Polish J. Chem., **77**, 137–145 (2003)

Synthesis and Magnetic Analysis of μ-Oxamido-Bridged Copper(II)–Iron(II) Heterodinuclear Complexes

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(Received July 29th, 2002; revised manuscript October 1st, 2002)

Five new copper(II)–iron(II) heterodinuclear complexes bridged by the dianion of N,N′-bis[3-(dimethylamino)propyl]oxamido (dmoxpn) and end-capped with 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 5-nitro-1,10-phenanthroline (NO_2-phen); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen); namely $[Cu(dmoxpn)FeL_2](ClO_4)_2$ (L = bpy, phen, NO_2-phen, Cl-phen, Br-phen), have been synthesized and characterized. Based on elemental analyses, magnetic moments (at room temperature), molar conductivity measurements, and spectroscopic studies, extended oxamido-bridged structures consisting of a copper(II) ion and an iron(II) ion, which have a square-planar environment and an octahedral environment, respectively, are proposed for these complexes. The $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$ (**1**) and $[Cu(dmoxpn)Fe(phen)_2](ClO_4)_2$ (**2**) complexes have been further characterized by variable temperature magnetic susceptibility (4.2~300 K) and the observed data were least-squares fitted to the susceptibility equation derived from the spin Hamiltonian including single-ion zero-field interaction for the iron(II) ion, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 - D\hat{S}_{Z1}^2$, giving the exchange integrals $J = -15.9\ cm^{-1}$ for (**1**) and $J = -17.5\ cm^{-1}$ for (**2**). These results indicated that the spin coupling between the adjacent copper(II) and iron(II) ions through oxamido-bridge in both complexes (**1**) and (**2**) is antiferromagnetic. The influence of methyl ($-CH_3$) substituents in the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

Key words: μ-oxamido-bridge, copper(II)–iron(II), heterodinuclear complexes, magnetism, synthesis

The studies on syntheses and magnetic investigations of heterodinuclear complexes containing two different paramagnetic centers have received much attention in recent years [1–5]. Interest in this field stems not only for gaining some insight into the electronic and geometric structure of metalloproteins and enzymes and thus correlating structure with biological function, but also for obtaining information about designing and synthesizing molecule-based magnets and investigating the spin-exchange mechanism between paramagnetic metal ions.

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It is known that 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 [6,7]. 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 [6–9]. So far, many dinuclear complexes containing oxamido-bridges have been synthesized and their magnetic properties studied [6–16]. The effective bridging function of the μ-oxamido moiety has been revealed by X-ray analysis for some of these complexes [10,12,13,15,16]. However, as far as we are aware, there are few studies on the influence of substituents in their amine groups of the bridging ligand 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 polynuclear complexes with bridging oxamide in order to gain some insight into the effect of substituents in this kind of ligand on magnetic interaction. In this paper, five new heterometal dinuclear complexes, $[Cu(dmoxpn)FeL_2](ClO_4)_2$ (L = bpy, phen, NO_2-phen, Cl-phen, Br-phen) have been synthesized and characterized by using N,N′-bis[3-(dimethylamino)propyl]oxamido (dmoxpn) as bridging ligand and the cryomagnetic properties of the $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$ (**1**) and $[Cu(dmoxpn)Fe(phen)_2](ClO_4)_2$ (**2**) complexes were measured in the temperature range 4.2–300 K to examine the effect of the substituents in oxamido bridge upon the magnetic interaction between Cu(II) and Fe(II) ions.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. The hydrated iron(II) perchlorate and N,N′-bis[3-(dimethylamino)propyl]oxamido (H_2dmoxpn) were prepared by the literature methods [17,18]. N,N-dimethylpropyldiamine, diethyl oxalate and the terminal ligands 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 5-chloro-1,10-phenanthroline (Cl-phen), 5-nitro-1,10-phenanthroline (NO_2-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were used as commercially available.

Synthesis of new heterodinuclear Cu(II)–Fe(II) complexes: The methods used to prepare the Cu(II)–Fe(II) dinuclear complexes are virtually identical and are exemplified by $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$. To a solution of H_2dmoxpn (0.258 g, 1 mmol) in methanol (20 mL) was added, successively, a solution of piperidine (0.170 g, 2 mmol) in the same solvent (20 mL), followed by a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.352 g, 0.950 mmol) in methanol (10 mL) with stirring at room temperature until the mixture became limpid. The resulting solution was then filtered. To the filtrate was added a methanol solution (15 mL) of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.184 g, 1 mmol) and a solution of bpy (0.312 g, 2 mmol) in the same solvent (20 mL) under N_2. The color of the solution turned from green to pale-brown immediately and a small amount of precipitate formed. After stirring for 8 h, the pale-brown microcrystals thus formed were filtered off, washed several times with methanol, water and diethyl ether and dried over P_2O_5 under reduced pressure. The results of elemental analyses confirmed the compositions indicated.

