

Synthesis and Magnetic Characterization of μ -Oxamido-Bridged Cu(II)–M(III) (M = Fe and Cr) Heterobinuclear Complexes

by Y.-T. Li^{1*}, C.-W. Yan² and H.-S. Guan¹

¹Marine Drug & Food Institute, Ocean University of China, 5 Yushan Road, Qingdao, Shandong, 266003, P. R. China

²College of Marine Life Sciences, Ocean University of China, Qingdao, 266003, P. R. China

(Received May 8th, 2003; revised manuscript June 30th, 2003)

Two new μ -oxamido-bridged heterobinuclear complexes have been synthesized and identified as [Cu(dmoxae)Cr(Ph₂phen)₂](ClO₄)₃ (**1**) and [Cu(dmoxae)Fe(Ph₂phen)₂](ClO₄)₃ (**2**), where dmoxae denotes N,N'-bis[2-(dimethylamino)ethyl]oxamido dianion and Ph₂phen represents 4,7-diphenyl-1,10-phenanthroline. Based on elemental analyses, IR, ESR and electronic spectra studies, and molar conductivity measurements, the complexes are proposed to have an extended oxamido-bridged structure consisting of planar copper(II) and octahedral chromium(III) or iron(III) ions. The two heterobinuclear complexes were further characterized by variable-temperature magnetic susceptibility (4.2–300 K) measurements and the magnetic data have been also used to deduce the indicated heterobinuclear structure. The results derived from least-squares fit of the experimental data have confirmed that the adjacent copper(II) and chromium(III) ions through the oxamido-bridge in complex (**1**) are ferromagnetically coupled with the exchange integral $J_{(\text{Cu-Cr})} = +13.6 \text{ cm}^{-1}$, while an intramolecular antiferromagnetic coupling is detected between the copper(II) and iron(III) ions through the oxamido-bridge in complex (**2**) with the exchange integral $J_{(\text{Cu-Fe})} = -17.5 \text{ cm}^{-1}$, on the basis of the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_{\text{Cu}} \cdot \hat{S}_{\text{M}}$ (M = Cr³⁺ and Fe³⁺). The influence of electronic-structural variation of the metal ions on the nature of spin-exchange interaction between the paramagnetic centers is also discussed.

Key words: oxamido-bridge, copper(II), iron(III), chromium(III), heterobinuclear complexes, magnetic properties, synthesis

The synthesis and magnetic investigations of transition-metal heterobinuclear complexes propagated by multiatom bridges are of current interest [1–4], not only for gaining some insight into the structural and electronic-structural factors causing spin-exchange interaction between paramagnetic centers and the pathway 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. So far, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions.

*Author to whom all correspondence should be addressed. E-mail: yantuanli@163.com

Among other more elaborate ligands employed in the study of magnetic interactions, N,N'-bis(substituent)oxamides could be good candidates in supporting magnetic exchange interactions, because their coordinating ability toward transition-metal ions can be modified and tuned by playing on the nature of the amide substituents, and the remarkable efficiency of the oxamido bridge to transmit electronic effects between the metal ions, and hence this family of ligands has played an important role in molecular magnetism [5–7]. Many polynuclear complexes, containing oxamido bridges, have been synthesized and their magnetic properties studied [5,8–10]. However, as far as we are aware, there are few studies on the influence of the electronic-structural variation of metal ions on magnetic interactions between the metal ions of this kind of complexes. Taking into account the above facts, it is of considerable interest to synthesize and study binuclear complexes with bridging oxamido in order to gain some insight into the molecular magnetism of this kind of complexes.

