

Conformational control of spin state in iron(II) tripodal imidazole complexes

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Abstract

Three new iron(II) N₆ tripodal complexes provide information on the role of ligand conformation on spin crossover behavior. The ligands (generated in situ) are the Schiff base condensate of tris(2-aminoethyl)amine (tren) with three equivalents of 4-methyl-5-imidazolecarboxaldehyde, H₃(1), and the condensates of tris(2-aminoethyl)methylammonium ion (N(Me)tren⁺) with three equivalents of 4-methyl-5-imidazolecarboxaldehyde, N(Me)H₃(1)⁺, or with 2-imidazole carboxaldehyde, N(Me)H₃(3)⁺. The structures of [FeH₃(1)](ClO₄)₂, [FeN(Me)H₃(1)](ClO₄)₃ and [FeN(Me)H₃(1)](ClO₄)₃ are reported. The central tren nitrogen atom in these complexes exhibits three different geometries, pyramidal with the nitrogen pointed toward the iron (“N in”, Fe–N distance of 3.050 Å), planar (Fe–N distance of 3.527 Å), and pyramidal with the nitrogen pointed away from the iron atom (“N out”, Fe–N distance of 3.921 Å). With iron(II) the “N in” geometry is high spin while the planar and “N out” geometries are low spin. [FeH₃(1)](ClO₄)₂ exhibits spin crossover behavior between room temperature and 77 K as determined by Mössbauer spectroscopy and also exhibits a conformational change from “N in” to planar over this same temperature range. The structures of [FeN(Me)H₃(1)](ClO₄)₃ and [FeN(Me)H₃(3)](ClO₄)₃ are locked into the “N out” geometry due to the quaternary nitrogen atom and are low spin even at room temperature. The LS planar and “N out” conformations place a strain on the bond angles of the aliphatic arms of the ligand, which are more pronounced in the “N out” case. The HS “N in” geometry lacks this strain.

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1. Introduction

Recent work in this laboratory [1] and others [2] has examined iron(II) and iron(III) complexes of the Schiff bases formed from reaction of tris-(2-aminoethyl)amine (tren) with three equivalents of various imidazole carboxaldehydes (Fig. 1). The protonation state of the ligand effects both the oxidation and spin state of the iron atom in the complex. Complexes containing an imidazole NH

bond exhibit reversible acid base chemistry, with iron(III) being stabilized with imidazolate and iron(II) with imidazole donors. Furthermore, the acid–base and redox chemistry are coupled as shown in Fig. 2.

Examples of proton-coupled electron transfer (PCET), or the coupling of proton transfer at a coordinated ligand with a metal-centered electron transfer, are abundant among transition metal complexes [3]. In the case of iron(III) both Fe(1) and Fe(2) are low spin (LS) while their protonated counterparts, [FeH₃(2)]³⁺ and [FeH₃(1)]³⁺, are spin crossover (SC) and high spin (HS), respectively.

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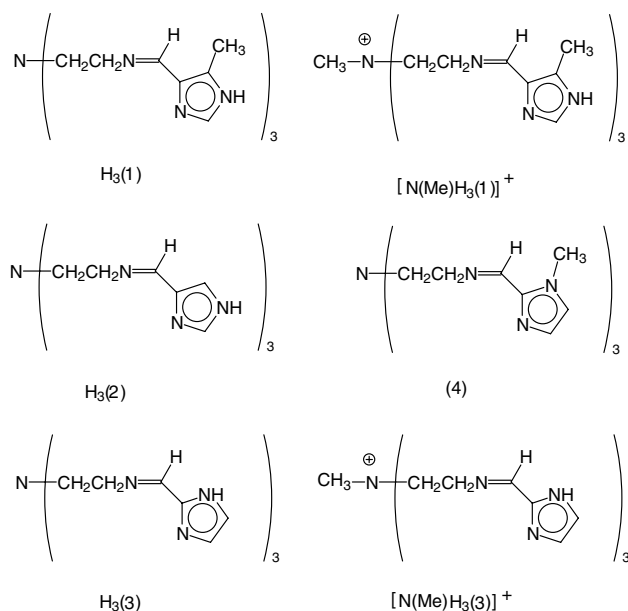
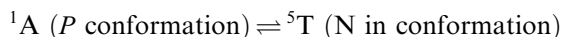
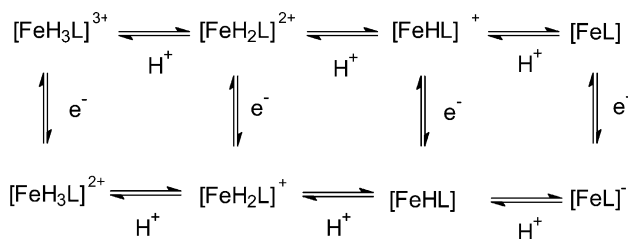


