

## Stable Eight-Coordinate Iron(III/II) Complexes

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The chemistry of unusual coordination numbers of transition-metal complexes has been of interest because of their presence in biology and catalytic systems. Herein we describe a systematic and predictable approach toward isolation of stable eight-coordinate (8C) iron(III/II) systems. The 8C ( $S = 2$ ; high-spin, HS) complex  $[\text{Fe}(\text{L}_{\text{N}_4})_2](\text{BF}_4)_2$  (**1**) has been synthesized and characterized, displaying a distorted square-antiprism structure. Complex **1** is a unique 8C iron complex that exhibits remarkable stability in solution under various unfavorable conditions. The  $E_{1/2}$  value of **1** (0.430 V vs Ag/AgCl, MeCN) supports the  $\text{Fe}^{\text{II}}$  oxidation state; however, the corresponding HS ( $S = 5/2$ ) 8C  $\text{Fe}^{\text{III}}$  analogue  $[\text{Fe}(\text{L}_{\text{N}_4})_2](\text{NO}_3)_3$  (**3**) has also been synthesized via the chemical oxidation of **1**. The structural, spectroscopic, and theoretical descriptions of these 8C iron complexes are reported in this work.

Classic inorganic chemistry demonstrates that coordination numbers (CNs) of four, five, and six are conventional for first-row transition-metals,<sup>1</sup> whereas CNs of three,<sup>2</sup> seven,<sup>3</sup> and eight<sup>4</sup> are rarely observed. Of these unique CNs, eight appears to be among the least abundant, accounting for < 1% of all transition-metal complexes reported in the *CSD*

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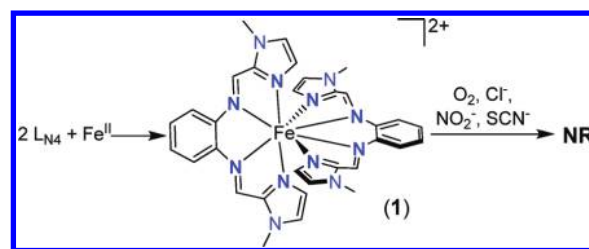
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**Scheme 1.** Synthesis and Reactivity of **1**



(version 5.30). Despite this rarity, there is a growing and broad interest in such systems because unusual CNs are observed in certain metalloproteins<sup>5</sup> and are also design targets for open-framework catalytic inorganic materials.<sup>6</sup> Because of its biological relevance and applications in catalysis, the fundamental coordination chemistry of iron is of particular importance.<sup>7</sup> Indeed, a handful of eight-coordinate (8C) iron complexes have been characterized.<sup>8,9</sup> The generation of such species is very much dependent on ligands with small bite angles or suitably disposed macrocycles. However, to date there has been no systematic study on such complexes, which could serve as templates for higher order materials. Herein we describe our results in this area and show that *stable* 8C iron(III/II) systems may be readily and predictably synthesized from our designed open-chain tetradentate imine/imidazole ligand,  $\text{L}_{\text{N}_4}$  (Scheme 1).

The dark-blue 8C iron(II) complex  $[\text{Fe}(\text{L}_{\text{N}_4})_2](\text{BF}_4)_2$  (**1**) was synthesized anaerobically in 85% yield by reacting an MeCN solution of  $\text{L}_{\text{N}_4}$  with  $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$  in a 2:1 molar ratio, respectively. The attempted sole isolation of the