In this paper two new heterobinuclear complexes bridged by N,N'-bis[2-(dimethylamino)ethyl]oxamido dianion (dmoxae) and end-capped with 4,7-diphenyl-1,10-phenanthroline (Ph₂phen), namely [Cu(dmoxae)Cr(Ph₂phen)₂](ClO₄)₃ (**1**) and [Cu(dmoxae)Fe(Ph₂phen)₂](ClO₄)₃ (**2**), have been synthesized and characterized. The cryomagnetic properties of the two heterobinuclear complexes were measured and studied 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 two heterobinuclear complexes have not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic studies and spectral data clearly demonstrates the presence of exchange coupling between the metal ions, reveals certain electronic properties of the heterobinuclear complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All of the reagents used in the synthesis were of analytical grade. The hydrated metal ion perchlorate salts and N,N'-bis[2-(dimethylamino)ethyl]oxamido (H₂dmoxae) were prepared by the literature [11,12] methods. N,N'-dimethylethylenediamine, diethyl oxalate and the terminal ligand 4,7-diphenyl-1,10-phenanthroline (Ph₂phen) were used as commercially obtained.

Synthesis of [Cu(dmoxae)Cr(Ph₂phen)₂](ClO₄)₃ (1**):** To a solution of H₂dmoxae (0.230 g, 1 mmol) stirred in absolute methanol (15 cm³) was added successively a solution of Cu(ClO₄)₂·6H₂O (0.352 g, 0.95 mmol) in absolute methanol (10 cm³) and a solution of triethylamine (0.102 g, 2 mmol). The stirring was continued at room temperature (about 20 minutes) until the mixture became limpid. It was then filtered to eliminate impurities. To the filtrate was added an absolute methanol solution (20 cm³) of Cr(ClO₄)₃·6H₂O (0.458 g, 1 mmol) and a solution of Ph₂phen (0.665 g, 2 mmol) in the same solvent (20 cm³). The color of the solution turned from blue to pale-brown immediately and a small amount of precipitate formed. The mixture was further refluxed for *ca.* 6 h, the brown microcrystals thus formed were filtered off, washed several times with methanol, water and diethyl ether and dried over P₂O₅ under reduced pressure. Recrystallization was carried out from a hot acetonitrile solution. Yield: 1.111 g (85%); m.p. 207.1°C.

Synthesis of [Cu(dmoxae)Fe(Ph₂phen)₂](ClO₄)₃ (2): This complex was obtained as pale-violet microcrystals by the same procedure as above but by using Fe(ClO₄)₃ · 6H₂O instead of Cr(ClO₄)₃ · 6H₂O. It was recrystallized from a DMF/ethanol (1:3) mixture. Yield: 1.049 g (80%); m.p. 197.1°C. Analyses confirmed the compositions.

Physical measurements: C, H and N elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were determined on an ICP-4300 isoionic emission spectrophotometer. IR spectra were recorded with a NICOLET FT-IR 5DX spectrophotometer using KBr pellets. The electronic spectra were measured on a Cary 300 spectrophotometer. Molar conductances were measured with a Shanghai DDS-11A conductometer. ESR spectra were recorded with a JES-FEIXG ESR apparatus using an X-band and Mn-reference. 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 SQUID-5 magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms [13] and effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Syntheses and coordination environment of the binuclear complexes: A promising method to design and synthesize heterobinuclear complexes is to use a heterobinucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions [14]. In this study, we have adopted this strategy to synthesize Cu(II)–Cr(III) and Cu(II)–Fe(III) heterobinuclear complexes. For this purpose, heterobinucleating ligand N,N'-bis[2-(dimethylamino)ethyl]oxamido (H₂dmoxae) was chosen as bridging ligand. Simultaneously, 4,7-diphenyl-1,10-phenanthroline (Ph₂phen) was used as terminal ligand. In the course of preparing these heterobinuclear complexes the use of triethylamine as base makes the bridging ligand coordinate to copper(II) ion through the deprotonated oxamido nitrogen atoms. By adding Cu(ClO₄)₂ · 6H₂O in less than stoichiometric amount, the formation of the binuclear copper(II) complexes is avoided. Indeed, elemental analyses indicate that the reaction of H₂dmoxae with Cu(ClO₄)₂ · 6H₂O, M(ClO₄)₃ · 6H₂O (M = Cr³⁺ and Fe³⁺) and Ph₂phen in *ca.* 1:1:1:2 mole ratio yielded the heterobinuclear complexes of the general formula [Cu(dmoxae)M(Ph₂phen)₂](ClO₄)₃ (M = Cr³⁺ and Fe³⁺), as expected. Although crystal structures of the two heterobinuclear complexes are not known, the magnetic and spectroscopic data are sufficient to deduce the occurrence of a magnetically coupled heterobinuclear unit containing one copper(II) and one chromium(III) or one iron(III) ions. On the basis of the physical and chemical evidence, the two binuclear complexes may be presumed to have the coordination environment as shown in Figure 1.

