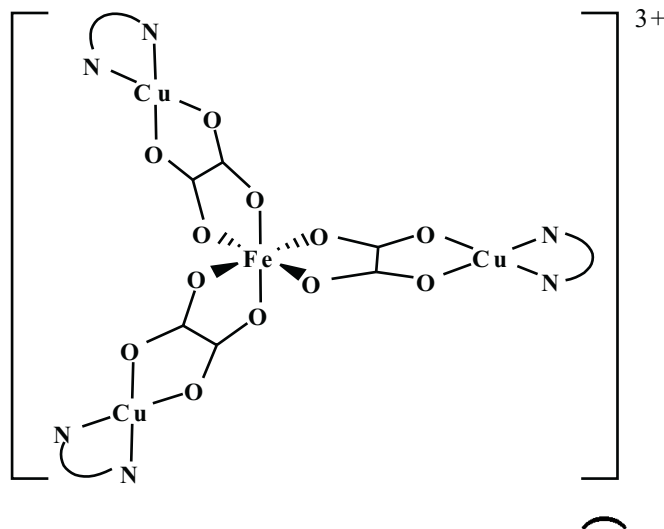
**Synthesis of  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{phen})_3](\text{ClO}_4)_3$  (**3**):** This complex was prepared as pale-violet powder in a manner similar to the synthesis of the complex (**1**) except that phen instead of  $\text{Me}_2\text{bpy}$  was used. Yield, 1012 mg (75%); m.p. 297.5°C. Anal. calc. for  $\text{Cu}_3\text{FeC}_{42}\text{H}_{24}\text{N}_6\text{O}_{24}\text{Cl}_3$  (M.W. 1349.52): C, 37.38; H, 1.79; N, 6.23; Fe, 4.14; Cu, 14.13%. Found: C, 37.16; H, 1.53; N, 6.06; Fe, 3.87; Cu, 14.37%.

**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  $\text{Hg}[\text{Co}(\text{SCN})_4]$  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 [14] for all the constituent atoms and effective magnetic moments were calculated, using the equation  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$ , where  $\chi_{\text{M}}$  is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

## RESULTS AND DISCUSSION

**Synthesis and coordination environment of the  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  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. The first is to use designed polynucleating ligand, which offers either the coordination geometry or the ligand field strength, suitable for dissimilar metal ions [15]. The second uses a complex as a "ligand", that contains a potential donor group capable of coordinating to another metal ion [10,11,16]. In this study, our aim was to obtain oxalato-bridged  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  heterotetranuclear complexes; therefore, the latter synthetic method was adopted. For this purpose, mononuclear fragment tris(oxalato)ferrate(III),  $[\text{Fe}(\text{ox})_3]^{3-}$ , was selected as "ligand complex", because (i) it can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes, (ii)  $[\text{Fe}(\text{ox})_3]^{3-}$  plays the key role in producing oxalato-bridged  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  heterotetranuclear complexes, since iron(III) ion generally leads to ill characterized materials, contaminated by the precipitation of  $\text{Fe}(\text{OH})_3$  rather than the corresponding complexes. In order to avoid this, in our synthetic approach to oxalato-bridged  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  heterotetranuclear complexes, the mononuclear fragment  $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  was used as the iron(III)-site component. Simultaneously, 4,4'-dimethyl-2,2'-bipyridine, 2,9-dimethyl-1,10-phenanthroline ( $\text{Me}_2\text{phen}$ ) or 1,10-phenanthroline (phen) 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  $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$  with  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the terminal ligand L (L =  $\text{Me}_2\text{bpy}$ ,  $\text{Me}_2\text{phen}$ , phen) in *ca.* 1:3:3 mole ratio yielded the heterotetranuclear complexes of the general formula  $[\text{Cu}_3\text{Fe}(\text{ox})_3\text{L}_3](\text{ClO}_4)_3$ , as expected. These complexes are the first examples of  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  species, bridged by tris(oxalato)ferrate(III). On the basis of the molar conductivity, room-temperature magnetic moment measurements, spec-

troscopic (IR, UV and ESR) characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.



