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# A CHELATE RING SIZE EFFECT ON SPIN STATES OF IRON(III) COMPLEXES WITH HEXADENTATE LIGANDS DERIVED FROM SALICYLALDEHYDE AND 4,8-DIAZAUNDECANE-1,11-DIAMINE(3,3,3-tet) OR 4,7-DIAZADECANE-1,10-DIAMINE(3,2,3-tet), AND THEIR X-RAY STRUCTURES [1)]

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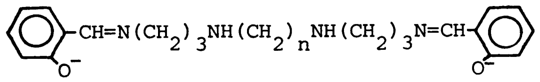
High- and low-spin Fe(III) complexes with the titled ligands, [Fe(Sal$_2$3,3,3-tet)](NO$_3$) (S=5/2) (**1**) and [Fe(Sal$_2$3,2,3-tet)](NO$_3$) (S=1/2) (**2**), have been synthesized. X-ray analyses for **1** and **2** show that, in each complex, the metal environment is pseudo octahedral with the two O atoms being trans. Difference of one CH$_2$ group in the methylene chain of the ligand causes a complete change in the spin state without changing coordination geometries. In methanol, **2** is essentially low spin with $\mu_{eff}$ = 1.95 BM(263.5 K), whereas **1** exhibits the behavior for the spin equilibrium [$\mu_{eff}$ = 3.00(244.5 K)-4.04(305.5 K) BM]. The equilibrium constant of **1**, K = [low-spin]/[high-spin]= 2.6±0.9 at 25 °C and $\Delta H = -11.8 \pm 2.5$ kJ mol$^{-1}$ were obtained from detailed analyses of the temperature dependent electronic spectra.

It has been known that pseudo octahedral Fe(III) complexes derived from triethylenetetramine (trien) and various salicylaldehydes,[2)] and their analogs,[3)] exhibit low-spin ($^2T_2$) $\rightleftharpoons$ high-spin ($^6A_1$) equilibria in solid and solution states. Since such complexes lie near the spin crossover, intramolecular steric effects which produce elongated metal-ligand bonds cause shifts of the equilibria toward the high-spin forms.[4)] In this study, the effects of chelate ring sizes on the spin states have been investigated. The title complexes, [Fe(Sal$_2$3,3,3-tet)](NO$_3$) (**1**) and [Fe(Sal$_2$3,2,3-tet)](NO$_3$) (**2**), ligand structures of which are shown, have been synthesized. The linear tetramine moieties in **1** and **2** form chelate rings with 6,6,6- and 6,5,6-members in these



n = 3 : Sal$_2$3,3,3-tet
n = 2 : Sal$_2$3,2,3-tet

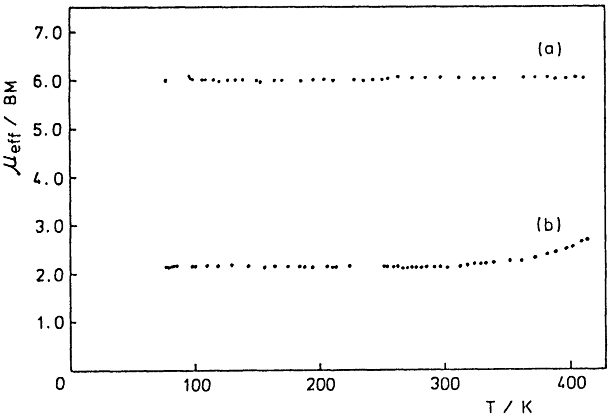


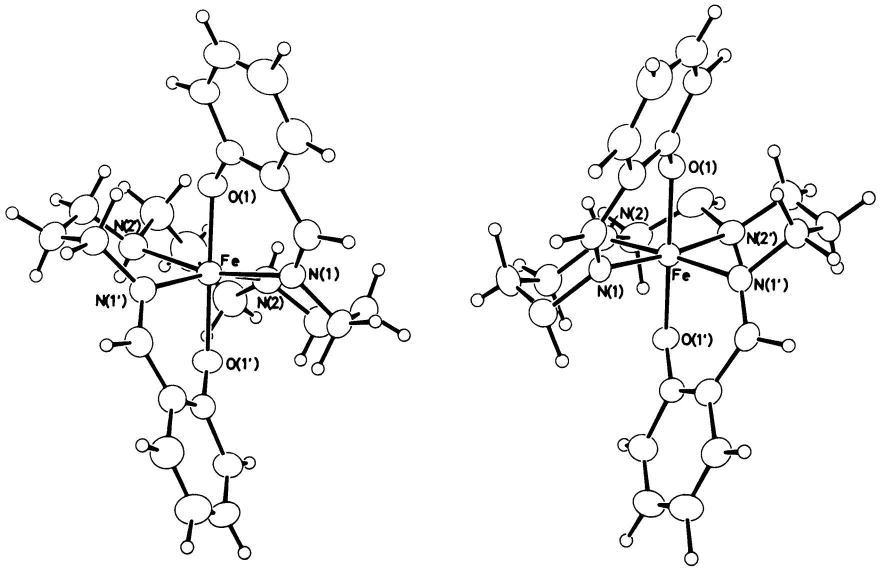
Fig. 1. Solid state $\mu_{eff}$ in BM vs. temperature data for **1** (a) and **2** (b).