General properties of the heterobinuclear complexes: All the two heterobinuclear complexes are sparingly soluble in water, ethanol, carbon tetrachloride, chloroform and benzene; but are soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature. In the solid state all of the complexes are fairly stable in air so as to facilitate physical measurements. For the two heterobinuclear complexes, the molar conductance values (1×10^{-3} mol · L⁻¹ acetonitrile solution) fall in

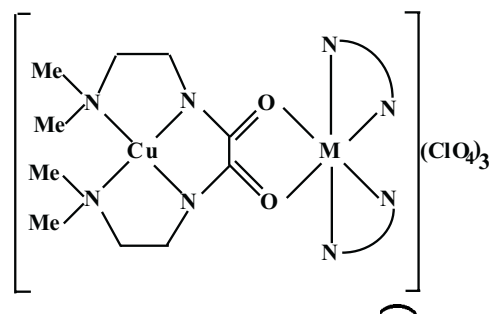


Figure 1. Plausible coordination environments of the complexes (N,N=Ph₂phen; M=Cr³⁺ and Fe³⁺).

the expected range ($405\sim 409\ \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) for 1:3 electrolytes [15], indicating that the three perchlorate anions are situated outside the metal coordination sphere. This is consistent with the presumed structure of the complexes shown in Fig. 1. The structure of the binuclear complexes was further supported by the spectroscopic characterization and magnetic studies.

Infrared spectra: The IR spectra taken in the region $4000\sim 400\ \text{cm}^{-1}$ provide some information regarding the mode of coordination in the complexes and were analyzed in a careful comparison with that of the free ligand (H₂dmoxae). It is noteworthy that the IR spectrum of the free ligand (H₂dmoxae) shows a sharp distinct band at $3280\ \text{cm}^{-1}$, which is attributed to $\nu(\text{N-H})$ stretching vibration band. However, in the IR spectra of the heterobinuclear complexes, the band had disappeared, accompanied by the appearance of a strong band in the $455\sim 458\ \text{cm}^{-1}$ range attributed to the $\nu(\text{Cu-N})$ stretching mode. These facts indicated that the free ligand (H₂dmoxae) is coordinated to copper(II) ion through the deprotonated oxamido group. On the other hand, it is noted that the carbonyl (C=O) stretching vibration for the free ligand remains at *ca.* $1650\ \text{cm}^{-1}$ in the IR spectra of the two heterobinuclear complexes. This might be due to the following reasons. In general, when the deprotonated amide nitrogen is coordinated with the metal ion to form mononuclear complex, its amide I band shifts considerably towards lower wave numbers. In the case of an oxamide dianions coordinated to two metal ions as bridging ligands, the amide I band reverts to near its original position (in the protonated species) [5,8]. Although the amide I band is the result of a composite N-C=O vibration, it can essentially be seen as $\nu(\text{C=O})$. It is likely that the bond order of C=O in binuclear complexes is higher than in its corresponding mononuclear complex. This shift has often been used as definite proof of an oxamido-bridge [5]. Thus, the above observations mean that the carbonyl oxygen atoms of the free ligand are coordinated with chromium(III) or iron(III) ion and are indicative of the oxamido-bridged structures. The facts that the C=O deformation at $728\ \text{cm}^{-1}$ of the free ligand had disappeared, and accompanied by the appearance of a new band at *ca.* $490\ \text{cm}^{-1}$ due to $\nu(\text{Cr-O})$ or $\nu(\text{Fe-O})$ further confirm the coordinated nature of the carbonyl oxygens in these heterobinuclear complexes. Furthermore, the -N=C- stretching vibration at *ca.* $1540\ \text{cm}^{-1}$ for the terminal ligand (Ph₂phen) was found in the two binuclear complexes, suggesting that the N atoms of the terminal ligand are coordinated with the chromium(III) or iron(III) ion. The additional band observed at aro-

