

# Synthesis, X-ray Crystal Structure, and Redox and Electronic Properties of Iron(III)–Polyimidazole Complexes Relevant to the Metal Sites of Iron Proteins

Anne-Sophie Chauvin,<sup>†,‡</sup> Yves-Michel Frapart,<sup>‡</sup> Jacqueline Vaissermann,<sup>§</sup> Bruno Donnadieu,<sup>||</sup> Jean-Pierre Tuchagues,<sup>||</sup> Jean-Claude Chottard,<sup>‡</sup> and Yun Li<sup>\*,‡</sup>

Laboratoire de chimie et biochimie pharmacologiques et toxicologiques (CNRS UMR8601), Université René Descartes, 45, rue des Saints Pères, 75270 Paris Cedex 06, France, Laboratoire de chimie inorganique et matériaux moléculaires (CNRS UMR7071), Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France, and Laboratoire de chimie de coordination du CNRS, UPR 8241, 205, route de Narbonne, 31077 Toulouse Cedex, France

Received June 14, 2002

A new tripod N<sub>3</sub> ligand (L), containing three imidazole rings, was synthesized in good yield. At variance with usual aromatic ligands with N<sub>2</sub> or N<sub>3</sub> donor sets such as pyridine or pyrazole derivatives, L stabilizes the Fe<sup>III</sup> oxidation state. The corresponding iron(III) complexes [Fe(L)Cl<sub>3</sub>] (1) and [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (2) were prepared and characterized by X-ray structural analysis and spectroscopic methods. The coordination environment around all the Fe<sup>III</sup> centers has a distorted octahedral geometry. [Fe(L)Cl<sub>3</sub>] (1) belongs to the monoclinic system, space group *P*2<sub>1</sub>/*n*, *a* = 9.7406(5) Å, *b* = 17.207(2) Å, *c* = 14.615(2) Å, β = 104.448(9)°, *Z* = 4, *V* = 2372.1(4) Å<sup>3</sup>; *R* = 0.044, *R*<sub>w</sub> = 0.055. [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (2) belongs to the monoclinic system, space group *P*2<sub>1</sub>/*c*, *a* = 16.1057(15) Å, *b* = 11.1079(12) Å, *c* = 26.283(2) Å, β = 102.062(10)°, *Z* = 4, *V* = 4598.2(8) Å<sup>3</sup>; *R* = 0.0465, *R*<sub>w</sub> = 0.0902. The Fe–N(Im) bond lengths are systematically longer than the Fe–N(Melm) ones. Compound 2 is a highly anisotropic low-spin Fe<sup>III</sup> complex displaying a rather unusual EPR spectrum with a sharp signal at *g* = 3.5 and a broad one at *g* ~ 1.6. The fitting of this EPR spectrum is discussed.

## Introduction

Non-heme iron metalloproteins with mono- and dinuclear active sites are involved in various biological processes.<sup>1–3</sup> Three histidyl nitrogen donors with a pyramidal coordination arrangement are often found at the metal sites. Such coordination structures have been established by X-ray crystallography for a number of non-heme metalloproteins, including lipoxxygenases,<sup>4,5</sup> Fe-superoxide dismutase (SOD),<sup>6–10</sup>

hemerythrin,<sup>11–13</sup> isopenicillin N-synthase (IPSN),<sup>14</sup> and the non-heme iron of photosynthetic reaction centers.<sup>15</sup>

Modeling the metal binding site of metalloproteins is a contribution to the understanding of their mechanism of action. Two objectives are often pursued simultaneously, i.e.,

\* To whom correspondence should be addressed. E-mail: Yun.Xu-Li@biomedicale.univ-paris5.fr.

<sup>†</sup> Present address: Laboratoire de chimie supramoléculaire des lanthanides (LCSL), Institut de chimie moléculaire et biologique (ICMB), EPFL, BCH 1405, CH-1015 Lausanne, France.

<sup>‡</sup> Université René Descartes.

<sup>§</sup> Université Pierre et Marie Curie.

<sup>||</sup> Laboratoire de chimie de coordination du CNRS.

(1) Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S. K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y. S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235.

(2) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239.

(3) Lippard, S. J.; Berg, J. M. *Principals of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.

(4) Minor, W.; Steckzko, J.; Stec, B.; Otwinowski, Z.; Bolin, J. T.; Walter, R.; Axelrod, B. *Biochemistry* **1996**, *35*, 10687.

(5) Skrzypczak-Jankun, E.; Amzel, L. M.; Kroa, B. A.; Funk, M. O. J. *Proteins: Struct., Funct., Genet.* **1997**, *29*, 15.

(6) Cooper, J. B.; McIntyre, K.; Badasso, M. O.; Wood, S. P.; Zhang, Y.; Garbe, T. R.; Young, D. *J. Mol. Biol.* **1995**, *246*, 531.

(7) Lah, M. S.; Dixon, M. M.; Patridge, K. A.; Stallings, W. C.; Fee, J. A.; Ludwig, M. L. *Biochemistry* **1995**, *34*, 1646.

(8) Ringe, D.; Petsko, G. A.; Yamakura, K.; Suzuki, D.; Ohmori, D. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3879.

(9) Stallings, W. C.; Powers, T. B.; Patridge, K. A.; Fee, J. A.; Ludwig, M. L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3884.

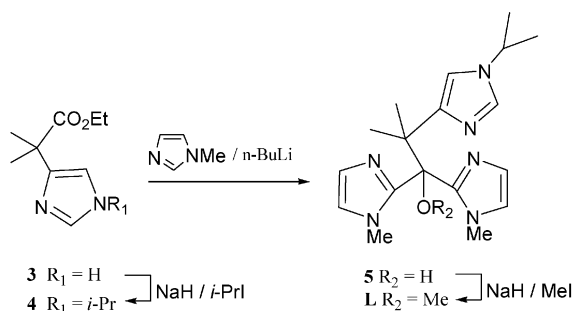
(10) Stoddard, B. L.; Howell, P. L.; Ringe, D.; Petsko, G. A. *Biochemistry* **1990**, *29*, 8885.

