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Synthesis and Magnetic Studies of Copper(II)–Iron(II) Heterodinuclear Complexes with N,N′-Bis[2-(dimethylamino)ethyl]oxamido Dianion as Ligand

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Three new copper(II)–iron(II) heterodinuclear complexes bridged by the dianions of N,N′-bis[2-(dimethylamino)ethyl]oxamido (dmoxae) and end-capped with 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO_2phen); namely [Cu(dmoxae)Fe(bpy)$_2$]SO_4 (**1**), [Cu(dmoxae)Fe(phen)$_2$]SO_4 (**2**) and [Cu(dmoxae)Fe(NO_2phen)$_2$]SO_4 (**3**), have been synthesized and characterized. The three dinuclear complexes have not yet been isolated in crystalline form suitable for X-ray structure analysis, but based on elemental analyses, IR and electronic spectra studies, magnetic moments at room-temperature and molar conductivity measurements, these complexes are proposed to have an extended oxamido-bridged structure consisting of planar copper(II) and octahedral iron(II) ions. The [Cu(dmoxae)Fe(bpy)$_2$]SO_4 (**1**) and [Cu(dmoxae)Fe(phen)$_2$]SO_4 (**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 = –20.9 cm^{-1} for (**1**) and J = –22.7 cm^{-1} for (**2**). These results indicated that the spin coupling between the adjacent copper(II) and iron(II) ions through the oxamido-bridge in both complexes (**1**) and (**2**) is antiferromagnetic. The influence of methyl substituents in the amine groups of the bridging ligand and the relative stability of the chelate ring arrangement around the copper(II) 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 design, synthesis and magnetic investigations of heterodinuclear complexes containing two different paramagnetic centers are of current interest, due to the hope of mimicking the active sites of some metalloenzymes containing dissimilar metal ions and thus correlating structure with biological function, and the mechanism of spin coupling between paramagnetic metal ions in view of the electronic structures of the interacting metal ions and to find appropriate systems applicable as building units for the design of molecular-based ferromagnet [1–10].

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Owing to their fundamental importance in the magnetic studies, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. 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 [11,12], 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 [11–14]. So far, many dinuclear complexes containing oxamido-bridges have been synthesized and their magnetic properties studied [11–22]. The effective bridging function of the μ-oxamido moiety has been revealed by X-ray analysis for some of these complexes [15,18–22]. 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 investigate further the structural variation effects upon magnetic interaction between the metal ions.

In this paper, three new heterometal dinuclear complexes formulated $[Cu(dmoxae)Fe(L)_2]SO_4$ (L = bpy, phen, NO_2phen) have been synthesized and characterized by using N,N′-bis[2-(dimethylamino)ethyl]oxamido (dmoxae) as bridging ligand and the cryomagnetic properties of the $[Cu(dmoxae)Fe(bpy)_2]SO_4$ (**1**) and $[Cu(dmoxae)Fe(phen)_2]SO_4$ (**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 copper(II) and iron(II) ions. At present, the three copper(II)–iron(II) heterodinuclear 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 these copper(II)–iron(II) dinuclear complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. N,N′-Bis[2-(dimethylamino)ethyl]oxamido (H_2dmoxae) were prepared by the literature methods [23,24]. $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, N,N-dimethylethyldiamine, diethyl oxalate and the terminal ligands 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO_2phen) were used as commercially available.

Synthesis of $[Cu(dmoxae)Fe(bpy)_2]SO_4$ (1): To a solution of H_2dmoxae (0.230 g, 1 mmol) in methanol (15 mL) was added, successively, a solution of piperidine (0.170 g, 2 mmol) in the same solvent (20 mL), followed by a solution of $CuSO_4 \cdot 5H_2O$ (0.237 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 $FeSO_4 \cdot 7H_2O$ (0.278 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 red-brown immediately and a small amount of precipitate formed. After stirring for 5 h, the red-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. Yield, 492 mg (65%), m.p. 293.1°C. Anal. Calc. for $CuFeC_{30}H_{36}N_8O_6S$ (m.w. 756.12): C, 47.66; H, 4.80; N, 14.82; Cu, 8.40; Fe, 7.39%. Found: C, 47.42; H, 4.65; N, 14.59; Cu, 8.21; Fe, 7.15%.