und 470 cm^{-1} due to $\nu(\text{Cr-N})$ or $\nu(\text{Fe-N})$ further supports this view. In addition, a broad and 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 [16,17], were observed for all the binuclear complexes, which coincides with the conductance data of the binuclear complexes.

Electronic spectra: In order to obtain further structural information, the electronic spectra of the binuclear complexes were measured in acetonitrile solution. For all two binuclear complexes, a strong band at $540\sim 545\text{ nm}$ may be attributed to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transition of copper(II) in a square-planar environment [18], while a stronger absorption in the $260\sim 265\text{ nm}$ range may be attributable to the charge-transfer absorption bands, which may be due to the spin-exchange interaction between the copper(II) and chromium(III) or iron(III) ions through the π -path orbital set up by an oxamido bridge [5]. Further investigations of these and similar systems are required in order to obtain more detailed assignment for charge transfer. In addition, in the spectrum of copper(II)–chromium(III) heterobinuclear complex, two weak bands centred at 432 nm and 705 nm are due to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^2\text{T}_2 + {}^2\text{E}$ transitions of chromium(III) and are characteristic of an octahedral configuration around chromium(III) ion [18]. On the other hand, in the spectrum of the copper(II)–iron(III) heterobinuclear complex, failure to observe any (d-d) bands of iron(III) ion may be due to the weakness of the absorption. The coordination environment of iron(III) ion in copper(II)–iron(III) heterobinuclear complex is most likely a distorted octahedron owing to the fact that two bidentate terminal ligands (Ph_2phen) coordinate with iron(III). Thus, according to ligand field theory, and assuming O_h symmetry, the ground state of iron(III) is ${}^6\text{A}_{1g}$. Because the d-d transitions of iron(III) [${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^4\text{T}_{2g}(\text{G})$, ${}^4\text{E}_g(\text{G})\dots$] are both Laporte and spin-forbidden, no characteristic iron(III) band was found in the spectrum of the copper(II)–iron(III) heterobinuclear complex [19].

ESR spectra: The X-band powder ESR spectra of the two heterobinuclear complexes have been recorded at room temperature. It is noted that the ESR spectrum of the copper(II)–chromium(III) binuclear 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 a detailed assignment of ESR spectra for copper(II)–chromium(III) binuclear system has so far been reported. Thus, at this stage, the dissymmetric broad band appeared for the complex may be rationalized by the following reasons. According to Kambe's approach [20] in copper(II)–chromium(III) binuclear system two spins, $S_{\text{Cu(II)}} = 1/2$ and $S_{\text{Cr(III)}} = 3/2$, are coupled to yield the total spin states of $S = 1$ and $S = 2$. On the basis of the Boltzmann distribution, the two states are both populated at room temperature owing to very weak interaction ($J = +13.6\text{ cm}^{-1}$, *vide infra*). Thus, the dissymmetric broad signals may be ascribed to the complex in these spin states [21]. On the other hand, for the copper(II)–iron(III) binuclear complex the ESR spectrum at room temperature showed no signals [22], indicating that the ground state of the binuclear complexes is $S = 2$, in accord with the following magnetically deduced conclusion.

