

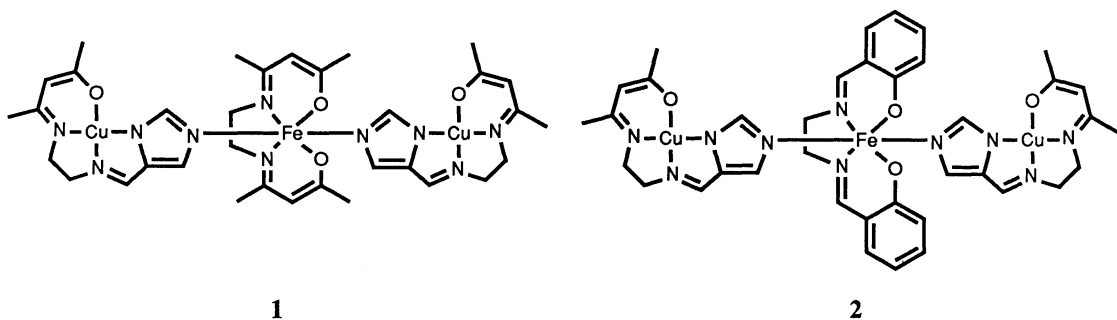
Synthesis and Magnetic Property of Imidazolate-Bridged Trinuclear Cu(II)-Fe(III)-Cu(II) Complexes.  
Effect of Fe(III) Spin-State Upon Spin-Coupling

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Imidazolate-bridged trinuclear Cu(II)-Fe(III)-Cu(II) complexes [Cu(A)Fe(acen)-Cu(A)]ClO<sub>4</sub>·2H<sub>2</sub>O (**1**) and [Cu(A)Fe(salen)Cu(A)]ClO<sub>4</sub>·2H<sub>2</sub>O (**2**) are synthesized and characterized by magnetic susceptibilities, Mössbauer spectra, and ESR spectra, where H<sub>2</sub>A=4-(6-methyl-8-oxo-2,5-diazanonane-1,5,7-trienylimidazole. The Fe(III) of **1** is in low-spin state ( $S = 1/2$ ) and the spin-coupling between the Fe(III) and Cu(II) ions is ferromagnetic. On the other hand, the Fe(III) of **2** is in high-spin state ( $S = 5/2$ ) and the spin-coupling is antiferromagnetic.

The elucidation of the structural and electronic-structural factors causing ferromagnetic spin-coupling between paramagnetic centers of polynuclear metal complexes is of current interests.<sup>1,2</sup> Ferromagnetic spin-coupling between the metal ions in hetero-metal system usually occurs when the magnetic orbitals of the interacting metal ions are orthogonal to each other.<sup>1,2</sup> Consider a hetero-metal system Fe(III)-Cu(II); if Fe(III) ion is in low-spin state, the magnetic orbitals of Fe(III) and Cu(II) ions are orthogonal to each other, because low-spin Fe(III) with (3d)<sup>5</sup> electronic configuration has one unpaired electron on a  $d_{\pi}$  type orbital under O<sub>h</sub> symmetry and Cu(II) with (3d)<sup>9</sup> has one unpaired electron on a  $d_{\sigma}$  type orbital. Therefore, ferromagnetic spin-coupling is expected for low-spin Fe(III)-Cu(II) pair. On the other hand, if Fe(III) is in high-spin state, the 3d shell is half-filled so that coupling with the copper unpaired electron could not lead to the strict orthogonality of the magnetic orbitals in any way. Thus, antiferromagnetic spin-coupling may occur for high-spin Fe(III)-Cu(II) pair. In order to investigate the effect of Fe(III) spin-state upon magnetic spin-coupling for Fe(III)-Cu(II) pair, in this study we have synthesized two imidazolate-bridged trinuclear Cu(II)-Fe(III)-Cu(II) complexes [Cu(A)Fe(acen)Cu(A)]ClO<sub>4</sub>·2H<sub>2</sub>O (**1**) and [Cu(A)Fe(salen)Cu(A)]ClO<sub>4</sub>·2H<sub>2</sub>O (**2**) (see drawings) where H<sub>2</sub>A=4-(6-methyl-8-oxo-2,5-diazanonane-1,5,7-trienyl)imidazole, H<sub>2</sub>acen=N,N'-bis(acetylacetylonylidene)-ethylenediamine, and H<sub>2</sub>salen=N,N'-bis(salicylidene)ethylenediamine and have shown that the spin-state of the Fe(III) is low-spin for **1** and high-spin for **2**. We report here ferromagnetic spin-coupling for **1** and antiferromagnetic spin-coupling for **2**.