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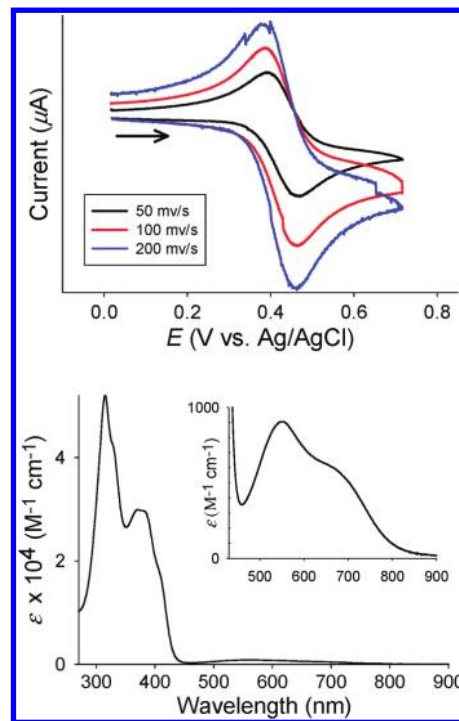
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mono-ligand  $[\text{Fe}(\text{L}_{\text{N}_4})_2(\text{MeCN})_2](\text{BF}_4)_2$  (**2**) species by employing a 1:1 ratio resulted in mixtures of **1** and **2** [for ESI-MS and X-ray results, see the Supporting Information (SI)], suggesting that when this ratio is employed, both species exist in equilibrium. Analogous to other iron complexes with neutral N-ligation like  $[\text{Fe}(\text{phen})_3]^{2+}$  (phen = 1,10-phenanthroline),<sup>10</sup> **1** is stable under aerobic conditions and does not form high oxidation-state derivatives. Additionally, **1** shows no reaction with potential anionic ligands like  $\text{Cl}^-$ ,  $\text{NO}_2^-$ , or  $\text{SCN}^-$  (Scheme 1). These results underscore the great stability of the 8C structure under competitive conditions that could conceivably lead to lower-coordinate structures or to the complete disintegration of the coordination unit as a whole. The robustness of the 8C structure is presumably due to the nature of the  $\text{L}_{\text{N}_4}$  ligand. As noted with tetradentate phen-based ligands of similar disposition,<sup>11</sup> it appears that the five-membered chelate rings formed by  $\text{L}_{\text{N}_4}$  favor bonding to cations with an ideal ionic radius close to 1.0 Å (8C  $\text{Fe}^{\text{II}}$  = 1.06 Å; 8C  $\text{Fe}^{\text{III}}$  = 0.92 Å),<sup>12</sup> resulting in relatively long Fe–N bonds. These predicted longer bonding interactions and ultimate 8C geometry of **1** appear to be favored in  $\text{L}_{\text{N}_4}$  because of the rigid cleft of the phenylenediamine backbone and limited movement of the flanking imidazole-nitrogens, essentially forcing coordination to all N-atoms. The stability of **1** may also be contrasted with the noted instability of the related N-ligated 8C complex  $[\text{Fe}(\text{TPA})_2]^{2+}$  [TPA = tris(2-pyridylmethyl)amine], which breaks down in donor solvents (S) to form  $[\text{Fe}(\text{TPA})(\text{S})_2]^{2+}$  six-coordinate species.<sup>9d</sup> The first example of a set of 8C iron(III/II) complexes reported by Krüger and co-workers containing diazapyridine macrocyclic ligands has also been described as stable entities.<sup>9c</sup> These complexes were reported to retain their 8C geometry in solution; however, the solutions utilized were not specified, nor were they presented with challenging competition reactions, thus making the comparison with our systems qualitative at best.

Complex **1** is soluble in polar organic solvents such as DMF and MeCN with slight solubility in pH 7.2  $\text{H}_2\text{O}$ , affording dark-blue solutions; the color is unlike that of any other reported 8C iron(II) complex with nitrogen ligands.<sup>9</sup> The UV–vis spectrum of **1** in MeCN exhibits two broad visible bands at 550 and 650 nm that appear to be of d–d origin with  $\epsilon < 1000 \text{ M}^{-1} \text{ cm}^{-1}$  (Figure 1). In fact, the finding that **1** and **2** exhibit very different UV–vis spectra suggests that **1** is stable even in donor solvents.

Complex **1** is redox-active with a reversible iron(III/II) couple at  $E_{1/2} = 0.430 \text{ V}$  ( $\Delta E_p = 0.073 \text{ V}$ ) in MeCN vs Ag/AgCl (Figure 1). The reversible electrochemistry suggested that an 8C  $[\text{Fe}^{\text{III}}(\text{L}_{\text{N}_4})_2]^{3+}$  complex should also be isolable. However, attempts to synthesize this complex directly from  $[\text{Fe}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$  and  $\text{L}_{\text{N}_4}$  in a 1:2 molar ratio, respectively, afforded the  $\text{ClO}_4^-$  salt of **1** (**1-ClO<sub>4</sub>**) as the primary product. The spontaneous reduction of the putative iron(III) complex to **1** in air was unexpected and indeed unprecedented. In retrospect, the stability of the  $\text{Fe}^{\text{II}}$  state is consistent with the high  $E_{1/2}$  value of **1**. In the end, using a strong chemical oxidant such as ceric ammonium nitrate ( $E_{1/2} = 1.65 \text{ V}$  vs Ag/AgCl) yielded the 8C iron(III) complex



**Figure 1.** Top: Cyclic voltammogram of a 2 mM MeCN solution of **1** at various scan rates (vs Ag/AgCl). Bottom: UV–vis spectrum of **1** in MeCN at 298 K. Inset: visible region of the spectrum.

