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Imidazolate-mediated Antiferromagnetic Coupling between Fe(III) Ions in Rigidly-linked Porphyrin Dimers and Trimers

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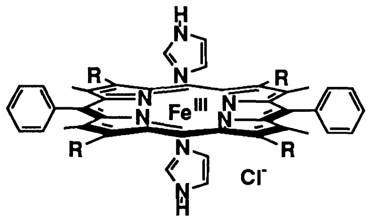
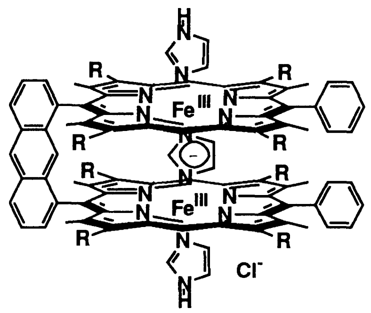
1,8-Anthracene- and *o*-phenylene-linked iron(III) porphyrin dimers and the trimer were synthesized. Their Fe(III) ions were ligated by imidazolate(s) in the molecular creft to form the corresponding low-spin complexes. Relatively large imidazolate-mediated antiferromagnetic exchange coupling ($-J$ = 15.3-29.4 cm^{-1}) between the Fe(III) ions is observed by means of their esr and magnetic susceptibility measurements.

Electronic and magnetic interactions between transition metal ions have been interesting from theoretical and experimental stand points in order to design high conducting or paramagnetic materials. Metalloporphyrins and metallophthalocyanines are known to be excellent candidates having large planar π ligands and two axial coordination sites, which potentially allow linear conducting polymers.1) Imidazole (Him) or imidazolate (im) are excellent donating ligands to iron and they allow electronic/magnetic interaction between metal ions. However, only a few examples of imidazole or imidazolate mediated magnetic coupling between the metalloporphyrins have been reported regarding simple metalloporphyrin complexes. From the results of such complexes, $[(\mathrm{M\text{-}TPP})(\mathrm{im})]_n$2) and urea-linked metalloporphyrin dimers,3) the imidazolate molecule is considered to be a relatively weak mediator of antiferromagnetic coupling as revealed by their magnetic susceptibility measurements. In this article, we show the preparation and structural determination of imidazolate-squeezed iron porphyrin dimers and trimer linked by a rigid backbone molecule and their relatively large antiferromagnetic coupling.

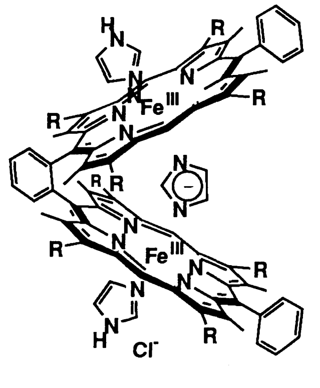
To realize strong magnetic interactions between two metal ions, we chose 1,8-anthrancene and *o*-phenylene as linker molecules. From CPK model study, they have suitable metal-metal separation and give the adequate molecular cavity between the porphyrins for the incorporation of im. According to this strategy, we prepared the iron(III) derivatives of 1,8-anthracene-linked porphyrin dimer (**2**, $[\mathrm{Fe_2\{An(TPP)\}]Cl_2}$), trimer (**4**, $[\mathrm{Fe_3\{An_2(TPP)_3\}]Cl_3}$), *o*-phenylene-bridged dimer (**3**, $[\mathrm{Fe_2\{Ph(TPP)_2\}]Cl_2}$), and the corresponding monomer (**1**, [Fe(TPP)]Cl) as the references.4,5) The imidazole complexes of these metalloporphyrins were prepared by the crystallization in acetonitrile-$\mathrm{CH_2Cl_2}$ solutions containing excess amounts of imidazole. The resultant iron(III) porphyrin-imidazole complexes, $[\mathrm{Fe(TPP)(Him)_2]Cl}$ (**5**), $[(\mu\text{-im})\mathrm{Fe_2\{An(TPP)_2\}(Him)_2]]Cl}$ (**6**), $[(\mu\text{-im})\mathrm{Fe_2\{Ph(TPP)_2\}(Him)_2]Cl}$ (**7**), and $[(\mu\text{-im})_2\mathrm{Fe_3\{An_2(TPP)_3\}(Him)_2]Cl}$ (**8**) were obtained as fine crystals.4) The X-ray crystallographic analysis of **6**6) at room temperature revealed that two Fe(III) ions were coordinated by an imidazolate molecule inside the molecular cavity (Fig. 1). The ligation of imidazolate caused a saddle-shaped deformation to the porphyrin rings by bending outside the plane rings. The $\mathrm{N_{ax}}$-Fe