The complex **1** was prepared as follows; To a methanol solution (20 cm<sup>3</sup>) of [Fe(acen)Cl] (313 mg, 1 mmol) was added a methanol solution (50 cm<sup>3</sup>) of [Cu(A)]0.5CHCl<sub>3</sub> (853 mg, 2.5 mmol). The mixture was kept at room temperature under stirring until the color of the solution turned from dark red to dark green, and then filtered. To the filtrate was added a methanol solution (20 cm<sup>3</sup>) of NaClO<sub>4</sub> (122 mg, 1 mmol) to give dark green microcrystals. Found: C, 41.05; H, 4.77; N, 14.33; Cu, 12.99; Fe, 5.48%. Anal. Calcd for [Cu(A)Fe(acen)Cu(A)]ClO<sub>4</sub>·2H<sub>2</sub>O, C<sub>34</sub>H<sub>50</sub>N<sub>10</sub>O<sub>10</sub>ClCu<sub>2</sub>Fe: C, 41.79; H, 5.16; N, 14.33; Cu, 13.00; Fe, 5.71%.  $\Lambda_M$  56 S mol<sup>-1</sup> cm<sup>2</sup> (in CH<sub>2</sub>Cl<sub>2</sub>). Electronic spectrum in CH<sub>2</sub>Cl<sub>2</sub>; 532 nm ( $\epsilon$  = 1560 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>) and 636 nm ( $\epsilon$  = 2100 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>).

A similar synthetic procedure of **1** was used to the synthesis of **2**, using [Fe(salen)Cl] instead of [Fe(acen)Cl]. Reddish black microcrystals. Found: C, 44.38; H, 4.31; N, 13.83; Cu, 12.05; Fe, 5.49%. Anal. Calcd for [Cu(A)Fe(salen)Cu(A)]ClO<sub>4</sub>·2H<sub>2</sub>O, C<sub>38</sub>H<sub>46</sub>N<sub>10</sub>O<sub>10</sub>ClCu<sub>2</sub>Fe: C, 44.69; H, 4.54; N, 13.71; Cu, 12.44; Fe, 5.47%.  $\Lambda_M$  41 S mol<sup>-1</sup> cm<sup>2</sup> (in CH<sub>2</sub>Cl<sub>2</sub>). Electronic spectrum in CH<sub>2</sub>Cl<sub>2</sub>; 498 nm ( $\epsilon$  = 3900).

The main subject of this work is to obtain Cu(II)-Fe(III)(*S*=5/2)-Cu(II) (with a high-spin Fe(III)) and Cu(II)-Fe(III)(*S*=1/2)-Cu(II) (with a low-spin Fe(III)) complexes and to investigate the magnetic interaction between Fe(III) and Cu(II) ions paying attention to the electronic configuration of Fe(III) ion. For this purpose we have adopted [Cu(A)] as a copper(II) component and [Fe(acen)]<sup>+</sup> and [Fe(salen)]<sup>+</sup> as a Fe(III) component to afford trinuclear [Cu(A)Fe(acen)Cu(A)]<sup>+</sup> and [Cu(A)Fe(salen)Cu(A)]<sup>+</sup> species. The choice of H<sub>2</sub>acen and H<sub>2</sub>salen as central ligands is due to our expectation that [Cu(A)Fe(acen)Cu(A)]<sup>+</sup> and [Cu(A)Fe(salen)Cu(A)]<sup>+</sup> species thus obtained may be of a low-spin Fe(III) and a high-spin Fe(III), respectively, because the related complexes [Fe(HIm)<sub>2</sub>(acen)]<sup>+</sup> and [Fe(HIm)<sub>2</sub>(salen)]<sup>+</sup> (HIm=imidazole) are known to be low-spin and high-spin complexes, respectively.<sup>3-7</sup> The spectrum of **1** is similar to that of low-spin [Fe(HIm)<sub>2</sub>(acen)]BPh<sub>4</sub> ( $\lambda_{\max}$  = 530 nm ( $\epsilon$  = 1230),  $\lambda_{\max}$  = 661 nm ( $\epsilon$  = 1540)). The spectral feature of **2** is similar to that of high-spin [Fe(HIm)<sub>2</sub>(salen)]BPh<sub>4</sub> ( $\lambda_{\max}$  = 518 nm ( $\epsilon$  = 3040)). The Mössbauer spectra of **1** and **2** were measured at room temperature. The Mössbauer parameters obtained for **1** are  $\Delta E$  = 2.32 mm sec<sup>-1</sup> and  $\delta_{Fe}$  = 0.24 mm sec<sup>-1</sup> which are typical of low-spin Fe(III), while those for **2** are  $\Delta E$  = 0.99 mm sec<sup>-1</sup>,  $\delta_{Fe}$  = 0.48 mm sec<sup>-1</sup> which are typical of high-spin Fe(III).<sup>8</sup>

