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Synthesis and Ferromagnetic Interaction in Oxalato-Bridged Copper(II)–Chromium(III)–Copper(II) Heterotrinuclear Complexes

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The strategy of "complex as ligand" allowed us to synthesize four new μ-oxalato-bridged copper(II)–chromium(III)–copper(II) heterotrinuclear complexes described by the overall formula $[Cu_2Cr(ox)_3L_2]ClO_4$, where ox represents the oxalato dianions; L stands for 5-phenyl-1,10-phenanthroline (Ph-phen); 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen). 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 oxalato-bridged structure consisting of two copper(II) ions and a chromium(III) ion, in which the chromium(III) ion has an octahedral environment, and the two copper(II) ions have a square-planar environment. The $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$ complex was 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, $\hat{H} = -2J(\hat{S}_{Cu1}\cdot\hat{S}_{Cr} + \hat{S}_{Cu2}\cdot\hat{S}_{Cr})$, giving the exchange integral $J = +12.8\ cm^{-1}$. The result indicates the presence of a ferromagnetic spin-exchange interaction between the copper(II) and chromium(III) ions through the oxalato-bridge in the complex.

Key words: oxalato-bridge, Cu(II)–Cr(III)–Cu(II), heterotrinuclear complexes, ferromagnetic interaction

The synthesis and magnetic investigations of heteropolynuclear complexes propagated by multiatom bridges are of current interest, 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 [1–3]. So far, much effort has been devoted to the design of high-spin molecules and several strategies have been proposed along this line [4–11]. The strict orthogonality of magnetic orbital can be attained by choosing an appropriate combination of paramagnetic metal ions, and hence the design of ferromagnetic complexes based on the concept of strict orthogonality seems promising [5–8]. It is known that a combination of chromium(III) and copper(II) ions can give rise to such strict orthogonality of magnetic

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orbitals [5–8,12]. The feasibility of the strategy has been revealed by magnetic analyses for some of copper(II)-chromium(III) complexes [5–8,12]. However, as far as we are aware, examples of such heteronuclear complexes are still few, especially comparatively little attention has been given to the copper(II)–chromium(III)–copper(II) heterotrinuclear systems with bridging oxalato. Taking into account above facts, it is of considerable interest to synthesize and study copper(II)–chromium(III)–copper(II) heterotrinuclear complexes bridged by oxalato group in order to gain some insight into the molecular magnetism of this kind of complexes.

In this paper, four new μ-oxalato-bridged heterometal trinuclear complexes, which have the general formula $[Cu_2Cr(ox)_3L_2]ClO_4$ (ox = oxalate dianion, L = Ph-phen, Ph_2-phen, Cl-phen, Br-phen) 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 magnetic properties of the complex $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$ were studied in detail. The main result of this investigation is that the copper(II) and chromium(III) ions are coupled in a weak ferromagnetic fashion *vis* isotropic coupling ($J = +12.8\ cm^{-1}$) through the oxalato bridge.

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 [13] method. The terminal ligands 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were used as commercially obtained.

Synthesis of $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$ (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 (10 mL) of $K_3[Cr(ox)_3]\cdot 3H_2O$ (1.0 mmol, 491.3 mg). The vigorous stirring was continued at room temperature until the mixture became limpid (about 1 h). It was then filtered. To the filtrate was added a methanol solution (15 mL) of Ph-phen (2.0 mmol, 512.6 mg). The solution changed colour immediately and a small amount of pale violet precipitate was formed. After stirring the mixture for *ca* 2 h the 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 an acetonitrile/ethanol (1:1) mixture. Yield, 823.1 mg (78%); m.p. 322.8°C. Anal. calc. for $Cu_2CrC_{42}H_{24}N_4O_{16}Cl$ (M.W. 1055.20): C, 47.81; H, 2.29; N, 5.31; Cr, 4.93; Cu, 12.04%. Found: C, 47.62; H, 2.10; N, 5.11; Cr, 4.74; Cu, 12.28%.

Synthesis of $[Cu_2Cr(ox)_3(Ph_2\text{-}phen)_2]ClO_4$ (2): This complex was obtained as pale brown microcrystals by the same procedure and the same amounts of reagents as above, but by using Ph_2-phen instead of Ph-phen. Recrystallization was carried out from DMF/ethanol (1:4) mixture. Yield, 965.9 mg (80%); m.p. 276.1°C. Anal. calc. for $Cu_2CrC_{54}H_{32}N_4O_{16}Cl$ (M.W. 1207.39): C, 53.72; H, 2.67; N, 4.64; Cr, 4.31; Cu, 10.53%. Found: C, 53.55; H, 2.46; N, 4.38; Cr, 4.56; Cu, 10.37%.