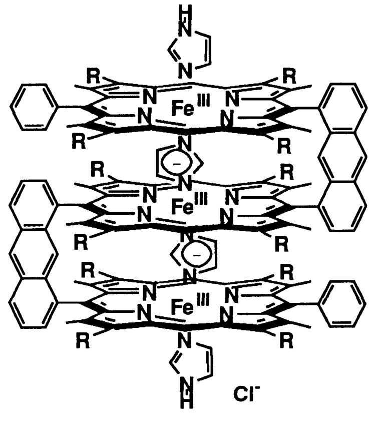
5 [Fe(TPP)(Him)$_2$]Cl



6 [(μ-im)Fe$_2${An(TPP)$_2$}(Him)$_2$]Cl



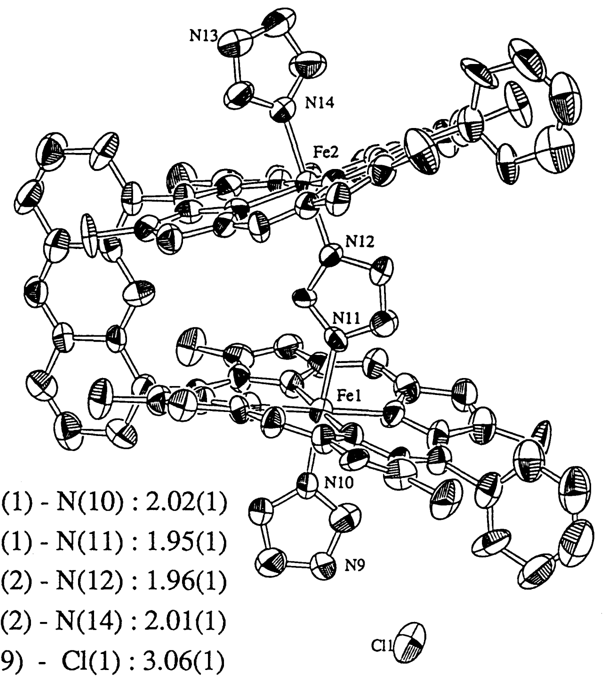
7 [(μ-im)Fe$_2${Ph(TPP)$_2$}(Him)$_2$]Cl



8 [(μ-im)$_2$Fe$_3${An$_2$(TPP)$_3$}(Him)$_2$]Cl

R = n-C_6H_{13}

bond distances were Fe-N(im) = 1.95 - 1.96 Å and Fe-N(Him) = 2.01 - 2.02 Å. Thus, the Fe-N(im) separation in this instance is smaller than the reported ones (2.186 - 2.280 Å) of the analogous Mn-im complexes.2) This implies that the strong magnetic and/or electronic interaction would be capable between the two Fe ions through the squeezed im molecule. These Fe-N$_{ax}$ distances are compatible with a low-spin iron(III) state.7) The other two complexes, **7** and **8**, would have similar structures regarding to imidazolate ligation based on the following spectroscopic data. The UV-vis spectrum of these imidazolate complexes showed their absorption maximum of the Soret band in the range from 407 to 411 nm in CH_2Cl_2 at 25 °C.8) This also supports the formation of low spin six-coordinate iron(III) porphyrin-imidazole complexes. ESR spectra of the anthracene-linked iron(III) porphyrins were measured in CH_2Cl_2 at 77 K. All the iron(III) porphyrins without an imidazole ligand exhibited absorption at g = 6.6 (**1**), 7.8 (**2**), 6.3 (**4**) which are characteristic to high-spin iron complexes. In these complexes, any magnetic interaction between the Fe ions was not observed. The iron(III) porphyrin monomer-imidazole complex **5** exhibited the ESR spectrum with g_1 = 2.9, g_2 = 2.4 which are characteristic to a low-spin complex. On the other hand, the imidazolate complexes, **7** and **8**, showed very broad signals and had none of such a distinct resonance. This could be due to the imidazolate-mediated antiferromagnetic exchange coupling