The magnetic susceptibility data of **1** and **2** are shown in Fig. 1, in the form of  $\mu_{\text{eff}}$  vs. *T* plots, where  $\mu_{\text{eff}}$  is the effective magnetic moment per trinuclear complex.

The  $\mu_{\text{eff}}$  value of **1** at room temperature is 3.33  $\mu_B$  which is somewhat larger than the spin-only value 3.00  $\mu_B$  for a system (*S*<sub>1</sub>, *S*<sub>2</sub>, *S*<sub>3</sub>=1/2, 1/2, 1/2) assuming no magnetic interaction. As the temperature is lowered, the  $\mu_{\text{eff}}$  decreases gradually from 3.33  $\mu_B$  at 290 K to 3.20  $\mu_B$  at 80 K, then increases gradually up to a maximum value 3.71  $\mu_B$  at 7 K, and finally decreases again to 3.62  $\mu_B$  at 4.2 K. The origin of the moderate

decrease of  $\mu_{\text{eff}}$  in 80–290 K must be due to the contribution of the orbital angular momentum of  $^2T_{2g}$  term of low-spin Fe(III). A similar trend was observed for mononuclear low-spin Fe(III) complexes  $[\text{Fe}(\text{HIm})_2(\text{acen})]\text{BPh}_4$  and  $[\text{Fe}(\text{CN})\text{L}]\text{BPh}_4$  ( $\text{H}_2\text{L}$ =4-azaheptamethylene-1,7-bis(salicylideneimine)).<sup>6,9)</sup> The increase of  $\mu_{\text{eff}}$  in 7–80 K must be due to intramolecular ferromagnetic spin-coupling. The maximum value  $3.71 \mu_{\text{B}}$  at 7 K is close to the spin-only value  $3.87 \mu_{\text{B}}$  expected for the spin ground state  $S_{\text{T}} = 3/2$  derived from ferromagnetic spin-coupling of a trinuclear system ( $S_1, S_2, S_3$ )=(1/2, 1/2, 1/2). The decrease of  $\mu_{\text{eff}}$  below 7 K may be due to intermolecular antiferromagnetic interaction. Hence, the magnetic property of **1** is effected by three magnetic interactions, *i.e.*, (i) the orbital angular momentum of  $^2T_{2g}$  term which contributes to  $\mu_{\text{eff}}$  in a high temperature region. (ii) intramolecular ferromagnetic interaction which is the predominant factor for the magnetic susceptibility. (iii) intermolecular antiferromagnetic interaction which contributes to  $\mu_{\text{eff}}$  only in very low temperature region. A conventional method was applied to interpret the magnetic data quantitatively in this work. The magnetic susceptibility data were analyzed on the basis of the spin-only expression (1) for the spin-system ( $S_1, S_2, S_3$ )=(1/2, 1/2, 1/2) ( $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3)$ ) including the contribution of the orbital angular momentum  $^2T_{2g}$  term,

$$\chi_{\text{M}} = \frac{Ng^2\beta^2(10x+x^{-2}+1)}{4kT(2x+x^{-2}+1)} + \frac{N\beta^2[8+\{3y-8\exp(-3y/2)\}]}{3kTy[2+\exp(-3y/2)]} - \frac{Ng^2\beta^2}{4kT} \quad (1)$$

where  $x = \exp(J/kT)$  and  $y = \lambda/kT$ . The first term corresponds to the spin-only expression and the second and third terms correspond to the correction term for higher temperature region due to the contribution of the orbital angular momentum of  $^2T_{2g}$ . Fitting parameters are  $g=1.95$ ,  $J=+12 \text{ cm}^{-1}$ , and  $\lambda = -560 \text{ cm}^{-1}$ .