$[\text{Fe}(\text{L}_{\text{N}_4})_2](\text{NO}_3)_3$  (**3**) in 98% yield, establishing that two  $\text{L}_{\text{N}_4}$  can support 8C ligation about an  $\text{Fe}^{\text{III}}$  center. The redox properties associated with **1** and **3** are reversible processes, and chemical reduction back to **1-NO<sub>3</sub>** with  $[\text{Co}(\text{Cp}^*)_2]$  ( $E_{1/2} = -1.56 \text{ V}$  vs Ag/AgCl) is nearly stoichiometric. Thus, the structural integrity of the 8C  $\text{FeN}_8$  core is retained during the  $\text{Fe}^{\text{III/II}}$  redox shuttle.

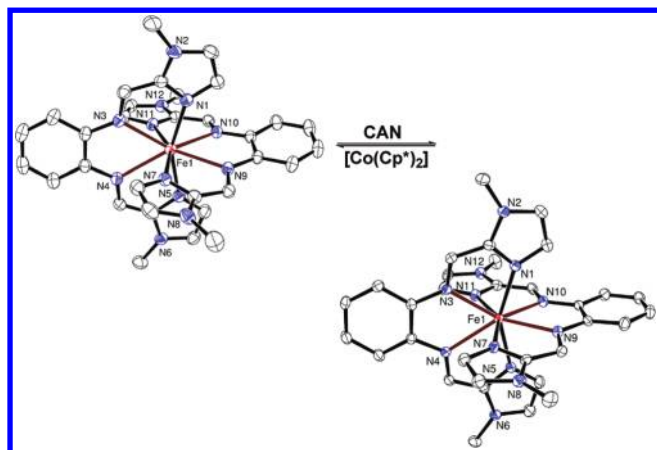
Crystallographic analysis unambiguously established the  $\text{FeN}_8$  coordination sphere of **1** and **3** (Figure 2). For both, the coordination geometry around the iron center may be described as a distorted square antiprism. The ligand  $\text{N}_4$  planes are nearly perpendicular to each other with interplanar angles of 88.5° for **1** and 89.9° for **3**. The average Fe– $\text{N}_{\text{imidazole}}$  distances [2.253(2) Å for **1**; 2.183(2) Å for **3**] are shorter by 0.17–0.19 Å than the corresponding Fe– $\text{N}_{\text{imine}}$  bonds [2.432(2) Å for **1**; 2.353(2) Å for **3**]. These bond distances are similar to those of the only other known set of structurally characterized 8C iron(II/III) complexes with neutral N-ligands ( $\text{Fe}^{\text{II}}$ , Fe– $\text{N}_{\text{py}} = 2.298 \text{ Å}$ , Fe– $\text{N}_{\text{amine}} = 2.382 \text{ Å}$ ;  $\text{Fe}^{\text{III}}$ , Fe– $\text{N}_{\text{py}} = 2.221 \text{ Å}$ , Fe– $\text{N}_{\text{amine}} = 2.307 \text{ Å}$ ).<sup>9c</sup> The four imidazole-N and four imine-N of two  $\text{L}_{\text{N}_4}$  ligands afford two sets of distorted planar coordination units at iron, which collectively form the 8C distorted square-antiprism polyhedron (Figure 2 and the SI). It appears that the two  $\text{L}_{\text{N}_4}$  ligands provide the metal with sufficient structural protection from potential competitive ligands by limiting access to the metal (see the space-filling model in Figure S1 in the SI), which could explain the unusual stability of these complexes with respect to other 8C iron systems.