Synthesis of $[Cu_2Cr(ox)_3(Cl\text{-}phen)_2]ClO_4$ (3): This complex was obtained as orange-tan powder by the same procedure and the same amounts of reagents as above, but by using Cl-phen instead of Ph-phen. Yield, 660.9 mg (68%); m.p. 288.3°C. Anal. calc. for $Cu_2CrC_{30}H_{14}N_4O_{16}Cl_3$ (M.W. 971.89): C, 37.08; H, 1.45; N, 5.76; Cr, 5.35; Cu, 13.08%. Found: C, 36.85; H, 1.30; N, 5.47; Cr, 5.19; Cu, 13.24%.

Synthesis of $[Cu_2Cr(ox)_3(Br\text{-}phen)_2]ClO_4$ (4): This complex was obtained as orange-red powder by the same procedure and the same amounts of reagents as above, but by using Br-phen instead of Ph-phen. Yield, 763.8 mg (72%); m.p. 259.0°C. Anal. calc. for $Cu_2CrC_{30}H_{14}N_4O_{16}Br_2Cl$ (M.W. 1060.81): C, 33.97; H, 1.33; N, 5.28; Cr, 4.90; Cu, 11.98%. Found: C, 33.81; H, 1.19; N, 5.57; Cr, 5.12; Cu, 11.75%.

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-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 Cary 300 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 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 $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, 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: One of the best strategies to design and synthesize polynuclear species is the "complex as ligand" approach, *i.e.* using mononuclear complexes that contain potential donor groups capable of coordinating to another metal ion. In this study, our aim was to obtain copper(II)–chromium(III)–copper(II) heterotrinuclear 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 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), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-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 $K_3[Cr(ox)_3]\cdot 3H_2O$ with $Cu(ClO_4)_2\cdot 6H_2O$ and the terminal ligand L (L = Ph-phen, Ph_2-phen, Cl-phen, Br-phen) in *ca* 1:2:2 mole ratio yielded the trinuclear complexes of the general formula $[Cu_2Cr(ox)_3L_2]ClO_4$, as expected. These complexes are the first examples Cu(II)–Cr(III)–Cu(II) 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 Figure 1.

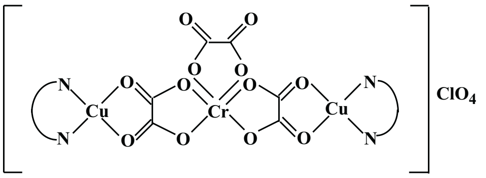

Figure 1. Suggested coordination environment of the complexes ($\overset{\frown}{N\,N}$ = Ph-phen, Ph_2-phen, Cl-phen, Br-phen).

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 complexes are fairly stable in air so as to allow physical measurements. For the four trinuclear complexes, the observed molar conductance values (145~150 $\Omega^{-1}\cdot cm^2 \cdot mol^{-1}$) in acetonitrile solution at 25°C are given in Table 1. These values are indicative of 1:1 electrolytic nature [15], in accord with the presumed structure of the trinuclear complexes shown in Figure 1. The trinuclear structure was further characterized by the following results.

Infrared 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)–Cu(II) heterotrinuclear 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 four trinuclear 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 trinuclear 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 $K_3[Cr(ox)_3]\cdot 3H_2O$ only shows typical of a bidentate coordination mode of the oxalato group. However, the IR spectra of the four trinuclear complexes exhibit bands corresponding to the bidentate oxalato ligand (*ca* 1710, 1680, 1650 cm^{-1} [$\nu_{as}(CO)$]; 790 cm^{-1} [$\delta(CO)$]) and also the bridging oxalato ligand (*ca* 1620 cm^{-1} [$\nu_{as}(CO)$]; 1380, 1340 cm^{-1} [$\nu_s(CO)$]) [11,16], 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 *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 of aromatic ring of the end-capping ligands (Ph-phen, Ph_2-phen, Cl-phen, Br-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 430 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 four trinuclear complexes, which coincides with the conductance data of these trinuclear 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 four trinuclear complexes are similar to each other. For all four trinuclear complexes, three d-d bands in the visible and infrared range are observed (see Table 2). The two weak bands centered at $(23.1{\sim}23.5)\times10^3$ cm^{-1} and $(14.0{\sim}14.4)\times10^3$ cm^{-1} are commensurate with a six-coordinated octahedral configuration around chromium(III) [19], whilst the strong band at $(16.2{\sim}16.5)\times10^3$ cm^{-1} may be attributed to the d-d transition of copper(II) in a square-planar environment. In addition, a stronger band at $(31.5{\sim}32.2)\times10^3$ cm^{-1} was also observed in the electronic spectra of the trinuclear complexes, which may be attributed to charge-transfer band.