sequences. The preparative methods for **1** and **2** were the same as that for the trien derivative [Fe(Sal$_2$trien)](NO$_3$),$^{2)}$ 3,3,3-tet and 3,2,3-tet being used in place of trien. Found for **1**: C, 53.09; H, 5.70; N, 13.87%. Calcd for $FeC_{23}H_{30}N_4O_2 \cdot NO_3$: C, 53.92; H, 5.90; N, 13.67%. Found for **2**: C, 53.14; H, 5.61; N, 14.43%. Calcd for $FeC_{22}H_{28}N_4O_2 \cdot NO_3$: C, 53.02; H, 5.66; N, 14.05%.

Figure 1 shows the temperature dependences of the magnetic moments of **1** and **2** in the solid states. Magnetic susceptibilities were measured by the Faraday method in a temperature range 77-420 K on unperturbed$^{5)}$ microcrystalline solids. The value of the compound **1** ($\mu_{eff}$ = 6.00 BM) is typical of high-spin pseudooctahedral Fe(III) complexes over the temperature range studied. On the other hand, the compound **2** is low-spin below 350 K ($\mu_{eff}$ = 2.15 BM) but undergoes a high- and low-spin equilibrium above 350 K. Of particular interest is the fact that increase in the methylene chain length from two to three carbon atoms in the central chelate ring of the tetramine moiety causes a complete change in spin state and promotes high-spin behavior.

Molecular structures of **1** and **2** have been determined by X-ray analyses$^{6)}$ (Fig. 2). In each compound, the metal environment in the complex cation is approximately octahedral, with the two oxygen atoms being trans to each other and the imino nitrogens cis. Interestingly enough, the observed trans-$FeO_2N_4$ geometries for **1** and **2** are in contrast with the coordination geometry reported for [Fe(Sal$_2$trien)]$^+$ having the similar hexadentate ligand, which is of cis-$FeO_2N_4$ type.$^{7)}$ This difference arises possibly from the difference in the preferred stereochemistries of the tetramine moieties.$^{8)}$

The coordination spheres of **1** and **2** have the following common structural features: (i) the two Fe-O bonds are by far the shortest among Fe-ligand bonds, coordination octahedron being compressed along the O-Fe-O direction; (ii) the bonds



(a) (b)

Fig. 2. Perspective views of [Fe(Sal$_2$3,3,3-tet)]$^+$ in **1** (a) and [Fe(Sal$_2$3,2,3-tet)]$^+$ in **2** (b). In [Fe(Sal$_2$3,3,3-tet)]$^+$ a twofold axis bisects the N(1)-Fe-N(1') angle.

to the amino nitrogens are slightly longer than those to imino nitrogens (see Table).

The average Fe-ligand distance in the high-spin complex **1** is 2.080 Å, whereas in the low-spin complex **2** the distance is 1.948 Å. This gives an average difference of ca. 0.13 Å. The high-spin complex **1** has an $N_4O_2$ coordination sphere that is much more distorted from an octahedral arrangement of donor atoms than for the low-spin complex **2**. This fact is evidenced by comparing the 12 angles subtened at Fe by adjacent donor atoms (see Table).

In each crystal, some of $NO_3^-$ oxygens were found to be within hydrogen bonding distance of the ligand amino nitrogens.

Solution state behaviors of **1** and **2** have also been studied in methanol by magnetic susceptibility (Evans' $^1$H NMR technique[9)]) and spectrophotometric measurements. The compound **2** is, as in the solid state, essentially low-spin with $\mu_{eff}$ = 1.95(263.5 K), 2.25(320 K) BM and showed only weak thermochromism. On the other hand, the compound **1** in methanol was found to exhibit the behavior for a spin equilibrium between high- and low-spin states: it is thermochromic [Fig. 3(a)] and exhibits temperature dependent magnetic susceptibility [$\mu_{eff}$ = 3.00(244.5 K), 3.38(263.0 K), 3.80(283.0 K), 4.04(305.5 K), and 4.29(322.0 K) BM]. Equilibrium constants at various temperatures, K = [low-spin]/[high spin], and ΔH were estimated from analyses of the electronic spectral data (based on 832 absorbance values at 52 wavelengths and at 16 temperatures) with a non-linear least-squares fitting program SALS[10)]. Electronic spectra of the pure high-spin and low-spin forms were determined simultaneously in this calculation [Fig. 3(b)]. The results were K = 2.6 ± 0.9 at 25 °C and ΔH = $-11.8 \pm 2.5$ kJ $mol^{-1}$. These values were close to those obtained from the solution magnetic susceptibility data.[11)] Remarkable change in the spin state behavior of **1** between solid and solution states arise undoutedly from the solvation, which surely involves hydrogen bond formation between solvent methanol and secondary amine groups of the ligand.[2)]