**Figure 1.** Suggested coordination environment of the tetranuclear complexes (N—N = Me<sub>2</sub>bpy, Me<sub>2</sub>phen, phen).

**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 ( $212\sim 220\ \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ) in DMF solution at  $25^\circ\text{C}$  are given in Table 1. These values are indicative of 1:3 electrolytic nature [17], in accord with the presumed structure of the tetranuclear complexes shown in Fig. 1. The  $[\text{Cu}_2^{\text{II}}\text{Fe}^{\text{III}}]$  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  $\text{K}_3[\text{Fe}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$  and the copper(II)–iron(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 vibrations in  $400\sim 4000\ \text{cm}^{-1}$  region in relation to the structure. The most relevant IR absorption bands of the heterotetranuclear complexes and the mononuclear fragment  $\text{K}_3[\text{Fe}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ , together with their assignments are given in Table 1. It is noteworthy that the spectrum of the mononuclear complex  $\text{K}_3[\text{Fe}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$  shows a broad band at *ca.*  $1720\ \text{cm}^{-1}$  and a medium band at  $805\ \text{cm}^{-1}$ , which are attributed to  $\nu(\text{CO})$  and  $\delta(\text{CO})$  of a bidentate coordination mode of the oxalato groups, respectively. However, the IR spectra of the three copper(II)–iron(III) tetranuclear complexes only exhibit bands corresponding to the typical bridging coordination mode of oxalato groups (*ca.*  $1650\ \text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{CO})$ ];

1370, 1340  $\text{cm}^{-1}$  [ $\nu_s(\text{CO})$ ] [7,9]), suggesting that the oxalato groups of the mononuclear fragment ( $\text{K}_3[\text{Fe}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ ) have coordinated with three copper(II) ions to form tetranuclear complexes. The appearance of a new band at *ca.* 560  $\text{cm}^{-1}$ , due to  $\nu(\text{Cu}-\text{O})$  has further proved the coordination mode of oxalato groups. On the other hand, the  $\delta(\text{C}-\text{H})$  deformation bands of aromatic ring of the end-capping ligands ( $\text{Me}_2\text{bpy}$ ,  $\text{Me}_2\text{phen}$ , phen) 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 around 580  $\text{cm}^{-1}$  due to  $\nu(\text{Cu}-\text{N})$  further supports this view. In addition, a broad intense band centered at *ca.* 1100  $\text{cm}^{-1}$  and a strong sharp band at *ca.* 630  $\text{cm}^{-1}$ , typical for a non-coordinated perchlorate group [18], were present for all the tetranuclear complexes, which coincides with the conductance data of these tetranuclear complexes.

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

Complexes	$\Lambda_M$ ( $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)	IR ( $\text{cm}^{-1}$ )					
			$\nu_{\text{as}}(\text{CO})$	$\nu_s(\text{CO})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Cu}-\text{O})$	$\nu(\text{ClO}_4^-)$	$\delta(\text{C}-\text{H})$
$[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$	215	6.35	1658	1376, 1346	587	565	1098, 628	860, 728
$[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$	212	6.26	1652	1373, 1340	584	562	1095, 630	857, 720
$[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{phen})_3](\text{ClO}_4)_3$	220	6.18	1650	1375, 1345	582	560	1099, 626	859, 730

**Table 2.** Electronic spectral bands and assignments of the tetranuclear complexes.

Complexes	UV-Vis $\nu(10^3 \text{ cm}^{-1})/\epsilon_{\text{max}} (\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$				
	CT	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$
$[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$	32.1(3480)	11.7(140)	18.5(136)	25.2(328)	16.7(282)
$[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$	31.5(3500)	11.5(150)	18.3(132)	25.4(330)	16.5(295)
$[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{phen})_3](\text{ClO}_4)_3$	31.6(3460)	11.8(148)	18.2(135)	25.3(335)	16.4(290)