Synthesis of [Cu(dmoxae)Fe(phen)$_2$]SO$_4$ (2): This complex was obtained as red-violet microcrystals by the same procedure as above but by using phen (0.360 mg, 2 mmol) instead of bpy. It was recrystallized from a DMF/ethanol (1:4) mixture and the needle crystals were collected. Yield, 563 mg (70%), m.p. 311.9°C. Anal. Calc. for $CuFeC_{34}H_{36}N_8O_6S$ (m.w. 804.16): C, 50.78; H, 4.51; N, 13.93; Cu, 7.90; Fe, 6.94%. Found: C, 50.52; H, 4.30; N, 13.68; Cu, 7.75; Fe, 6.73%.

Synthesis of [Cu(dmoxae)Fe(NO$_2$phen)$_2$]SO$_4$ (3): This complex was obtained as pale-violet powder by the same procedure as described for complex **(1)**, except that NO_2phen (0.450 mg, 2 mmol) was used instead of bpy. Yield, 724 mg (81%); m.p. 286.5°C. Anal. Calc. for $CuFeC_{34}H_{34}N_{10}O_{10}S$ (m.w. 894.16): C, 45.67; H, 3.83; N, 15.66; Cu, 7.11; Fe, 6.25%. Found: C, 45.43; H, 3.59; N, 15.34; Cu, 7.36; Fe, 6.43%.

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 Cary 300 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 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [25] 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: 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. 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 [26]. In this study, our purpose was to obtain iron(II)–copper(II) bimetallic species, therefore, this synthetic method was adopted and N,N′-bis[2-(dimethylamino)ethyl]oxamido (H_2dmoxae) was chosen as a heterodinucleating ligand. Simultaneously, 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen) and 5-nitro-1,10-phenanthroline (NO_2phen) were used as terminal ligands, respectively. In the course of preparing these heterodinuclear complexes the use of piperidine as base makes the bridging ligand (H_2dmoxae) coordinate to copper(II) ion through the deprotonated oxamido nitrogen atoms. In addition, by adding $CuSO_4 \cdot 5H_2O$ in less than stoichiometric amount, the formation of the dinuclear copper(II) complexes is avoided. Indeed, elemental analyses indicate that the reaction of H_2dmoxae with $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$ and L (L = bpy, phen, NO_2phen) in *ca.* 1:1:1:2 mole ratio has yielded the heterodinuclear complexes of the general formula [Cu(dmoxae)Fe(L)$_2$]SO$_4$, as expected. The general synthetic pathway for the complexation reaction taking place may be represented as follows:

$$\mathrm{H_2dmoxae + Cu^{2+} \xrightarrow{piperidine} [Cu(dmoxae)] + 2\ H^+}$$

$$\mathrm{[Cu(dmoxae)] + Fe^{2+} + 2\ L \longrightarrow [Cu(dmoxae)Fe(L)_2]^{2+}}$$

where L = bpy, phen, NO_2phen. These complexes are the first examples of copper(II)–iron(II) heterodinuclear complexes bridged by N,N′-bis[2-(dimethylamino)ethyl] 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 Figure 1.

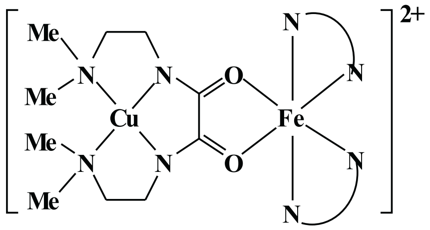

Figure 1. Plausible coordination environments of the complexes ($\widehat{\mathrm{N\ N}}$ = bpy, phen, NO_2phen).