TABLE Bond Distances(l/Å) and Angles(φ/°) about the Fe

| | Compound **1** | Compound **2** |
|---|---|---|
| Fe -O(1) | 1.937(2) | 1.879(4) |
| Fe -O(1´) | | 1.876(4) |
| Fe -N(1) | 2.121(3) | 1.959(4) |
| Fe -N(1´) | | 1.958(4) |
| Fe -N(2) | 2.181(3) | 2.009(5) |
| Fe -N(2´) | | 2.005(5) |
| O(1) -Fe -O(1´) | 174.2(1) | 173.9(2) |
| O(1) -Fe -N(1) | 83.7(1) | 90.1(2) |
| O(1´)-Fe -N(1´) | | 90.0(2) |
| O(1) -Fe -N(1´) | 101.6(1) | 90.8(2) |
| O(1´)-Fe -N(1) | | 90.2(2) |
| O(1) -Fe -N(2) | 82.5(1) | 85.3(2) |
| O(1´)-Fe -N(2´) | | 84.9(2) |
| O(1) -Fe -N(2´) | 92.4(1) | 94.0(2) |
| O(1´)-Fe -N(2) | | 94.2(2) |
| N(1) -Fe -N(2) | 87.7(1) | 90.4(2) |
| N(1´)-Fe -N(2´) | | 90.2(2) |
| N(1) -Fe -N(2´) | 90.3(1) | 85.9(2) |
| N(1´)-Fe -N(2) | 165.4(1) | 174.1(2) |
| N(2) -Fe -N(2´) | | 173.5(2) |
| N(1) -Fe -N(1´) | 97.8(1) | 93.9(2) |

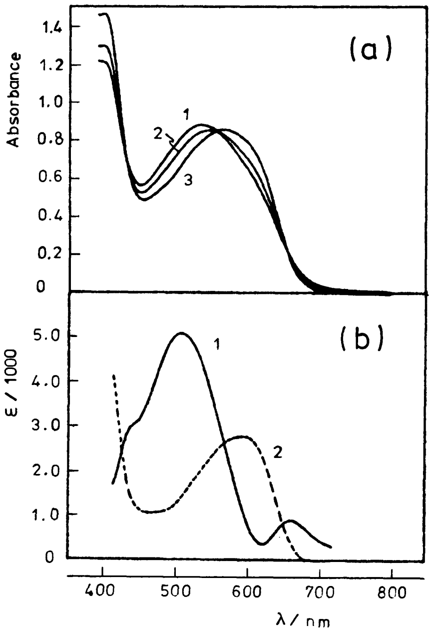


Fig. 3. (a) Temperature dependence of the electronic absorption spectrum of a 3.45 x $10^{-4}$ mol $dm^{-3}$ solution of **1** in methanol: (1) 322.0 K, (2) 299.4 K, (3) 268.3 K. (b) Spectra separated into the high-spin (1) and low-spin (2) form of **1**.

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## References

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6) Intensity data were collected on a Rigaku four-circle diffractometer AFC-5 with graphite monochromatized Mo Kα radiation at room temperature. The procedures used for data collection as well as the methods used in the solution and refinement of the structure were standard and have been described previously [T. Ito, K. Toriumi, and H. Ito, Bull. Chem. Soc. Jpn., 54, 1096 (1981)]. X-ray data. Compound **1**: orthorhombic, Pbnb, a = 16.430(2), b = 18.739(2), c = 7.915(2) Å, U = 2437(1) Å, Z = 4, $D_x$ = 1.396 g $cm^{-3}$, μ(Mo Kα) = 6.8 $cm^{-1}$, R = 0.039 for 1315 independent reflections [Fo > 3σ(Fo)]. Compound **2**: monoclinic, $P2_1/a$, a = 19.060(4), b = 16.073(2), c = 7.608(2) Å, β = 90.98(2)°, U = 2330(1) $Å^3$, Z = 4, $D_x$ = 1.420 g $cm^{-3}$, μ(Mo Kα) = 7.1 $cm^{-1}$, R = 0.051 for 2412 independent reflections [Fo > 3σ(Fo)].

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8) It has been known that, in complexes of the type $[Co^{III}X_2L]^{n+}$ where L is 3,2,3-tet or trien and X is unidentate ligand, the 3,2,3-tet ligand takes a structure with four nitrogens in plane [M. D. Alexander and H. G. Hamilton, Jr., Inorg. Chem., 8, 2131 (1969)], while trien adopts usually non-planar cis form.

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