The colors, yields and melting points of the complexes are collected in Table 1.

Table 1. Yields, colors and melting points (M.p) of the complexes.

No	Complex	Color	Yield (%)	M.p (°C)
(1)	$[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$	pale-brown	76	263.2
(2)	$[Cu(dmoxpn)Fe(phen)_2](ClO_4)$	brown	82	218.9
(3)	$[Cu(dmoxpn)Fe(NO_2\text{-phen})_2](ClO_4)_2$	pale-red	90	207.6
(4)	$[Cu(dmoxpn)Fe(Cl\text{-phen})_2](ClO_4)_2$	violet-red	85	189.1
(5)	$[Cu(dmoxpn)Fe(Br\text{-phen})_2](ClO_4)_2$	violet	80	275.3

Physical measurements: Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. Metal contents were determined on an ICP-4300 isoionic emission spectrophotometer. IR spectra were recored with a NICOLET FT-IR 5DX spectrophotometer using KBr pellets. The electronic spectra (acetonitrile solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured 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 were measured using a Quantum Design MPMS-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [19] for all the constituent atoms and effective magnetic moments were calculated by 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 dinuclear complexes: One strategy for the synthesis of heterodinuclear complexes is to use heterodinucleating ligand, which offers either the coordination geometry or the ligand field strength suitable for dissimilar metal ions [20]. In this study, our purpose was to obtain Fe(II)–Cu(II) bimetallic species. Therefore, this synthetic method was adopted and N,N′-bis[3-(dimethylamino)propyl]oxamido (H_2dmoxpn) was chosen as a "heterodinucleating ligand", simultaneously, 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 5-chloro-1,10-phenanthroline (Cl-phen); 5-nitro-1,10-phenanthroline (NO_2-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were used as terminal ligands. In the course of preparing these dinuclear complexes the use of piperidine as base makes the bridging ligand (H_2dmoxpn) coordinate to copper(II) ion through the deprotonated oxamido nitrogen atoms. In addition, by adding $Cu(ClO_4)_2 \cdot 6H_2O$ in less than stoichiometric amount, the formation of the dinuclear copper(II) complexes is avoided. Indeed, elemental analyses indicate that the reaction of H_2dmoxpn with $Cu(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_2 \cdot 6H_2O$ and L (L = bpy, phen, NO_2-phen, Cl-phen, Br-phen) in *ca.* 1:1:1:2 mole ratio has yielded the heterodinuclear complexes of the general formula $[Cu(dmoxpn)FeL_2](ClO_4)_2$, as expected. These complexes are the first examples of Cu(II)–Fe(II) heterodinuclear complexes bridged by N,N′-bis[3-(dimethylamino)propyl]oxamido group. On the basis of molar conductance measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

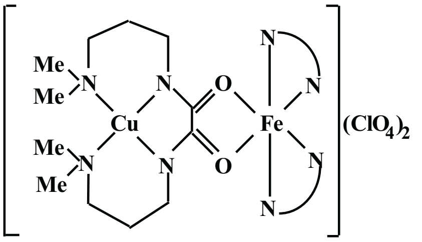

Figure 1. Plausible coordination environment of the complexes (N⁀N = bpy, phen, NO_2-phen, Cl-phen, Br-phen).

General properties of the dinuclear complexes: All the Cu(II)–Fe(II) dinuclear complexes are sparingly soluble in water, ethanol, carbon tetrachloride, chloroform and benzene; but soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature. The complexes $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$ and $[Cu(dmoxpn)Fe(phen)_2](ClO_4)_2$ can be recrystallized from an acetonitrile/ethanol (1:1) and DMF/ethanol (1:3) mixture, respectively. In the solid state all the complexes are fairly stable in air, thus facilitating physical measurements. For the five Cu(II)–Fe(II) dinuclear complexes, the observed molar conductance values in acetonitrile solution at 25°C fall in the expected range for 1:2 electrolytes [21] (see Table 2), indicating that the two perchlorate anions are situated outside the metal coordination sphere, in accord with the measured IR data of these heterodinuclear complexes. Furthermore, the dinuclear complexes were further characterized by the spectroscopic analyses and magnetic studies.

