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Spin-Equilibrium Behavior of Iron(III) Complexes with Various Monodentate Ligands and Bis(*N,N'*-3-Methoxysalicylideneaminopropyl) Methylamine

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The syntheses, structures, and magnetic properties of iron(III) complexes with the chemical formula of $[Fe(X)L]Bph_4$ are reported, where X = monodentate ligand such as pyridine and imidazole derivatives, H_2L = bis(*N,N'*-(3-methoxy-salicylideneaminopropyl)methylamine, and Bph_4^- = tetraphenylborate, respectively. The magnetic susceptibilities were measured by a SQUID susceptometer in the temperature range 4–350 K under an external magnetic field of 1 T. On the basis of the magnetic susceptibility data, the complexes are classified into three groups (**1**) – (**3**). (**1**): high-spin complexes; The effective magnetic moments of $[Fe(Im)L]Bph_4$ and $[Fe(4\text{-}MeIm)L]Bph_4$ are constant at ca. 5.7 μ_B over the temperature range measured. (**2**): spin-equilibrium complexes between S =5/2 and S =1/2; $[Fe(4\text{-}NH_2py)L]Bph_4$ showed an ideal spin-equilibrium behavior, as the μ_{eff} decreased from 5.5 μ_B at 300 K to 2.1 μ_B at 60 K. Hysteresis was not observed, indicating that the complex is classified as continuous type. The thermodynamic model of Slichter and Drickamer was applied and the intermolecular interaction parameter Γ, the enthalpy ΔH, and the entropy ΔS were estimated to be Γ = 2 kJ / mol, ΔH = 5.99 kJ / mol, and ΔS = 49.99 J/ mol K, respectively. (**3**): $[Fe(py)L]Bph_4$ showed an unusual magnetic behavior. On lowering the temperature, the μ_{eff} decreased gradually from 5.69 μ_B at 300 K and reached to a plateau value of 3.89 μ_B at 60 K, whose value is too large for low-spin state and rather close to that of S = 3/2.

INTRODUCTION

Iron(III) complex with $3d^5$ electronic configuration can assume versatile spin-states, that is, high-spin (S = 5/2), intermediate-spin (S = 3/2), low-spin (S = 1/2), and spin-equilibrium.[1] The spin-equilibrium behavior, which can be driven by external constrains such as

temperature, pressure, and photo-irradiation, has attracted much attention not only for the potential use as molecular-based electronic devices such as optical memory and switches, but also for precise understanding how some iron-containing protein tunes the electronic state of its prosthetic group.[2-7]

In the previous paper,[8] we have shown that the iron(III) complexes with a pentadentate Schiff-base ligand derived from the 2:1 condensation of salicylaldehyde and di(3-aminopropyl)amine can afford a ligand field so as to give a spin-equilibrium behavior. In the present work, the analogous iron(III) complexes with the general formula $[Fe(X)L]Bph_4$ (see Chart 1) have been prepared by the use of the pentadentate ligand of the 2:1 condensation product of 3-methoxy salicylaldehyde and di(3-aminopropyl)-methylamine. Since the magnetic behavior for the series of the complexes were found to be versatile, we report the synthesis, crystal structure, and magnetic properties.

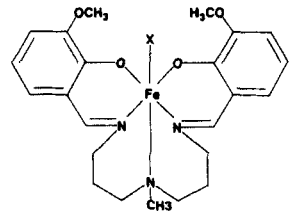

CHART 1 Structure of $[Fe(X)L]^+$, where X = pyridine, 3-methylpyridine, 3,5-dimethylpyridine, 4-aminopyridine, imidazole, 2-methylimdazole, and the analogous compounds.

RESULTS AND DISCUSSION

The pentadentate Schiff-base ligand H_2L was prepared through the 2:1 condensation reaction of 3-methoxysalicylaldehyde with di(3-aminopropyl)methylamine in methanol. The reaction mixture was subsequently used for the synthesis of the precursor iron(III) complex [Fe(Cl)L] without isolation of the ligand. The precursor complex [Fe(Cl)L] was prepared by the reaction of anhydrous iron(III) chloride, the methanol solution of pentadentate ligand, and triethylamine with the 1:1:2 molar ratio in methanol. A series of iron(III) complexes with the chemical formula of $[Fe(X)L]Bph_4$ (X = pyridine and imidazole derivatives) were prepared by the substitution reaction of [Fe(Cl)L] with the corresponding monodentate ligand, and subsequently by the addition of a methanol solution of $NaBph_4$. The complexes were obtained as black crystals. The infrared spectra showed the characteristic absorption bands attributable to the Schiff-base $\nu_{C=N}$ and tetraphenylborate anion.[9] The molar electrical conductivities in the 10^{-3} M dichloromethane solutions were in the range of ca. 50 S cm^{-1} mol^{-1}. The values of the complexes $[Fe(X)L]BPh_4$ (X = neutral ligand) are in the expected range for 1:1