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} (B.M.)	ν(ox) (bidentate)		ν(ox) (bridging)					
			ν_{as}(CO)	δ(CO)	ν_{as}(CO)	ν_s(CO)	ν(Cu–O)	ν(Cu–N)	ν(ClO_4^-)	ν(C–H)
(1)	145	4.69	1710, 1680, 1645	788	1620	1375, 1340	465	425	1100, 630	853, 720
(2)	150	4.75	1715, 1682, 1650	790	1628	1380, 1335	463	420	1098, 630	850, 725
(3)	148	4.72	1718, 1685, 1648	786	1625	1380, 1342	460	430	1100, 628	852, 728
(4)	150	4.70	1712, 1688, 1652	792	1623	1378, 1339	462	427	1099, 629	856, 730

(1) = [$Cu_2Cr(ox)_3$(Ph-phen)$_2$]ClO_4, **(2)** = [$Cu_2Cr(ox)_3$(Ph_2-phen)$_2$]ClO_4,
(3) = [$Cu_2Cr(ox)_3$(Cl-phen)$_2$]ClO_4, **(4)** = [$Cu_2Cr(ox)_3$(Br-phen)$_2$]ClO_4.

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

Complexes	UV-Vis ν(10^3 cm^{-1})/ε_{max} (L·mol^{-1}·cm^{-1})				ESR
	CT	$^4A_2 \rightarrow {}^4T_1$	$^4A_2 \rightarrow {}^4T_2 + {}^2E$	$^2B_{1g} \rightarrow {}^2E_g$	g values
[$Cu_2Cr(ox)_3$(Ph-phen)$_2$]ClO_4	31.7(197500)	23.3(18)	14.4(26)	16.5(218)	2.00
[$Cu_2Cr(ox)_3$(Ph_2-phen)$_2$]ClO_4	31.9(183500)	23.4(15)	14.0(22)	16.2(190)	1.98
[$Cu_2Cr(ox)_3$(Cl-phen)$_2$]ClO_4	31.5(217800)	23.1(20)	14.1(28)	16.3(205)	2.01
[$Cu_2Cr(ox)_3$(Br-phen)$_2$]ClO_4	32.2(195900)	23.5(12)	14.3(19)	16.4(182)	1.99

ESR spectra: In order to obtain further information on the structure of the trinuclear complexes, the X-band powder ESR spectra of the four trinuclear complexes have been recorded at room temperature. It is noted that the ESR spectra of the four trinuclear complexes are similar and exhibit a dissymmetric broad band around g = 2.0 (see Table 2). Since there is a lack of structural data for these complexes, it is difficult to interpret quantitatively this broad band. In addition, to the best of our knowledge, no a detailed assignment of ESR spectra for Cu(II)–Cr(III)–Cu(II) trinuclear 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 [20], in Cu(II)–Cr(III)–Cu(II) trinuclear systems, first couple the spins of the two copper(II) ions ($S_{Cu1} = S_{Cu2} = 1/2$) to give two spin states of S' = 1 and 0. Then couple S' to the chromium(III) ion ($S_{Cr} = 3/2$) to yield four total spin states of $S_T = 5/2, 3/2, 1/2, 3/2$. On the Boltzmann distribution, these states are at thermal population at room temperature owing to a weak interaction ($J = +12.8\ cm^{-1}$, *vide infra)*. Thus, the dissymmetric broad signals may be ascribed to the complexes in these spin states [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 infrared, electronic and ESR spectra, conductivity measurements and magnetic studies (*vide infra*), these complexes are proposed to have an extended ox-bridged structure and to contain two copper(II) and a chromium(III) ions, in which the chromium(III) ion has an octahedral environment and the two copper(II) ions have a square-planar environment, as shown in Figure 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 trinuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, the plausible binuclear structure is supported by the following magnetic studies.