General properties of the heterodinuclear complexes: All the copper(II)–iron(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. In the solid state all the complexes are fairly stable in air, thus facilitating physical measurements. For the three copper(II)–iron(II) dinuclear complexes, the observed molar conductance values in acetonitrile solution at 25°C fall in the expected range for 1:1 electrolytes [27] (see Table 1), indicating that the sulfate anion is situated outside the metal coordination sphere and in accord with the measured IR data of these heterodinuclear complexes. Furthermore, the heterodinuclear 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_2dmoxae). The most relevant IR absorption bands from the IR spectra of the complexes, along with their assignments are shown in Table 1. We will only discuss here the selected infrared bands. It is noteworthy that the spectrum of the free ligand (H_2dmoxae) shows a sharp distinct band at 3250 cm^{-1}, which is attributed to υ(N–H) stretching vibration band. However, in the IR spectra of all copper(II)–iron(II) heterodinuclear complexes, this band had disappeared, accompanied by the appearance of a strong band in the 488–492 cm^{-1} range attributed to the υ(Cu–N) stretching mode. These facts indicated that the free ligand (H_2dmoxae) 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.* 1650 cm^{-1} in the IR spectra of the three heterodinuclear complexes, implying that the carbonyl oxygen atoms of the free ligand are coordinated with iron(II) ion and are indicative of the oxamido-bridged structures [12,16]. 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. However, 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) [12]. Although the amide I band is the result of a composite N–C=O vibration, it can essentially be seen as υ(C=O). It is likely that the bond order of C=O in dinuclear complexes is higher than in its corresponding mononuclear complex. Thus, this shift has often been used as definite proof of an oxamido-bridge [12]. The facts that the C=O deformation at 728 cm^{-1} of the free ligand had disappeared, and accompanied by the appearance of a new band at *ca.* 520 cm^{-1} due to υ(Fe–O) further confirm the coordinated nature of the carbonyl oxygens in these heterodinuclear complexes. Furthermore, the –N=C– stretching vibration for the terminal ligands (bpy, phen, NO_2phen) were found in the corresponding dinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands are coordinated with the iron(II) ion. The additional band observed at around 490 cm^{-1} due to υ(Fe–N) also supports this view. In addition, a broad and intense band centered at *ca*. 1120 cm^{-1}, typical for a non-coordinated sulphate group [28], were observed for all the dinuclear complexes. This is consistent with the conductance data of the dinuclear complexes.

Electronic spectra: In order to obtain further structural information of these heterodinuclear complexes, the electronic spectra of these complexes are measured in acetonitrile solutions and the spectral data are given in Table 1. As shown in this table, the electronic spectra of the three complexes are similar to each other. Two d-d bands centred at (11.1~11.3)×10^3 cm^{-1} and (19.2~19.0)×10^3 cm^{-1} are observed. The weak band at (11.1~11.3)×10^3 cm^{-1} is due to the $^5T_{2g} \rightarrow {}^5E_g$ transition of iron(II) and is characteristic of a high spin octahedral configuration around iron(II) [29,30], while the strong band at (19.2~19.0)×10^3 cm^{-1} is characteristic of copper(II) in a square-planar environment [30], 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 1) may be attributable 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 [12]. Further investigations of these and similar systems are required in order to obtain more detailed assignment for the charge transfer.

In spite of our many attempt, 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 [15,18–22], 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.

Table 1. Physical data for the copper(II)–iron(II) heterodinuclear complexes.

Complex	μ_{eff} (B.M.)	Λ_M*	IR (cm^{-1})					UV $\upsilon(10^3cm^{-1})/\varepsilon_{max}$ ($mol^{-1}cm^{-1}L$)	
			υ(C=O)	υ(N=C)	υ(Fe–N)	υ(Fe–O)	$\upsilon(SO_4^{2-})$	d-d	CT
(**1**)	4.93	155	1650	1530	492	520	1123	19.1(242), 11.1(21)	29.9(21900)
(**2**)	4.89	148	1652	1528	488	524	1125	19.0(235), 11.2(30)	30.1(19800)
(**3**)	4.84	150	1650	1526	490	528	1120	19.2(258), 11.3(24)	30.2(23800)

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

Magnetic studies: The observed magnetic moment per dinuclear complex at room temperature, shown in Table 1, is less than the spin-only value (5.20 B.M.) for heterodinuclear complexes of copper(II)–iron(II) in the absence of exchange interaction. This suggests the operation of an antiferromagnetic spin-exchange interaction in these complexes [31]. 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. From Figure 2 it is evident that the magnetic moments decrease steadily with decreasing temperature, implying the existence of an antiferromagnetic spin-exchange interaction within each molecule.