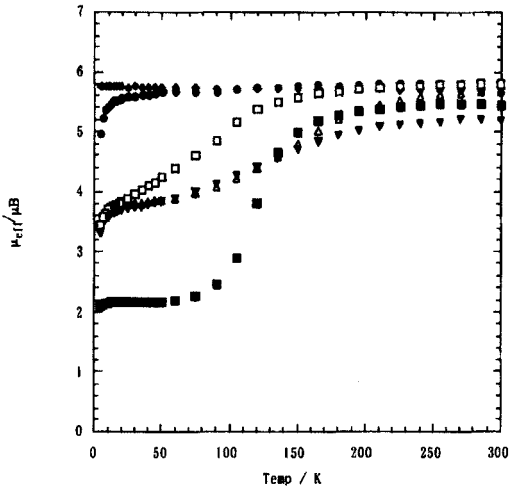

FIGURE 1 Plots of the effective magnetic moment μ_{eff}/μ_B versus T for the complexes [Fe(X)L]Bph_4; X = 2-methylimidazole (▲), imidazole (●), 3,5-dimethylpyridine(□), pyridine(△), 3-methylpyridine(▼), and 4-aminopyridine(■).

electrolytes.[10] The color is an easy indicator for spin-states, i.e., black for high-spin and green for low-spin in the solid state, and red for high-spin and green or blue-green for low-spin in the solution state. For example, the ground solid of [Fe(4-NH_2py)L]Bph_4 exhibits black color at room temperature and dark green color at liquid nitrogen temperature, demonstrating a thermochromism associated with spin-equilibrium.

Magnetic susceptibilities were measured with a MPMS5 SQUID susceptometer (Quantum Design Inc.) in the 4–350 K temperature range under an externally applied magnetic field of 1 T. Fig. 1 shows the graph of effective magnetic moment μ_{eff} vs T for the selected complexes. (1) high-spin complex: The effective magnetic moment of [Fe(Cl)L], [Fe(Im)L]Bph_4 and [Fe(2-methylIm)L]Bph_4 are typical values of high-spin (S = 5/2) over the temperature range studied. (2) spin-equilibrium complex between S = 1/2 and 5/2: The magnetic behavior of [Fe(4-NH_2py)L]Bph_4 is typical for spin-equilibrium between S =1/2 and S = 5/2, because the μ_{eff} decreased from 5.5 μ_B at 300 K to 2.1 μ_B at 4 K. This complex was subjected to further experimental and theoretical study to reveal the spin-equilibrium behavior in more detail. (3) unusual magnetic behavior: The effective

magnetic moments of [Fe(3,5-dimethylpy)L]Bph_4, [Fe(py)L]Bph_4, and [Fe(3-methylpy)L]Bph_4 decreased gradually from ca. 5.5 μ_B at 300 K to ca. 3.8 μ_B at 60 K, and reached the plateau value at ca. 60 K, and then abruptly decreased. The value of 3.8μ_B at the plateau region is too large expected for the low-spin state and rather close to the value of intermediate spin-state of S = 3/2. The further investigation is necessary.

The crystal structure of [Fe(4-NH_2py)L]Bph_4 was determined by the single-crystal X-ray diffraction method at 296 K. ORTEP drawings of the cation are given in Fig. 2 with the 50 % thermal ellipsoid. The carbon atoms of the di(3-aminopropyl)methylamine moiety exhibit large thermal motions. The Fe–N and Fe–O bond distances are compatible with those of the previously reported high-spin Fe(III) complexes.[8]

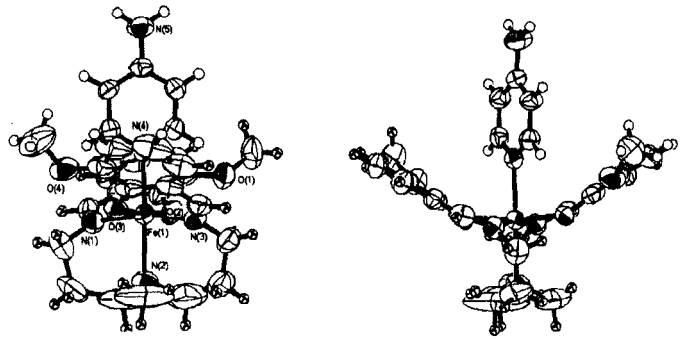

FIGURE 2 ORTEP drawings of the cation of [Fe(4-NH_2py)L]Bph_4, showing the 50% thermal ellipsoid. The Fe–N, Fe–O bond distances are Fe–O(2) = 1.922(5), Fe–O(3) = 1.904(5), Fe–N(1) = 2.091(7), Fe–N(2) = 2.250(7), Fe–N(3) = 2.055(6), Fe–N(4) = 2.147(6).