Based on the composition of these complexes, their infrared spectra, electronic spectra, ESR spectra, conductivity measurements and magnetic studies (*vide infra*), these complexes are proposed to have an extended oxamido-bridged structure and to contain a copper(II) and a chromium(III) or an iron(III) ions, in which the chromium(III) or iron(III) ion has an octahedral environment and the copper(II) ion has 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 binuclear 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 studies: The observed effective magnetic moment (μ_{eff}) of complex **(1)** is 4.32 B.M. at room temperature, which is slightly higher than the spin-only value (4.24 M.B.) for a copper(II)–chromium(III) binuclear complex with two spin-system ($S_{\text{Cu}}, S_{\text{Cr}} = 1/2, 3/2$) 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} value (5.57 B.M.) of complex **(2)** at room temperature is less than the spin-only value ($6.16 \mu_{\text{B}}$) of the magnetically non-interacting copper(II)–iron(III) spin-system ($S_{\text{Cu}}, S_{\text{Fe}} = 1/2, 5/2$), indicating the presence of an antiferromagnetic spin-exchange interaction in the copper(II)–iron(III) binuclear complexes.

Being interested in the magnetic behavior of the two binuclear complexes, variable-temperature (4.2–300 K) magnetic susceptibility data were further collected for complexes $[\text{Cu}(\text{dmoxae})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ **(1)** and $[\text{Cu}(\text{dmoxae})\text{Fe}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ **(2)** in order to investigate the electronic-structural variation of the metal ions effects upon the nature of spin-exchange interaction between the paramagnetic centers of this kind of complexes, and the results are shown in Figures 2 and 3, respectively, in the forms plots of χ_{M} vs. T and μ_{eff} vs. T. As shown in Figure 2, when the temperature is lowered, the curve of the effective magnetic moment (μ_{eff}) for complex **(1)** increases gradually from 4.35 B.M. at 300 K, reach a maximum value of 4.85 B.M. at 17.5 K, and then sharply decrease to 4.38 B.M. at *ca.* 4 K. The maximum value (4.85 B.M.) is comparable to the spin-only value 4.90 B.M. for the spin-state $S = 2$, which should arise from a ferromagnetic spin-coupling of the spin system Cu(II)–Cr(III) ($S_{\text{Cu}} = 1/2, S_{\text{Cr}} = 3/2$). 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 Figure 3, the variation of μ_{eff} with temperature for complex **(2)** decreases slightly on lowering of 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 variable-temperature clearly demonstrates the operation of a weak intramolecular ferromagnetic spin-exchange interactions between chromium(III) and copper(II) ions through the oxamido-bridge within the binuclear unit

[23], while the spin-coupling between the copper(II) and iron(III) ions within complex **(2)** is antiferromagnetic.

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 equation (1) [24] which includes a parameter θ to correct for the contribution from an intermolecular magnetic interaction based on the spin-Hamiltonian $\hat{H} = -2J\hat{S}_{Cu} \cdot \hat{S}_{Cr}$ ($S_{Cu} = 1/2$, $S_{Cr} = 3/2$):

$$\chi_M = \frac{N\beta^2 g^2}{k(T - \theta)} \left[\frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT)} \right] + N\alpha \quad (1)$$

Where χ_M denotes the molecular susceptibility per binuclear 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 **(1)**. 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 $J = +13.6 \text{ cm}^{-1}$, $g = 2.01$, $\theta = -0.13 \text{ K}$, $N\alpha = 100 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$, $F = 6.9 \times 10^{-4}$. The results indicate that the complex undergo ferromagnetic spin-exchange interaction between the copper(II) and chromium(III) ions.

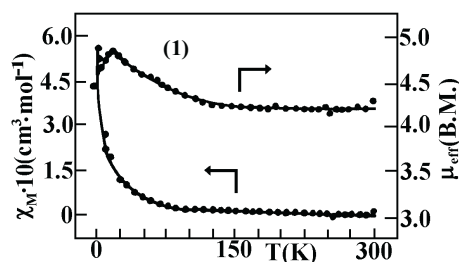


Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complex $[\text{Cu}(\text{dmoxae})\text{-Cr}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ (**1**). The curves are based on equation (1) using the parameters given in the text. (•), experimental data; (—), calculation curves as described in the text.