Infrared spectra: The IR spectra taken in the region 4000–400 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 (H_2dmoxpn). The most relevant IR absorption bands from the IR spectra of the complexes, along with their assignments are shown in Table 2. We will only discuss here the selected infrared bands. It is noteworthy that the spectrum of the free ligand (H_2dmoxpn) shows a sharp distinct band at 3320 cm^{-1}, which is attributed to ν(N–H) stretching vibration band. However, in the IR spectra of all Cu(II)–Fe(II) dinuclear complexes, this band had disappeared, accompanied by the appearance of a strong band in the 485–490 cm^{-1} range attributed to the ν(Cu–N) stretching mode. These facts indicated that the free ligand (H_2dmoxpn) is coordinated to the copper(II) ion through the deprotonated oxamido group. On the other hand, the carbonyl (C=O) stretching vibration for the free ligand remains at *ca.* 1630 cm^{-1} in the IR spectra of the five dinuclear complexes, which is similar to the band exhibited by analogous complexes [10,11]. This observation means that the carbonyl oxygen atoms of the ligand are coordinated with iron(II) ion and are indicative of the oxamido-bridged structures [7,11]. Because the deprotonated amide nitrogen is coordinated with the metal ion to form mononuclear complex, its amide I band shifts considerably towards lower wave numbers, however, in the case of an oxamide dianion coordinated to two metal ions as a bridging ligands, the amide I band reverts to near its original position (in the protonated species) [7]. Although the amide I band is the result of a composite N-C=O vibration, it can essentially be seen as ν(C=O). It is likely that the bond order of C=O in binuclear complexes is higher than in its corresponding mononuclear complex. Thus, this shift has often been used as definite proof of an oxamido-bridge [7]. The facts that the C=O deformation at 725 cm^{-1} of the free ligand had disappeared, and accompanied by the appearance of a new band at *ca.* 590 cm^{-1} due to ν(Fe–O) further confirm the coordinated nature of the carbonyl oxygens in these dinuclear complexes. Furthermore, the -N=C- stretching vibration for the terminal ligands (bpy, phen, NO_2-phen, Cl-phen, Br-phen) were found in the corresponding dinuclear complexes (see Table 2), suggesting that the N atoms of the terminal ligands are coordinated with the Fe(II) ion. The additional band observed at around 490 cm^{-1} due to ν(Fe–N) also 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 [22,23], were observed for all the dinuclear complexes. This is consistent with the conductance data of the binuclear complexes.

Electronic spectra: In order to obtain further structural information of these dinuclear complexes, the electronic spectra of these complexes are measured in acetonitrile solutions and the spectral data are given in Table 2. As shown in this Table, the electronic spectra of the five complexes are similar to each other. Two d-d bands centered at (11.2~11.0)×10^3 cm^{-1} and (19.2~19.0)×10^3 cm^{-1} are observed. The weak band at (11.2~11.0)×10^3 cm^{-1} is due to the $^5T_{2g} \rightarrow {}^5E_g$ transition of Fe(II) and is characteristic of a high spin octahedral configuration around iron(II) [24], while the strong band at (19.2~19.0)×10^3 cm^{-1} is characteristic of copper(II) in a square-planar environment [25], which can be unambiguously assigned to the $^2B_1 \rightarrow {}^2A_1$ local transition in C_{2v} site symmetry. In addition, a stronger absorption in the short wavelength range (see Table 2) may be attributed to the charge-transfer absorption bands, which may be due to the spin-exchange interaction between the copper(II) and iron(II) ions through the π-path orbital set up by an oxamido bridge [7]. Further investigations of these and similar systems are required in order to obtain more detailed assignment for charge transfer.

Table 2. Physical data for the Cu(II)–Fe(II) dinuclear complexes.