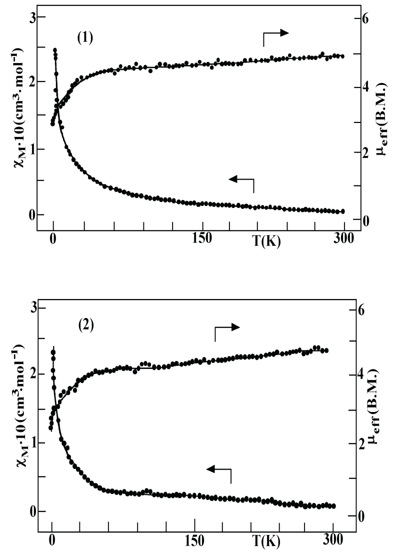

Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complexes [Cu(dmoxae)Fe(bpy)$_2$]SO$_4$ (**1**) and [Cu(dmoxae)Fe(phen)$_2$]SO$_4$ (**2**). The curves are based on equation (2) using the parameters given in the text. (•), experimental data; (–), calculation curves as described in the text.

This is consistent with the room-temperature magnetic moments of the heterodinuclear 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 copper(II)–iron(II) heterodinuclear complexes:

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

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 [31]. Considering the zero-field splitting of iron(II), we, therefore, adopted a susceptibility equation based on the modified Heisenberg operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 - D\hat{S}^2_{Z1}$, where D is axial zero-field splitting parameter for the iron(II) ion. In this case, the expression for the molar magnetic susceptibility (χ_M) is given by equation (2) [31]:

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

$A = (35J/4 + 4D)/kT$,
$B = [25J/4 + 5D/2 + (25J^2/4 - 9DJ/2 + 9D^2/4)^{1/2}]/kT$,
$C = [25J/4 + D/2 + (25J^2/4 - DJ/2 + D^2/4)^{1/2}]/kT$,
$G = [25J/4 + 5D/2 - (25J^2/4 - 9DJ/2 + 9D^2/4)^{1/2}]/kT$,
$E = [25J/4 + D/2 - (25J^2/4 - DJ/2 + D^2/4)^{1/2}]/kT$.

As shown in Figure 2, good least-squares fit to the experimental data was attained with equation (2). The magnetic parameters thus determined are $J = -20.9$ cm^{-1}, $g = 2.05$, $D = -1.25$ cm^{-1} for [Cu(dmoxae)Fe(bpy)$_2$]SO$_4$ (**1**) and $J = -22.7$ cm^{-1}, $g = 2.07$, $D = -1.36$ cm^{-1} for [Cu(dmoxae)Fe(phen)$_2$]SO$_4$ (**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 7.1×10^{-5} (**1**) and 8.2×10^{-5} (**2**). The results indicated that the complexes showed an antiferromagnetic spin-exchange interaction within each dinuclear unit. The 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 [32–34]. 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 [15,18,21] 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 [34] 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 $S = \langle b_1(Cu)|b_1(Fe)\rangle \neq 0$, antiferromagnetic exchange interactions should be observed in these complexes.

Table 2. Magnetic data of the copper(II)–iron(II) heterodinuclear complexes.

Complexes	–J (cm^{-1})	g	–D (cm^{-1})	10^5F	Ref.
[Cu(dmoxpn)Fe(bpy)$_2$](ClO$_4$)$_2$	15.9	2.03	1.01	7.5	16
[Cu(dmoxpn)Fe(phen)$_2$](ClO$_4$)$_2$	17.5	2.02	1.16	3.6	16
[Cu(oxae)Fe(bpy)$_2$]SO$_4$	30.6	2.06	1.8	6.5	17
[Cu(oxae)Fe(phen)$_2$]SO$_4$	31.8	2.04	2.0	3.2	17
[Cu(dmoxae)Fe(bpy)$_2$]SO$_4$	20.9	2.05	1.25	7.1	This work
[Cu(dmoxae)Fe(phen)$_2$]SO$_4$	22.7	2.07	1.36	8.2	This work