Magnetic properties of [$Cu_2Cr(ox)_3(Ph\text{-}phen)_2$]$ClO_4$: The observed magnetic moment per trinuclear complex at room temperature, shown in Table 1, is slightly higher than the spin-only value (4.58 B.M) for a copper(II)–chromium(III)–copper(II) trinuclear complex with 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 these complexes. Being interested in the magnetic behavior of these complexes, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for complex [$Cu_2Cr(ox)_3(Ph\text{-}phen)_2$]$ClO_4$, and the results are shown in Figure 2 in the form of plots of χ_M *vs.* T and μ_{eff} *vs.* T, where χ_M, μ_{eff} and T denote molar susceptibility, effective magnetic moment and absolute temperature respectively. From Figure 2 it is evident that the curve of the effective magnetic moment (μ_{eff}) increases steadily when the temperature is lowered, indicating the operation of intramolecular ferromagnetic interaction through the ox-bridge within the complex. The rapid decrease of the magnetic moment at low temperature may be attributed to an intermolecular antiferromagnetic interaction.

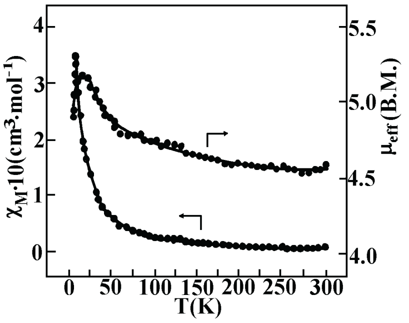

Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complex $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$. The curves are based on equation (1) using the magnetic parameters given in the text. (•), experimental data; (–), calculated curve as described in the text.

Thus, as noted above, the observed magnetic behaviour both at room-temperature and variable-temperature clearly demonstrates the operation of a weak intramolecular ferromagnetic spin-exchange interactions between Cr(III) and Cu(II) ions through the ox-bridge within the trinuclear unit [12].

In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic susceptibility data were analyzed on the basis of equation (1) [6,22–24], which includes a parameter θ to correct for the contribution from an intermolecular magnetic interaction based on the spin-Hamiltonian

$$\hat{H} = -2J(\hat{S}_{Cu1} \cdot \hat{S}_{Cr} + \hat{S}_{Cu2} \cdot \hat{S}_{Cr})(S_{Cu1} = S_{Cu2} = 1/2,\ S_{Cr} = 3/2),\ \chi_M = \frac{N\beta^2 g^2}{4k(T-\theta)}\left[\frac{A}{B}\right] \quad (1)$$

$A = 10 + \exp(-5J/kT) + 10\exp(-2J/kT) + 35\exp(3J/kT)$, $B = 2 + 2\exp(-5J/kT) + 2\exp(-2J/kT) + 3\exp(3J/kT)$, 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 $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$. 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 $J = +12.8\ cm^{-1}$, $g = 1.99$, $\theta = -1.02$ K, $F = 2.7\times10^{-4}$. The results indicate that the complex undergo weak ferromagnetic spin-exchange interaction between the copper(II) and chromium(III) ions.

We also previously investigated the magnetic behaviour of the analogous μ-oxalato complex $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$ [25] and observed antiferromagnetic coupling ($J = -9.89\ cm^{-1}$) between the copper(II) and iron(III) ions in this complex. In fact, $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$ complex and the present complex $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$ have the same skeleton of the oxalate bridging structure and the same terminal ligand, thus, their IR and electronic spectra are also similar.

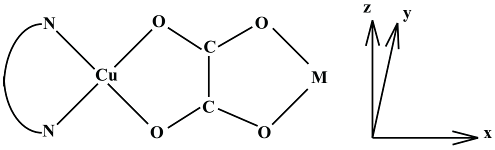

Figure 3. The structure of the [M(ox)Cu] (M = Fe, Cr) skeleton.

The only difference between $[Cu_2Fe(ox)_3(Ph\text{-}phen)_2]ClO_4$ and $[Cu_2Cr(ox)_3(Ph\text{-}phen)_2]ClO_4$ is that the metal ion is iron(III) in the former case and chromium(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 ions may affect the nature of the exchange interaction. The magnetic behaviour for the two complexes can be rationalized on the basis of the method of magnetic orbital interaction between the metal ions, as proposed by Kahn [26,27]. Considering the symmetry of the [M(ox)Cu] (M = Fe, Cr) skeleton of the oxalate bridging network close to C_{2V} (for the definition of X and Y coordinates, see Figure 3), if M = Fe(III) ion, the 3d metallic orbitals of copper(II) and iron(III) ions transform [26] 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 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. 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 [5,6], since there is no orbital interaction is feasible between the magnetic orbitals of the metal centers, namely $\langle b_1(Cu)|a_2(Cr)\rangle = 0$, $\langle b_1(Cu)|b_2(Cr)\rangle = 0$. This may be the reason for a ferromagnetic spin-exchange interaction observed in the copper(II)–chromium(III)–copper(II) complex.

Acknowledgments

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