The cryomagnetic property of complex **(2)** is showed in Figure 3. The magnetic analysis was carried out with the susceptibility equation [25,26] based on a symmetrical two-spin system derived from a spin-Hamiltonian operator $\hat{H} = -2J\hat{S}_{Cu} \cdot \hat{S}_{Fe}$ ($S_{Cu} = 1/2$, $S_{Fe} = 5/2$).

$$\chi_M = \frac{N\beta^2 g^2}{k(T - \theta)} \left[\frac{28 + 10\exp(-6J/kT)}{7 + 5\exp(-6J/kT)} \right] \quad (2)$$

where each symbol has its usual meaning. As shown by the trace in Figure 3, good fitting to the experimental data is attained with equation (2) for complex (2) using magnetic parameters $J = -17.5 \text{ cm}^{-1}$, $g = 2.02$, $\theta = -0.16 \text{ K}$, $F = 8.8 \times 10^{-4}$. The results (negative and small J value) have confirmed that the spin coupling between iron(III) and copper(II) ions through an oxamido group in complex (2) is antiferromagnetic.

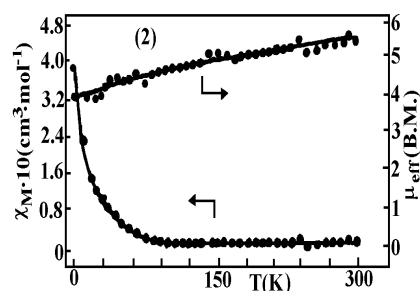


Figure 3. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complex $[\text{Cu}(\text{dmoxae})\text{Fe}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ (2). The curves are based on equation (2) using the parameters given in the text. (•), experimental data; (—), calculation curves as described in the text.

On the basis of the above discussion of magnetic properties of complexes (1) and (2), it has shown that the two complexes (1) and (2) differ in magnetic properties from each other. That is, ferromagnetic spin-coupling occurs in complex (1), whereas an antiferromagnetic spin-coupling in complex (2). In fact, the present complexes $[\text{Cu}(\text{dmoxae})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ (1) and $[\text{Cu}(\text{dmoxae})\text{Fe}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ (2) have the same skeleton of the oxamido bridging structure and the same terminal ligand, thus, their IR and coordination environment are also similar. The only difference between $[\text{Cu}(\text{dmoxae})\text{Cr}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ (1) and $[\text{Cu}(\text{dmoxae})\text{Fe}(\text{Ph}_2\text{phen})_2](\text{ClO}_4)_3$ (2) is that the 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 kinds of metal ions may affect the nature of the exchange interaction. The magnetic behavior for the two complexes can be rationalized by several models which have so far been proposed [27,28]. According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise antiferromagnetic coupling ($J < 0$) should be involved in the system. On the basis of the crystal structure of complex [9] that is analogous to the present complexes, if the whole molecular symmetry is considered to be C_{2v} , the 3d metallic orbitals of copper(II) and chromium(III) ions transform [29] 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 chromium(III) ion there are three unpaired electrons which populate the a_1 , a_2 , b_1 and b_2 orbitals. According to the point group theory, because there is no orbital interaction to be feasible between the magnetic orbitals of the metal centers, namely, $\langle b_1(\text{Cu}) | a_1(\text{Cr}) \rangle = 0$, $\langle b_1(\text{Cu}) | a_2(\text{Cr}) \rangle = 0$, $\langle b_1(\text{Cu}) | b_2(\text{Cr}) \rangle = 0$, therefore, the ferromagnetic interaction between the copper(II) and chromium(III) ions within the copper(II)–chromium(III) complex should be observed. On the other

hand, for complex **(2)** the 3d metallic orbitals of copper(II) and iron(III) ions transform as $a_1(d_{z^2}$ and $d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{zx})$ [29]. 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, that is, $S = \langle b_1(\text{Cu}) | b_1(\text{Fe}) \rangle \neq 0$. This may be the reason for an antiferromagnetic interaction between the copper(II) and iron(III) ions within complex **(2)**.

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 [27,6,30]. 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.

Acknowledgments

This project was supported by the National Natural Science Foundation of China and the Natural Science Foundation of Shandong Province.