The magnetic behavior of [Fe(4-NH_2py)L]Bph_4 is typical for spin-equilibrium between S =1/2 and S = 5/2. The spin-transition is smooth, occurring within a large temperature range, the transition is completed both at low temperature (C_{hs} = 0) and at high temperature (C_{hs} = 1), where C_{hs} is the fraction of high-spin species. The C_{hs} = f(T) curves are strictly identical in the cooling and heating modes exhibiting no hysteresis. Thermodynamical parameters associated with the spin equilibrium process can be estimated by applying the model of Slichter and Drickamer.[11] This model can be applied by the assumption that the high- and low-spin molecules are statistically distributed and form regular solution. At equilibrium, this model leads to the implicit equation,

$$\ln[(1-C_{hs})/C_{hs}] = [\Delta H + \Gamma(1-2C_{hs})]/RT - \Delta S/R \qquad (1)$$

Here Γ, is a term that reflects the strength of the cooperative intermolecular interactions. The high-spin molar fraction C_{hs} is calculated at each temperature from the magnetic measurements using the equation (2).

$$C_{hs} = [\chi_M T - (\chi_M T)_{ls}]/[(\chi_M T)_{hs} - (\chi_M T)_{ls}] \quad (2)$$

The values of $(\chi_M T)_{hs}$ and $(\chi_M T)_{ls}$ for the pure high-spin (hs) and low-spin (ls) forms are obtained from the plateau values at high- and low-temperature regions of the magnetic data, respectively. The solution of equation (1) is provided by the intersects of the logarithmic curve $y = \ln[(1-C_{hs})/C_{hs}]$ and the straight line $y = [\Delta H + \Gamma(1-2C_{hs})]/RT - \Delta S/R$ which at any temperature passes through the point P defined by $C_{hs} = 1/2 + \Delta H/2\Gamma$ and $y = -\Delta S/R$. Figure 3 shows the plot of y vs. C_{hs}. The entropy ΔS and the enthalpy ΔH, was estimated to be ΔS = 49.92 J/mol K and ΔH=6 kJ / mol K. The value of Γ = 2 kJ / mol was taken, because the graph of ln K vs 1/T deviate strongly from straight line, curving upward higher temperature. These data contrast with the straight line which results from Γ = 0. On the basis of the parameters obtained from the Slichter Drickmier model, there is no cooperativity in $[Fe(4\text{-}NH_4py)L]Bph_4$.

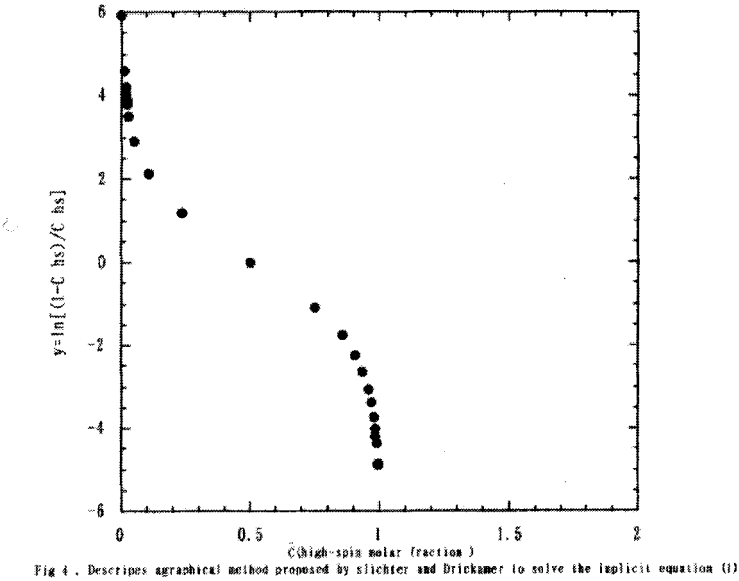

FIGURE 3 Plots of $y = \ln[(1-C_{hs})/C_{hs}]$ versus high-spin molar fraction C_{hs}

ACKNOWELEDGEMENT

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