If we compare the present magnetic data with those previously reported for the analogous μ-oxamido dinuclear copper(II)–iron(II) complexes [Cu(dmoxpn)Fe(L)$_2$](ClO$_4$)$_2$ [16] and [Cu(oxae)Fe(L)$_2$]SO$_4$ [17] (where oxae and dmoxpn denote the N,N′-bis(2-aminoethyl)oxamido and N,N′-bis[3-(dimethylamino)propyl]oxamido dianions, respectively; L = bpy and phen), which are given in Table 2, we can obtain the following results for the magnetic interactions in these heterodinuclear complexes: [Cu(dmoxae)Fe(bpy)$_2$]SO$_4$ ($J = -20.9$ cm^{-1}) < [Cu(oxae)Fe(bpy)$_2$]SO$_4$ ($J = -30.6$ cm^{-1}); [Cu(dmoxae)Fe(phen)$_2$]SO$_4$ ($J = -22.7$ cm^{-1}) < [Cu(oxae)Fe(phen)$_2$]SO$_4$ ($J = -31.8$ cm^{-1}); [Cu(dmoxpn)Fe(bpy)$_2$](ClO$_4$)$_2$ ($J = -15.9$ cm^{-1}) < [Cu(dmoxae)Fe(bpy)$_2$]SO$_4$ ($J = -20.9$ cm^{-1}); [Cu(dmoxpn)Fe(phen)$_2$](ClO$_4$)$_2$ ($J = -17.5$ cm^{-1}) < [Cu(dmoxae)Fe(phen)$_2$]SO$_4$ ($J = -22.7$ cm^{-1}). In fact, these copper(II)-iron(II) heterodinuclear complexes have essentially the same skeletal structure and the same terminal ligand (bpy and phen), thus, their IR and electronic spectra are also similar. The only difference between [Cu(dmoxae)Fe(L)$_2$]SO$_4$ and [Cu(oxae)Fe(L)$_2$]SO$_4$ (L = bpy and phen) is that there are four methyl (-CH$_3$) substituents in their amine groups of the bridging ligand in the former. Their presence may have effects on both electronic and molecular structure [35]. 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. In addition, 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. Thus, the antiferromagnetic interaction between iron(II) and copper(II) in complexes [Cu(oxae)Fe(L)$_2$]SO$_4$ is larger than that of complexes [Cu(dmoxae)Fe(L)$_2$]SO$_4$ (L = bpy, phen). On the other hand, the main difference between [Cu(dmoxpn)Fe(L)$_2$](ClO$_4$)$_2$ and [Cu(dmoxae)Fe(L)$_2$]SO$_4$ (L = bpy and phen) is that the chelate ring around the copper(II) consists 6-5-6 members in [Cu(dmoxpn)Fe(L)$_2$](ClO$_4$)$_2$ and 5-5-5 members in [Cu(dmoxae)Fe(L)$_2$]SO$_4$. It is known that the relative stabilities of copper(II) complexes consisting of 6-5-6 member fused chelates are always higher than those of the 5-5-5 complexes [36]. Ojima and Nonoyama [12] pointed out, the higher the relative stability of the chelate ring arrangement; the less extensive is the delocalization of the π electrons in the oxamido bridge [12]. In other words, lower relative stability of the ligand field in an oxamido dimeric molecule makes the magnetic interaction through the oxamido bridge stronger [12]. Therefore, the J values (absolute value) of $[Cu(dmoxae)Fe(L)_2]SO_4$ should be larger than that of $[Cu(dmoxpn)Fe(L)_2](ClO_4)_2$. This would explain the difference in J values for the complexes $[Cu(dmoxae)Fe(L)_2]SO_4$ and $[Cu(dmoxpn)Fe(L)_2](ClO_4)_2$ (L = bpy and phen).

From the above discussion, it has shown that in this system the magnitude of the spin-exchange interaction between iron(II) and copper(II) ions may be tunable by playing the nature of the substituents in the bridging ligands, and this strategy opens vast perspectives. Further investigation using various substituents is required in order to confirm this effect and is in progress in our laboratory.

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