REFERENCES

1. Kahn O., "Molecular Magnetism", Verlag-Chemie: N.Y., 1993.
2. Winpenny R.E.P., *Chem. Soc. Rev.*, **27**, 447 (1998).
3. Benelli C. and Gatteschi D., *Chem. Rev.*, **102**, 2369 (2002).
4. Kahn M.L., Mathoniere C. and Kahn O., *Inorg. Chem.*, **30**, 3692 (1999).
5. Ojima H. and Nonoyama K., *Coord. Chem. Rev.*, **92**, 85 (1988).
6. Yu P., Kahn O., Nakatani K., Codjovi E., Mathoniere C. and Sletten J., *J. Am. Chem. Soc.*, **113**, 6558 (1991).
7. Lloret F., Julve M., Ruiz R., Journaux Y., Nakatani K., Kahn O. and Sletten J., *Inorg. Chem.*, **32**, 27 (1993).
8. Li Y.T., Liao D.Z., Jiang Z.H. and Wang G.L., *Polyhedron*, **14**, 2209 (1995).
9. Mathoniere C., Kahn O., Daran J.-C., Hilbig H. and Kohler H., *Inorg. Chem.*, **32**, 4057 (1993).
10. Benelli C., Fabretti A.C. and Giusti A., *J. Chem. Soc., Dalton Trans.*, 409 (1993).
11. Bethrent J.R. and Madan S.K., *J. Inorg. Nucl. Chem.*, **20**, 195 (1950).
12. Ojima H. and Yamada Y., *Bull. Chem. Soc. Jpn.*, **43**, 3018 (1970).
13. Selwood P.W., "Magnetochemistry", Interscience, N.Y., p. 78 (1956).
14. Gunter M.J., Berry K.J. and Murray K.S., *J. Am. Chem. Soc.*, **106**, 4227 (1984).
15. Geary W.J., *Coord. Chem. Rev.*, **7**, 81 (1971).
16. Radecka-Paryzek E., *Inorg. Chim. Acta*, **34**, 5 (1979).
17. Nakamoto K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd. edn., Wiley Intersciences, N.Y., 1978.
18. Lever A.B.P., "Inorganic Electronic Spectroscopy", Elsevier Publishing Co., Amsterdam, 1984.
19. Tanabe Y. and Sugano S., *J. Phys. Chem. Jpn.*, **9**, 735 (1954).
20. Kambe K., *J. Phys. Soc. Jpn.*, **5**, 48 (1950).
21. Suzuki M., Oshio H., Uenara A., Endo K., Yanaga M., Kida S. and Saito K., *Bull. Chem. Soc. Jpn.*, **61**, 3907 (1988).
22. Tweedle M.F., Wilson L.J., Garcis-Iriguez L., Babcock G.T. and Palmer G.J., *J. Biol. Chem.*, **253**, 8065 (1987).
23. Li Y.T., Yan C.W., Miao S.H. and Liao D.Z., *Polyhedron*, **15**, 2491 (1998).

24. Zhong J.Z., Okawa H., Matsumoto N., Sakiyama H. and Kida S., *J. Chem. Soc., Dalton Trans.*, 497 (1991).
25. Liao D.Z., Shi J., Jiang Z.H., Yan S.P., Cheng P. and Wang G.L., *Polyhedron*, **11**, 2621 (1992).
26. Li Y.T., Yan C.W. and Miao S.H., *Polish J. Chem.*, **75**, 223 (2001).
27. Kahn O., *Struct. Bond.*, **68**, 89 (1987).
28. Kahn O. and Charlot M.F., *Nouv. J. Chem.*, **4**, 567 (1980).
29. Morgenstern-Badarau I., Rerat M., Kahn O., Jaud J. and Galy J., *Inorg. Chem.*, **21**, 3050 (1982).
30. Journaux Y., Kahn O., Zarembowitch J., Galy J. and Jaud J., *J. Am. Chem. Soc.*, **105**, 7585 (1983).