Spin States of Mono- and Dinuclear Iron(II) Complexes with Bis(imidazolylimine) Ligands

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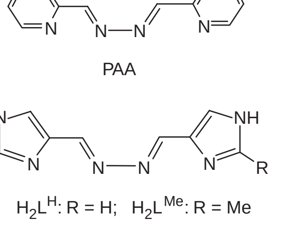
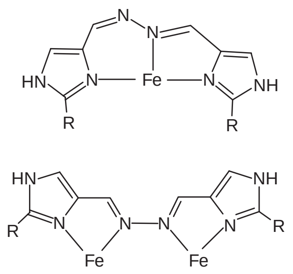
Bis(imidazolylimine) ligands, H_2L^H and H_2L^{Me}, were prepared from hydrazine and 4-formylimidazole or 2-methyl-4-formylimidazole (1:2), respectively. Mononuclear iron(II) complexes, $[Fe(H_2L^H)_2](ClO_4)_2 \cdot MeOH$ and $[Fe(H_2L^{Me})_2](ClO_4)_2 \cdot 2H_2O$, were in the LS and HS states, respectively, in the temperature range 5–300 K. A triple-helicate $[Fe_2(H_2L^H)_3](ClO_4)_4$, showed an abrupt [LS–HS] to [HS–HS] spin transition at 240 K, while $[Fe_2(H_2L^{Me})_3](ClO_4)_4$ remained in the LS state in the temperature range 5–300 K.

As early as 1958, Busch and Stratton[1] reported that the pyridylaldazine ligand, PAA (Scheme 1), could form two types of metal complexes, $[M(PAA)_2]^{2+}$ (M^{II} = Fe, Ni) and $[M_2(PAA)_3]^{4+}$ (see Scheme 2). In the former mononuclear complex, PAA acts as an unsymmetrical tridentate ligand with two pyridyl nitrogen atoms and one azine nitrogen atom. In the latter complex, PAA acts as a dinucleating ligand employing all four nitrogen atoms to form a triple helicate. Both the iron(II) complexes, $[Fe(PAA)_2]^{2+}$ and $[Fe_2(PAA)_3]^{4+}$, are reported to be in the low spin state. Because an imidazole nitrogen atom usually exhibits a weaker ligand field strength than a pyridine nitrogen atom does, we expected that the imidazole analog of PAA, H_2L^H, and its methyl derivative, H_2L^{Me}, would have the necessary ligand field strength to form spin-crossover (SCO) iron(II) complexes. Dinuclear iron(II) SCO complexes are particularly interesting since the iron centers are coupled by intramolecular interactions.[2] In diiron(II) complexes, three different spin-pair states are possible: [LS–LS], [LS-HS], and [HS–HS]. Here, we report that $[Fe_2(H_2L^H)_3](ClO_4)_4$ shows an abrupt [LS–HS] to [HS–HS] spin transition, and that H_2L^H and H_2L^{Me} afford a different order of the ligand field strength between the mononuclear and dinuclear Fe^{II} complexes.

The bis(imidazolylimine) ligands, H_2L^H and H_2L^{Me}, were prepared by condensation of hydrazine and 4-formylimidazole or 2-methyl-4-formylimidazole in a 1:2 mole ratio in methanol.[3] The mononuclear complex, $[Fe(H_2L^H)_2](ClO_4)_2 \cdot MeOH$ (**1H**), was prepared by the reaction of H_2L^H and $Fe(ClO_4)_2 \cdot 6H_2O$ in methanol in a 2:1 mole ratio.[3] The color of the mixture changed from orange to dark purple on heating, and on addition of diethyl ether, **1H** was isolated as dark purple crystals. The corresponding methyl derivative, $[Fe(H_2L^{Me})_2](ClO_4)_2 \cdot 2H_2O$ (**1Me**), was prepared in a similar manner and isolated as orange crystals.[3] The distinct color difference, dark purple (**1H**) versus orange (**1Me**), suggested that the complexes were in different spin states. The dinuclear complexes, $[Fe_2(H_2L^H)_3](ClO_4)_4$ (**2H**) and $[Fe_2(H_2L^{Me})_3](ClO_4)_4$ (**2Me**), were prepared by the reaction of the respective ligand and $Fe(ClO_4)_2 \cdot 6H_2O$ in nitromethane in a 3:2 mole ratio.[3] Once again, the color of the two compounds was different: orange (**2H**) and dark brown (**2Me**).



Scheme 1. Ligands, PAA, H_2L^H, and H_2L^{Me}.



Scheme 2. Two coordination modes adopted by H_2L^R (R = H, CH_3).