The  $\mu_{\text{eff}}$  of **2** at room temperature is  $6.44 \mu_{\text{B}}$  which is comparable to the spin-only value  $6.40 \mu_{\text{B}}$  of a trinuclear complex with three spin-system ( $S_1, S_2, S_3$ )=(1/2, 5/2, 1/2) assuming no magnetic interaction. As the temperature is lowered, the  $\mu_{\text{eff}}$  decreases gradually from  $6.44 \mu_{\text{B}}$  at 291.8 K and reaches a plateau of  $3.80 \mu_{\text{B}}$  below 16 K, indicating the operation of intramolecular antiferromagnetic

interaction. The observed magnetic moment *ca.*  $3.80 \mu_{\text{B}}$  at the plateau region 6–16 K is close to the spin-only value  $3.87 \mu_{\text{B}}$  expected for  $S_{\text{T}}=3/2$ , the smallest total-spin generated by antiferromagnetic spin-coupling in Cu(II)-Fe(III)( $S=5/2$ )-Cu(II) system. The magnetic susceptibility data were analyzed on the basis of Eq. 2 for

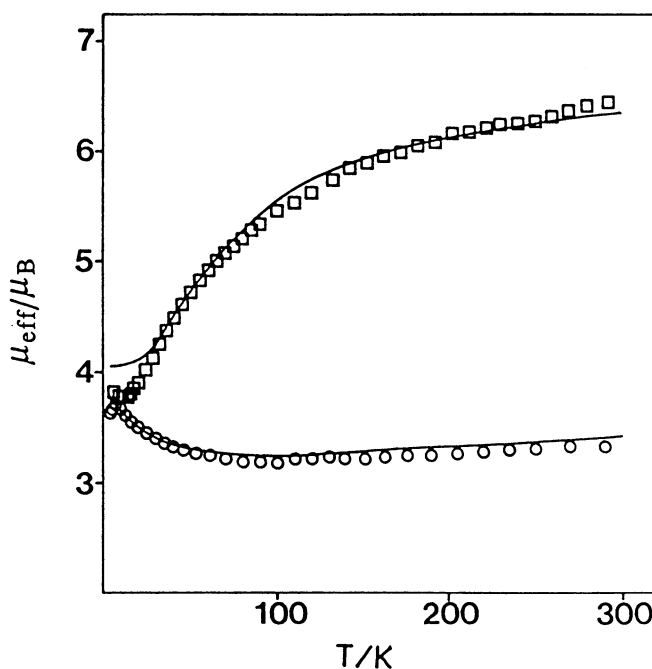


Fig. 1. Plot of  $\mu_{\text{eff}}$  vs.  $T$  for **1**(○) and **2**(□). Solid lines represent theoretical curves.

a symmetrical three-spin system derived from a spin-Hamiltonian  $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3)$  ( $S_1 = S_3 = 1/2$ ,  $S_2 = 5/2$ ). The best-fit was attained with  $g = 2.03$ , and  $J = -11 \text{ cm}^{-1}$ .

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \frac{10x^{-7} + 35(x^{-2}+1) + 84x^5}{2x^{-7} + 3(x^{-2}+1) + 4x^5} + N\alpha, \quad x = \exp(J/kT) \quad (2)$$

Two complexes **1** and **2** differ in magnetic property from each other. That is, ferromagnetic spin-coupling occurs in **1**, whereas an antiferromagnetic spin-coupling in **2**. ESR spectra of [Cu(A)] and [Fe(HIm)<sub>2</sub>(acen)]<sup>+</sup> showed that the Cu(II) and Fe(III) ions have an unpaired electron on  $\sigma$  and  $\delta$  character orbitals with respect to the Cu-N(imidazole nitrogen) and Fe-N(imidazole nitrogen) bonds, respectively.<sup>3,10</sup> Therefore, the ferromagnetic spin-coupling in **1** can be explained in terms of the  $\delta/\sigma$  orthogonality of the interacting magnetic orbitals, as we and others discussed on hetero-metal systems.<sup>1,2,10,11</sup> On the other hand, the Fe(III) of (**2**) is in high-spin state of a  $(3d)^5$  electronic configuration. And no strict orthogonality of the magnetic orbitals between Cu(II) and Fe(III) ions can be realized. In the case of, one of the five magnetic orbitals of Fe(III) brings about a finite overlap integral in the Cu-Im-Fe MO system, and this provides an antiferromagnetic contribution that is usually dominant.<sup>12</sup>

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