Fe(1) - N(10) : 2.02(1)
Fe(1) - N(11) : 1.95(1)
Fe(2) - N(12) : 1.96(1)
Fe(2) - N(14) : 2.01(1)
N(9) - Cl(1) : 3.06(1)

Fig. 1. ORTEP drawing for **6** and selected bond-lengths in Å. The hexyl groups are omitted for clarity.

Table 1. Best fit parameters of iron(III) porphyrin-imidazole complexes analyzed according to the Bleaney-Bowers equation[a)]

Compound.	J / cm^{-1}	g	θ/K	$N\alpha$ /10^{-4} emu mol^{-1}	γ/%	r
6	-29.4	2.14	8.7	11.2	1.38	0.9996
7	-19.8	2.27	8.3	1.7	8.3	0.9917
8	-15.3	2.26	0.345	2.41	-	0.9999

a) J; Exchange integral. g; Spectroscopic splitting factor. θ; Weiss constant. $N\alpha$; Temperature-independent paramagnetic term. γ: Impurity of monomer. r: Correlation coefficient of least squre fit.

between the irons. To determine the degree of the exchange coupling, the temperature-dependent magnetic susceptibility (χ) was measured for microcrystalline samples of iron(III) porphyrins and the corresponding imidazole complexes on a SQUID susceptometer at 2.39×10^5 or 7.96×10^5 A m^{-1} in the temperature range 5-300 K. The resultant χ of the imidazole-free complexes, **1**, **2**, **3**, and **4**, follows the Curie law (χ = C/T) and their effective magnetic moments were estimated to be μ_{eff} = 5.97, 5.93, 5.98 and 5.71 μ_{B} per iron(III), respectively, which are in good accordance with the spin only value μ_{eff}(theory) = 5.92 μ_{B} (S = 5/2) expected for high-spin iron(III) complexes. Thus, there is no magnetic interaction between Fe(III) ions in these imidazole-free complexes. The magnetic susceptibility of **5** also follows the Curie law, and the effective magnetic moment was μ_{eff} = 1.89 μ_{B}, expected for a low-spin (S = 1/2) iron(III) complex compared with μ_{eff}(theory) = 1.73 μ_{B} (S = 1/2). However, the susceptibility data of **6** is completely different from the monomer as shown in Fig. 2a.[9)] The magnetic behavior can be well simulated according to the equation (1)[10)] by assuming the general isotropic exchange Hamiltonian $H = -2J\, S_1 \cdot S_2$ with $S_1 = S_2 = 1/2$,[11)] where $2J$ is a singlet-triplet energy gap. The observed magnetic behavior shows that the complex takes the singlet ground state to give the best fit parameters in Table 1. The estimated value $-J$ = 29.4 cm^{-1} was larger than the reported values of Mn(II)-(μ-im)-Mn(II) complexes ($-J$ < 8 cm^{-1}),[11)] which have isoelectronic structures with the corresponding Fe(III) complexes. The result of the magnetic susceptibility measurement of **8** is shown in