Complex	μ_{eff}	Λ_M*	IR (cm^{-1})					UV ν(10^3 cm^{-1})/ε_{max} (mol^{-1} cm^{-1} L)		
	(B.M.)		ν(C=O)	ν(N=C)	ν(Fe–N)	ν(Fe–O)	$\nu(ClO_4^-)$	d-d		CT
(1)	4.92	265	1632	1536	490	590	1100 628	19.0 (212)	11.0 (22)	29.8 (21600)
(2)	4.87	260	1635	1528	485	595	1100 624	19.2 (215)	11.2 (25)	32.0 (18900)
(3)	4.85	262	1640	1527	488	592	1100 630	19.1 (226)	11.1 (18)	30.7 (19400)
(4)	4.76	258	1628	1530	490	596	1100 625	19.1 (242)	11.0 (20)	29.7 (18700)
(5)	4.80	260	1630	1520	490	594	1100 632	19.2 (256)	11.2 (27)	30.5 (26800)

*Values for 1×10^{-3} mol·L^{-1} acetonitrile solution, unit: $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

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 IR and electronic spectra, conductivity measurements, magnetic studies (*vide infra*) and the crystal structure of the analogous complexes [10,12,13,15,16], these complexes are proposed to have an extended oxamido-bridged structure and to contain an iron(II) ion and a copper(II) ion, which have an octahedral environment and a square-planar environment, respectively, as shown in Figure 1. The plausible structure is further supported by the following magnetic studies.

Magnetic studies: The observed magnetic moment per dinuclear complex at room temperature, shown in Table 2, is less than the spin-only value (5.20 B.M.) for heterodinuclear complexes of Cu(II)–Fe(II) in the absence of exchange interaction. This suggests the operation of an antiferromagnetic spin-exchange interaction in these complexes [26]. In order to obtain further information on the structure of the complexes, variable-temperature dependence molar magnetic susceptibility (4.2~300 K) data were collected for complexes (**1**) and (**2**), and the results are shown in Figure 2 in the form of the μ_{eff} *versus* T and χ_M *versus* T plots, χ_M being the temperature dependence of the susceptibilities, μ_{eff} effective magnetic moments and T the absolute temperature for both dinuclear complexes. From Figure 2 it is evident that the magnetic moments decrease steadily with decreasing temperature, implying the

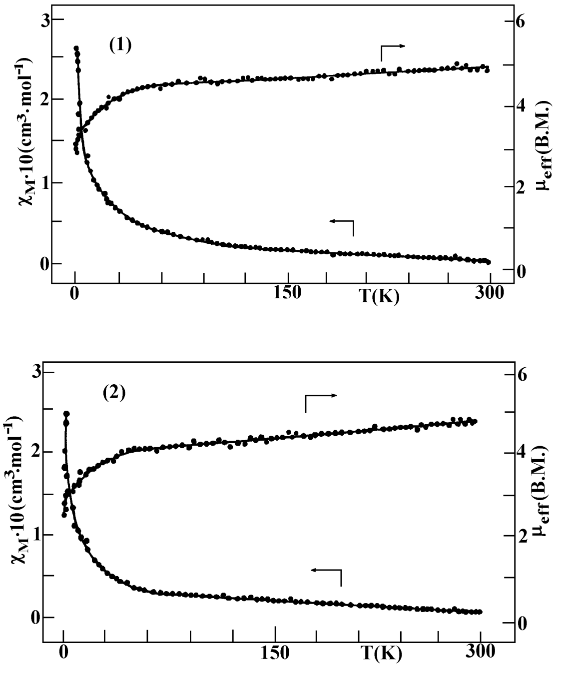

Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complexes $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$ (**1**) and $[Cu(dmoxpn)Fe(phen)_2](ClO_4)_2$ (**2**). The curves are based on equation (2) using the parameters given in the text. (●), experimental data; (–), calculation curves as described in the text.

existence of an antiferromagnetic spin-exchange interaction within each molecule. This is consistent with the room-temperature magnetic moments of the complexes.

In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic analysis for the complexes was initially carried out with the susceptibility equation (1) based on the spin Hamiltonian, which include only an isotropic magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$) for the Cu(II)–Fe(II) dinuclear complexes:

$$\chi_M = \frac{N\beta^2 g^2}{4kT}\left[x\,\frac{10 + 35\exp(5J/kT)}{2 + 3\exp(5J/kT)}\right] \tag{1}$$

However, the observed and calculated values do not satisfactorily fit this equation, especially at low temperature range, because it neglects the single ion zero-field interaction of the iron(II) ion [26]. Considering the zero-field splitting of iron(II), we, therefore, adopted a susceptibility equation based on the modified Heisenberg operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 - D\hat{S}_{Z1}^2$, where D is axial zero-field splitting parameter for the Fe(II) ion. In this case, the expression for the molar magnetic susceptibility (χ_M) is given by equation (2) [26]:

$$\chi_M = \frac{N\beta^2 g^2}{4kT}\left[\frac{25\exp(A) + 9\exp(B) + \exp(C) + 9\exp(G) + \exp(E)}{\exp(A) + \exp(B) + \exp(C) + \exp(G) + \exp(E)}\right] \tag{2}$$