Fig. 1. Line drawings of ligands.

The iron(II) complexes of H₃(1–3) and (4) exhibit a thermal equilibrium between the LS ¹A and HS ⁵T states as demonstrated by Mössbauer and/or magnetic susceptibility measurements. In addition, structural studies reveal a conformational change about the central tren nitrogen atom from planar (P) to “N in” (pyramidal with the nitrogen atom pointed toward the iron atom).



The observation that a thermal spin equilibrium coincides with a conformational change led to the investigation of the effect that a quaternary tren nitrogen atom would have on spin state selection. Methylation of the central tren nitrogen atom should lock its conformation into the “N out” (pyramidal with the nitrogen atom pointed away from the iron atom) due to both the change in coordination number of the nitrogen atom from three to four and the electrostatic repulsion between the positive nitrogen and iron atoms. Since the conformation is now fixed this should force the iron(II) atom to adopt a single spin state. Presented in this work are the syntheses and characterization of three new

Fig. 2. Acid–base and redox chemistry of iron complexes of H₃(1)–H₃(3).

iron(II) complexes of H₃(1), N(Me)H₃(1)⁺, and N(Me)H₃(3)⁺. The data indicate that [FeH₃(1)]²⁺ participates in the ¹A (P conformation) ⇌ ⁵T (“N in” conformation) equilibrium. In contrast N(Me)H₃(1)⁺ and N(Me)H₃(3)⁺ impose the “N out” conformation in [FeN(Me)H₃(1)]³⁺ and [FeN(Me)H₃(3)]³⁺ which results in stabilization of the LS state exclusively for these complexes.

2. Experimental

Elemental analyses were determined by MHW Laboratory, Phoenix, AZ. Mass spectral analyses were obtained from HT Laboratories, San Diego, CA. Tris(2-aminoethyl)amine, 4-methyl-5-imidazole carboxaldehyde, 2-imidazole carboxaldehyde, salicylaldehyde, and anhydrous ferric chloride were obtained from Aldrich. Ferrous perchlorate hexahydrate was obtained from Alfa. Sodium perchlorate monohydrate was obtained from Fisher. All solvents were of reagent grade and used without further purification. [N(Me)tren-H₃]I(tfa)₃ [4] and [FeH₃(1)](ClO₄)₃ [1] were prepared as described previously.

2.1. Spectra

The ⁵⁷Fe Mössbauer spectra were recorded from powdered samples with a constant acceleration MS1200 Ranger Scientific spectrometer and a ca. 1.85 GBq ⁵⁷Co/Rh source. The sample thickness was 50–80 mg/cm². The line width of the calibration spectrum was 0.29 mm/s. The chemical isomer shift data are quoted relative to the centroid of the metallic iron spectrum at room temperature. The data were analyzed by a constrained least squares fit to Lorentzian shaped lines. UV–visible spectra were obtained on a Perkin–Elmer Lambda 4 spectrometer. IR spectra were obtained as KBr pellets on a Perkin–Elmer 1600 FT IR spectrometer.

2.2. Structure determinations

Crystal data were collected on a Bruker SMART 1 K four circle diffractometer. All structures were solved using the direct methods program SHELXS [5]. All nonsolvent heavy atoms were located using subsequent difference Fourier syntheses. The structures were refined against *F*² with the program SHELXL [6], in which all data collected were used including negative intensities. All nonsolvent heavy atoms were refined anisotropically. All nonsolvent hydrogen atoms were idealized using the standard SHELXL idealization methods. Complete crystallographic details are given in the Supporting Information and are summarized in Table 1.

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