**Electronic spectra:** The electronic spectral data of these complexes (in acetonitrile 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, four d-d bands in the visible and infrared range are observed (see Table 2). The band at  $(16.4\sim 16.7) \times 10^3 \text{ cm}^{-1}$  may be attributed to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  transition of copper(II) in a square-planar environment [19], while the other three d-d bands, appearing in the  $(11.8\sim 11.5) \times 10^3 \text{ cm}^{-1}$ ,  $(18.5\sim 18.2) \times 10^3 \text{ cm}^{-1}$  and  $(25.4\sim 25.2) \times 10^3 \text{ cm}^{-1}$  regions, may be assigned to the  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$

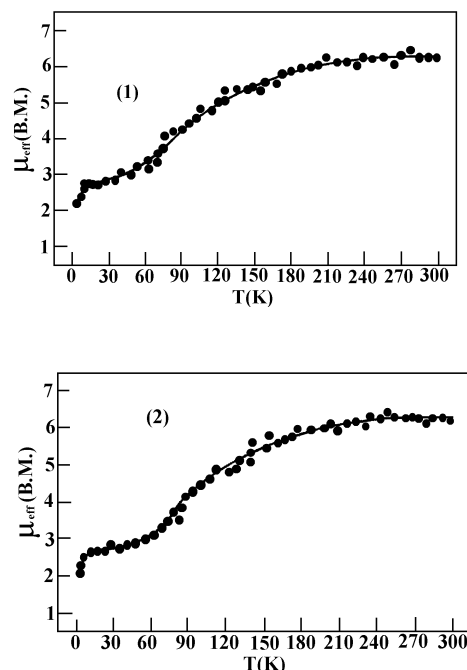
transitions, in the order of increasing energy, consistent with the presence of a six-coordinated octahedral configuration around iron(III) ion [19]. These formally spin-forbidden bands for iron(III) ion may be activated by an exchange mechanism [20]. In addition, the stronger band at  $(31.5\sim32.1)\times10^3\text{ cm}^{-1}$ , observed in the electronic spectra of the three tetranuclear complexes, may be attributable to charge-transfer band. Further investigation of these and similar systems is still required, in order to obtain more detailed assignment for the 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 have been recorded at room temperature. It is noted, that the ESR spectra of the three tetranuclear complexes are similar and the ESR spectra showed no signals, indicating that the ground state of the three heterotetranuclear complexes is  $S = 2$ , in accord with the following magnetically deduced conclusion [21]. 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 complexes.

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 an iron(III) ions, in which the iron(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 less than the spin-only value (6.63 B.M) for a  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  tetranuclear complex with four spin-system ( $S_{\text{Cu1}}, S_{\text{Cu2}}, S_{\text{Cu3}}, S_{\text{Fe}} = (1/2, 1/2, 1/2, 5/2)$ ) in the absence of an exchange interaction. This result suggests the presence of a weak antiferromagnetic spin-exchange interaction in these complexes. In order to obtain further information on the structure of the complexes, the magnetic data have been used to deduce the indicated tetranuclear structure. Therefore, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for the complexes  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$  (**1**) and  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$  (**2**), by way of example, and the results are shown in Fig. 2 in the form of plot of  $\mu_{\text{eff}}$  vs.  $T$ , where  $\mu_{\text{eff}}$  and  $T$  denote molar effective magnetic moment per molecule and absolute temperature. From Fig. 2 it can be seen that the magnetic behavior of the two heterotetranuclear complexes is similar. It decreases smoothly upon cooling and reaches a plateau in the low temperature range 10~20 K with  $\mu_{\text{eff}}$  between 2.78 and 2.81 B.M. The plateau corresponds to the temperature range, where only the triplet ground state is thermally populated. The rapid decrease of the magnetic moment below 10 K may be attributed to secondary effects, such as zero-field splitting and/or to an intermole-

cular 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 antiferromagnetic spin-exchange interactions between iron(III) and copper(II) ions through the ox-bridge within the  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  tetranuclear unit [22].



**Figure 2.** Temperature variation of  $\mu_{\text{eff}}$  for the complexes  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Mebpy})_3](\text{ClO}_4)_3$  (**1**) and  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$  (**2**). The curves are based on equations (1) and (2) using the magnetic parameters given in the text. (•), experimental data; (—), calculated curve as described in the text.