Temperature-dependent molar susceptibility measurements on powdered samples of **1H**, **1Me**, **2H**, and **2Me** were carried out in an applied field of 0.5 T in the temperature range 5–300 K. Complex **1H** remained in the low-spin (LS) state over the entire temperature range, while **1Me** was in the high-spin (HS) state. The dinuclear complexes, **2H**, and **2Me**, were in different spin states from those of the corresponding mononuclear complexes, **1H** and **1Me**. At 300 K, **2H** and **2Me** were in the HS and LS state, respectively. The magnetic behavior of **2H** and **2Me** are shown in Figure 1 in the form of a $\chi_M T$ versus T plot, where χ_M is the molar magnetic susceptibility and T is the absolute temperature. Complex **2H** exhibited the abrupt SCO behavior at ca. 240 K. Above 250 K, the $\chi_M T$ value was nearly constant at 6.6 $cm^3\,K\,mol^{-1}$, which is close to the calculated value for the [HS–HS] system ($\chi_M T = 6.0\,cm^3\,K\,mol^{-1}$). In the temperature range 30–220 K, the value of $\chi_M T$ was nearly constant at 3.3 $cm^3\,K\,mol^{-1}$, indicating that 50% of the Fe^{II} sites were in the HS state. The half-SCO state was trapped, and the complex was locked into it, and it does not change into the [LS–LS] state on further reducing the temperature. The decrease in $\chi_M T$ observed below ca. 20 K is probably due to a combination of zero-field splitting of the HS Fe^{II} center and low-symmetry ligand field splitting effects. Similar behavior was shown by other SCO complexes.[2e,2h] The temperature dependence of the Mössbauer spectra agrees with the magnetic susceptibility results.[3]

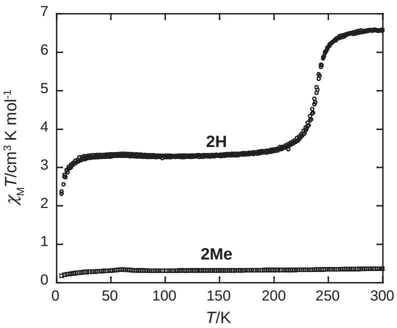


Figure 1. Magnetic behaviors of $[Fe_2(H_2L^H)_3](ClO_4)_4$ (**2H**) and $[Fe_2(H_2L^{Me})_3](ClO_4)_4$ (**2Me**) in the form of a $\chi_M T$ versus T plot.

The X-ray crystal structure of **2H** was determined at both 103 and 293 K, because this complex undergoes a spin transition at ca. 240 K. There is no crystallographic phase transition, and the same space group, $P2_1/c$, is retained at both temperatures. Figure 2 shows an ORTEP drawing of the cation of **2H** at 293 K. The structure is a dinuclear triple-helicate, with each ligand bound as a bis-didentate to two different iron centers. Each Fe^{II} center binds to three ligand strands to attain a pseudo-octahedral coordination geometry. All the Fe–N coordinate bond distances (2.116(2)–2.238(2) Å) are typical for HS Fe^{II}.[4] The two iron centers, Fe1 and Fe2, are in different environments. The average Fe1–N bond length (2.153 Å) is smaller than that of Fe2–N (2.197 Å).

At 103 K, the average Fe1–N bond length (1.975 Å) shortens by 0.178 Å than that at 293 K (2.153 Å), demonstrating that the SCO occurs at the Fe1 site, while the Fe2 site remains in the HS state (average Fe2–N bond length = 2.189 Å), to form a mixed-spin state [LS–HS] complex. The Fe1···Fe2 distance decreases from 4.0362(7) Å at 293 K to 3.8507(8) Å at 103 K. The unit cell volume of 5610.1(3) Å^3 at 293 K decreases to 5344.3(5) Å^3 at 103 K (4.7%).

As described above, **1Me** is in the HS state while **1H** is in the LS state at room temperature. The difference in the spin state may be explained in terms of a steric effect. The X-ray molecular structure of $[Fe(H_2L^H)_2]^{2+}$ (**1H**) shows that each H_2L^H ligand serves as an unsymmetrical tridentate ligand.[5] Inspection of the molecular structure indicates that **1Me** involves intramolecular steric repulsion between a methyl group of an H_2L^{Me} ligand and the other ligand. The steric crowding will lengthen the Fe–N bond resulting in the HS state. None of the other complexes, **1H**, **2H**, or **2Me**, involves such a steric congestion. Thus, a different order of the ligand field strength between the mononuclear and dinuclear Fe^{II} complexes results. The SCO behavior is known to depend on many factors such as the nature of the counter ion and solvent of crystallization. It is to be noted that the present complexes are in different spin states not only in the solid state but also in solution at room temperature. This suggests that the different order of the ligand field strength between the mono- and dinuclear complexes is intrinsic.

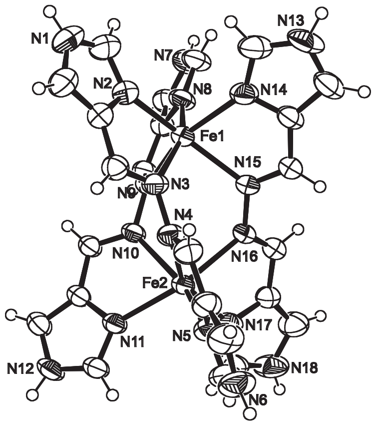


Figure 2. X-ray molecular structure of the cation of $[Fe_2(H_2L^H)_3](ClO_4)_4\cdot5MeNO_2$ (**2H**) at 293 K, with an atom numbering scheme showing the 50% probability ellipsoids.

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3 Detailed synthetic methods, Mössbauer spectral data, and crystallographic data of **2H** were deposited in Supporting Information.[6] Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-647353 and 647354. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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5 The structure of **1H** proved difficult to refine to an acceptable level because of the low quality of the crystal but the gross stereochemical features are clearly identified.

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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