$A = (35J/4 + 4D)/kT$,

$B = [25J/4 + 5D/2 + (25J^2/4 - 9DJ/2 + 9D^2/4)^{1/2}]/kT$,

$C = [25J/4 + D/2 + (25J^2/4 - DJ/2 + D^2/4)^{1/2}]/kT$,

$G = [25J/4 + 5D/2 - (25J^2/4 - 9DJ/2 + 9D^2/4)^{1/2}]/kT$,

$E = [25J/4 + D/2 - (25J^2/4 - DJ/2 + D^2/4)^{1/2}]/kT$.

As shown in Figure 2, good least-squares fit to the experimental data was attained with equation (2). The magnetic parameters thus determined are $J = -15.9\ \text{cm}^{-1}$, $g = 2.03$, $D = -1.01\ \text{cm}^{-1}$ for $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$ (**1**) and $J = -17.5\ \text{cm}^{-1}$, $g = 2.02$, $D = -1.16\ \text{cm}^{-1}$ for $[Cu(dmoxpn)Fe(phen)_2](ClO_4)_2$ (**2**). The agreement factors R, defined here as $R = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$, are then equal to 7.5×10^{-5} (**1**) and 3.6×10^{-5} (**2**). The results indicated that the complexes showed an antiferromagnetic spin-exchange interaction within each dinuclear unit. The weak antiferromagnetic spin-exchange interaction between iron(II) and copper(II) ions within each molecule may be explained by several models which have so far been proposed [27–29]. According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise an antiferromagnetic coupling ($J < 0$) should be involved in the system. On the basis of the crystal structure of complexes [10,12,13,15,16] 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 iron(II) ions transform [29] as $a_1(d_{z^2}$ and $d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$ and $b_2(d_{zx})$. Around the copper(II) ion, there is just one unpaired electron which occupies the b_1 orbital, and around iron(II) there are four unpaired electrons which populate the a_1, a_2, b_1 and b_2 orbitals. Because there is no orthogonality between b_1(Cu) and b_1(Fe), namely $S = \langle b_1(\mathrm{Cu})|b_1(\mathrm{Fe})\rangle \neq 0$, antiferromagnetic exchange interactions should be observed in these complexes.

We have previously investigated the magnetic behavior of the analogous μ-oxamido heterodinuclear copper(II)–iron(II) complexes [11] $[Cu(oxpn)Fe(bpy)_2]SO_4$ and $[Cu(oxpn)Fe(phen)_2]SO_4$, where oxpn denotes the N,N′-bis(3-aminopropyl)oxamido dianion and obtained the following results for the magnetic interactions: $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_2$ ($J = -15.9$ cm^{-1}) < $[Cu(oxpn)Fe(bpy)_2]SO_4$ ($J = -21.8$ cm^{-1}); $[Cu(dmoxpn)Fe(phen)_2](ClO_4)_2$ ($J = -17.5$ cm^{-1}) < $[Cu(oxpn)Fe(phen)_2]SO_4$ ($J = -23.2$ cm^{-1}). In fact, these Cu(II)–Fe(II) heterodinuclear complexes have essentially the same skeletal structure and the same terminal ligand, thus, their IR and electronic spectra are also similar. The main difference between $[Cu(dmoxpn)FeL_2](ClO_4)_2$ and $[Cu(oxpn)FeL_2]SO_4$ (L = bpy, phen) is that there are four methyl ($-CH_3$) substituents in the former compound. Their presence may have effects on both electronic and molecular structures [30]. However, the electronic influence of the methyl groups on overlap between the magnetic orbitals should be small in view of their remoteness from the bridging site. On the other hand, the presence of this substituent will cause a decrease in coplanarity between the coordination environment of copper(II) and that of the adjacent iron(II) ion, resulting in a decrease in overlap between the two magnetic orbitals. This would explain the difference in J values for these complexes.

The above discussion has shown that in this system the magnitude of the spin-exchange interaction between Fe(II) and Cu(II) ions may be tunable by playing the nature of the substituents in the bridging ligands, and this strategy opens vast perspectives.

Acknowledgments

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

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