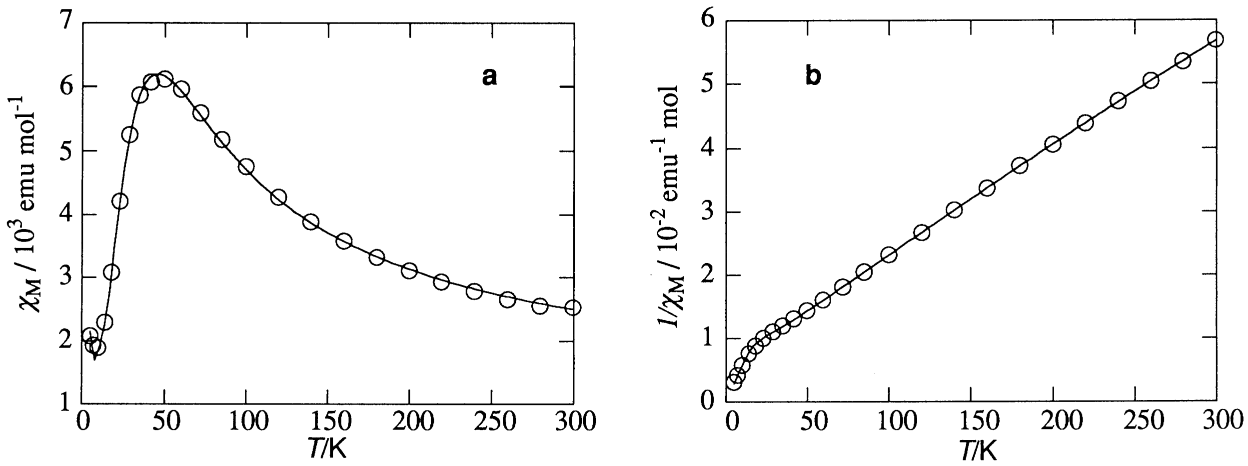


Fig. 2. Temperature dependence of magnetic susceptibility of **6** (a) and **8** (b). The circles are observed data points after correction of diamagnetic and paramagnetic impurities. The curve is a calculated best fit according to equations (1) and (2) for **6** and **8**, respectively.

Fig. 2b. If the intramolecular spin coupling between the terminal Fe(III) ions is negligibly small, the spin-spin interaction of this trimer system can be expressed by the general isotropic exchange Hamiltonian $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3)$ with $S_1 = S_2 = S_3 = 1/2$. The simulation of the resultant data according to the equation (2)10) showed good fitting with experimental data, and the estimated $-J$ value ($-J$ = 15.3 cm^{-1}) was comparable with those of the dimers. Thus, the very rigid structure of the porphyrin oligomers with the appropriate distances and the arrangement of the metal ions can give the corresponding stable imidazolate complexes. The resultant short Fe-N(im) distances allow that imidazolate stabilizes the singlet ground state2,3,11) and becomes a good mediator of the antiferromagnetic exchange coupling between Fe(III) ions .

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6) Crystal Data for **6**: $C_{131}H_{161}N_{14}Fe_2Cl$, F_W = 2078.95, monoclinic, space group $P2_1/n$, a = 19.46(1), b = 23.84(1), c = 25.45(2) Å, β = 94.72(6)°, V = 11765(12) $Å^3$, Z = 4, D_o = 1.180, D_c = 1.174 g cm^{-3}, R = 0.069, R_W = 0.076 for 4731 observed reflections. Equivalent temperature factors (B_{eq}) were calculated according to the following equation.

$$B_{eq} = \frac{8}{3}\pi^2\left[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha\right]$$

7) W. R. Scheidt and C. A. Reed, *Chem. Rev.*, **81**, 543 (1981).

8) UV-vis spectra of the iron porphyrin dimers and trimer in the presence of excess amounts of imidazole showed their λ_{max} at this region. The isolated imidazolate complexes also gave the same spectra in CH_2Cl_2. Thus, the isolated imidazolate complexes were stable in the solution.

9) Phenylene-linked iron porphyrin dimer **7** also showed a similar temperature-dependent magnetic susceptibility.

10)
$$\chi = \frac{Ng^2\beta^2}{3k(T-\theta)}\frac{3}{3+\exp(-2J/kT)} + N\alpha + \gamma\frac{C}{T} \qquad (1)$$

$$\chi = \frac{Ng^2\beta^2}{12k(T-\theta)}\frac{1+\exp(-2J/kT)+10\exp(J/kT)}{1+\exp(-2J/kT)+2\exp(J/kT)} + N\alpha \qquad (2)$$

where C is Curie constant. For other notation of each parameter, see the footnotes of Table 1.

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