In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic analysis was carried out using equation (1) based on the spin Hamiltonian operator ( $\hat{H} = -2J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Fe}} + \hat{S}_{\text{Cu2}} \cdot \hat{S}_{\text{Fe}} + \hat{S}_{\text{Cu3}} \cdot \hat{S}_{\text{Fe}})$  ( $S_{\text{Cu1}} = S_{\text{Cu2}} = S_{\text{Cu3}} = 1/2$ ,  $S_{\text{Fe}} = 5/2$ ) with molecular field exchange model [23]:

$$\chi_M = \frac{Ng^2\beta^2}{kT} \left[ \frac{A}{B} \right] + N\alpha \quad (1)$$

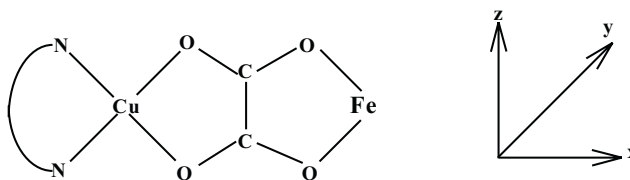
$$A = 2 + 10\exp(4J/kT) + 20\exp(7J/kT) + 28\exp(10J/kT) + 56\exp(13J/kT) + 60\exp(18J/kT)$$

$$B = 3 + 5\exp(4J/kT) + 10\exp(7J/kT) + 7\exp(10J/kT) + 14\exp(13J/kT) + 9\exp(18J/kT)$$

$$\chi'_M = \chi_M/[1 - 2ZJ'\chi_M/N\beta^2g^2] \quad (2)$$

where  $\chi_M$  is the molecular susceptibility per tetranuclear complex in the absence of the molecular exchange field (1),  $J$  is the exchange integral and  $ZJ'$  is the product of the molecular field-exchange constant and the number of interacting nearest neighbours,  $N_\alpha$  is the temperature-independent paramagnetism ( $460 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ ), and the remaining symbols have their usual meanings. As shown in Fig. 2, good least-square fits to the experimental data were obtained with (1) and (2) for the complexes  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{bpy})_3](\text{ClO}_4)_3$  (**1**) and  $[\text{Cu}_3\text{Fe}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3$  (**2**). The magnetic parameters, thus determined, and the agreement factor  $F$ , defined here as  $F = \sum[(\chi_M)_{\text{calc.}} - (\chi_M)_{\text{obs.}}]^2 / \sum(\chi_M)_{\text{obs.}}$  are  $J = -9.15 \text{ cm}^{-1}$ ,  $ZJ' = -0.57 \text{ cm}^{-1}$ ,  $g = 2.03$ ,  $F = 1.7 \times 10^{-4}$  for (**1**) and  $J = -8.79 \text{ cm}^{-1}$ ,  $ZJ' = -0.62 \text{ cm}^{-1}$ ,  $g = 2.06$ ,  $F = 3.6 \times 10^{-4}$  for (**2**). The results indicate, that the complexes undergo weak antiferromagnetic spin-exchange interaction between the copper(II) and iron(III) ions through an oxalato-bridge within each tetranuclear molecule.

To describe the mechanism of the exchange interaction, several models have been proposed [8,24–26]. 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  $[\text{Fe}(\text{ox})\text{Cu}]$  skeleton of the oxalate bridging network close to  $C_{2v}$  (for the definition of X and Y coordinates, see Fig. 3), in  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  heterotetranuclear system, the 3d metallic orbitals of copper(II) and iron(III) ions transform [27] 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 the point group theory, because there is no strict orthogonality of the magnetic orbitals between copper(II) and iron(III) ions can be realized, namely,  $S = \langle b_1(\text{Cu}) | b_1(\text{Fe}) \rangle \neq 0$ , therefore, the antiferromagnetic interaction between the copper(II) and iron(III) ions within complexes (**1**) and (**2**) should be observed. This may be the reason for an antiferromagnetic spin-exchange interaction observed in these  $[\text{Cu}_3^{\text{II}}\text{Fe}^{\text{III}}]$  heterotetranuclear complexes.



**Figure 3.** The structure of the  $[\text{Fe}(\text{ox})\text{Cu}]$  skeleton.



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