The iron center in **1** is high-spin (HS), as demonstrated by the solution magnetic susceptibility value ( $\mu_{\text{eff}}$  for **1** = 4.94  $\mu_{\text{B}}$ ;  $S = 2$ ) and the Fe–L distances. The Mössbauer spectrum of **1** at 4.2 K consists of a large quadrupole splitting ( $\Delta E_{\text{Q}}$ ) of

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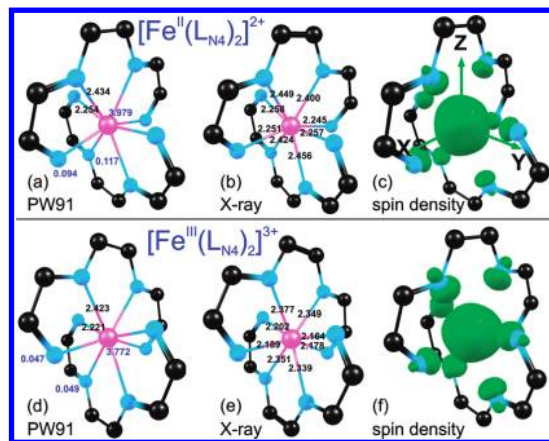


**Figure 2.** ORTEP diagrams at 30% thermal ellipsoids of the cations of **1** (left) and **3** (right), demonstrating their chemical interconversion.

3.85(2) mm/s and an isomer shift ( $\delta$ ) of 1.56(6) mm/s, consistent with a HS Fe<sup>II</sup> center in an asymmetric N<sub>8</sub> coordination environment (see Figure S11 in the SI).<sup>9a,c</sup> Complex **3** also contains HS Fe<sup>III</sup>, as evidenced by its EPR spectrum at 4.2 K (1:1 toluene/DMF glass), affording the typical HS ( $S = 5/2$ ) Fe<sup>III</sup> isotropic signal at  $g = 4.28$  with an additional signal at  $g = 6.22$  due to the distorted ligand environment (see the SI). To the best of our knowledge, this spectrum is the first reported EPR of an 8C iron(III) species.

DFT (PW91/TZP) calculations (for details, see the SI) on **1** and **3** yielded optimized structures with exact  $D_{2d}$  symmetry and Fe–N distances and other geometric parameters in close agreement with the crystal structures (Figure 3). Other functionals such as OLYP and B3LYP, which generally give better spin-state energetics relative to classic pure functionals,<sup>13</sup> significantly overestimated the Fe–N distances. PW91, OLYP, and B3LYP all clearly indicated HS ground states for both **1** and **3**. The high CN implies that all five d orbitals entail comparable levels of antibonding interactions with the ligand lone pairs and are therefore of rather similar energy. The coordinating imidazole nitrogen atoms, which are the strongest-field ligands, define the orientations of the d-orbital axes. The electronic configuration of **1** may be described as  $d_{xy}^2 d_{xz}^1 d_{yz}^1 d_{z^2}^1 d_{x^2-y^2}^1$ , where the lobes of the doubly occupied  $d_{xy}$  orbital point between the imidazole nitrogen atoms. The lack of unpaired spin in this orbital is manifested by dimples in the overall spin-density profile of **1** (Figure 3c).

In summary, we have synthesized and characterized a set of 8C iron complexes in both the 2+ (**1**) and 3+ (**3**) oxidation states. Complex **1** exhibits exceptional stability in the solid and solution states, retaining its 8C structure under a variety



**Figure 3.** Selected PW91/TZP results for **1** (top) and **3** (bottom): distances (in Å are in black, in parts a, b, d, and e); Mulliken spin populations (in blue, in parts a and d); spin-density plots (in green, in parts c and f). Only bound L<sub>N4</sub> ligand atoms and their carbon connectivity are shown for clarity.

of conditions. Even pH 7.2 anaerobic solutions of **1** and **3** do not readily [ $k_{\text{obs}}$  for **1** =  $(1.06 \pm 0.02) \times 10^{-4} \text{ s}^{-1}$ ; that for **3** =  $(7.02 \pm 0.36) \times 10^{-4} \text{ s}^{-1}$ ] afford oxo- or hydroxo-bridged polymeric species (UV–vis; see the SI). These species are recognized as thermodynamically stable entities in the hydrolytic coordination chemistry of iron, which is a further testament to their remarkable stability.<sup>14</sup> The tetradentate imine/imidazole donor frame thus appears to provide a *systematic and predictable* route toward *stable* 8C metal complexes. Collectively, this work establishes the crucial synthetic, structural, spectroscopic, theoretical, and reactivity benchmarks for future 8C metal complexes in general. Such research efforts are currently in progress in our laboratory.

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**Supporting Information Available:** Experimental details for the synthesis and reactivity of **1–3**, X-ray crystallographic data (CIF), computational results, and Mössbauer spectral analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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