(11) Pulver, S.; Froland, W. A.; Fox, B. G.; Lipscomb, J. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1993**, *115*, 12049.

(12) Reem, R. C.; McCormick, J. C.; Richardson, D. E.; Devin, F. J.; Stephens, P. J.; Musselman, R. L.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 8.

(13) Stenkamp, R. E. *Chem. Rev.* **1994**, *94*, 715.

Scheme 1



to mimic both the spectral features and the reactivity of protein active sites using low molecular weight compounds. One of the difficulties of the model approach is to synthesize complexes with biologically relevant ligands. The imidazole of histidine is a ubiquitous ligand present at the active site of many metalloproteins. Because of the synthetic difficulties in preparing imidazoles, aliphatic amines, imines, pyridines, pyrazoles, and benzimidazoles are commonly used to synthesize model compounds, and significantly less work has been done with polyimidazole ligands.<sup>16–20</sup>

Concerning tripod aromatic N ligands, previous work has been reported on the synthesis and characterization of some mononuclear structural model complexes of non-heme iron proteins using various pyridine derivatives<sup>21</sup> or more or less hindered tripod tris(pyrazolyl)borate (Tpz) derivatives as ligands.<sup>22–25</sup> Although pyrazole is a good structural analogue of histidine for its size, it is not a good mimic for its electronic properties since it is significantly less donating than imidazole. Reactivity studies of complexes involving imidazole ligands are a valuable complement to the work previously reported for pyridyl and pyrazole complexes. The purpose of this work was to develop the synthesis of a new tripod ligand L (Scheme 1) containing three imidazole groups as N donors and to study some of its iron(III) complexes. All three imidazole rings of L are *N*-alkylated, providing high solubility in noncoordinating organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and EtOAc. Usually, nonalkylated polyimidazole ligands are soluble only in protic solvents, such as MeOH or  $\text{H}_2\text{O}$ , which are also potential ligands. Owing to its electron donating property, L was found to exhibit a

remarkable ability to stabilize iron(III) species. Thus, two monomeric iron(III) complexes,  $[\text{Fe}(\text{L})\text{Cl}_3]$  (**1**) and  $[\text{Fe}(\text{L})_2](\text{ClO}_4)_3$  (**2**), were prepared and fully characterized. These complexes may be used as building blocks in the preparation of mono or dinuclear iron(III) complexes with coordination spheres containing three imidazoles and various additional ligands.

## Experimental Section

All reagents and solvents were purchased from commercial sources and used as received. The following solvents were distilled and stored under argon: methanol, from  $\text{Mg}(\text{OMe})_2$ ; tetrahydrofuran (THF), from sodium benzophenone ketyl; acetonitrile, from  $\text{CaH}_2$ ; methylene chloride, from  $\text{CaH}_2$ ; *N,N*-dimethylformamide (DMF), from  $\text{CaH}_2$ . The imidazole derivative **3**<sup>26</sup> and  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ <sup>27</sup> were prepared according to reported procedures.

**Synthesis of Ligands. (1) *N*-Isopropylation of 3.** NaH (60% in mineral oil, 1.76 g, 44 mmol) was added in small portions to a solution of **3** (5.27 g, 29 mmol) and 2-iodopropane (7.48 g, 44 mmol) in anhydrous DMF (100 mL) cooled to 0 °C. After 16 h at room temperature, the usual workup with  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  gave a crude product which was purified by distillation to afford *N*-isopropylimidazole (*i*PrIm) **4** as a pale yellow oil (5.74 g, 88%). Bp: 134 °C/3.5 mm Hg.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.40 (d, 1 H,  $J$  1.2 Hz), 6.76 (d, 1 H,  $J$  1.2 Hz), 4.26 (m, 1 H), 4.10 (q, 2 H,  $J$  7.1 Hz), 1.51 (s, 6 H), 1.42 (d, 6 H,  $J$  6.7 Hz); 1.17 (t, 3 H,  $J$  7.1 Hz).  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 176.12 (C), 145.96 (C), 134.02 (CH), 112.10 (CH), 60.37 ( $\text{CH}_2$ ), 48.88 (CH), 42.90 (C), 25.91 ( $\text{CH}_3$ ), 23.42 ( $\text{CH}_3$ ), 13.88 ( $\text{CH}_3$ ). HRMS Calcd for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2$  ( $\text{MH}^+$ ): 225.1603. Found: 225.1600.

**(2) Synthesis of Carbinol 5.** *n*-BuLi (1.6 M in hexane, 30 mL, 48 mmol) was added under argon to a solution of *N*-methylimidazole (Melm) (3.94 g, 48 mmol) in anhydrous THF (80 mL) cooled to  $-78$  °C. After 0.5 h at  $-78$  °C, 2.7 g (12 mmol) of **4** in THF (20 mL) was added to the solution. After 16 h at room temperature, the usual workup with  $\text{H}_2\text{O}$  and EtOAc gave a crude product which was purified by crystallization (3:7 EtOAc/cyclohexane) to afford carbinol **5** as colorless crystals (3.32 g, 81%). Mp: 159–161 °C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.73 (s, 1H,  $\text{D}_2\text{O}$  exchangeable), 7.35 (s, 1 H), 6.82 (s, 2 H), 6.77 (s, 1 H), 6.65 (s, 2 H), 4.24 (m, 1 H), 3.29 (s, 6 H), 1.67 (s, 6 H), 1.43 (d, 6 H,  $J$  6.7 Hz).  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 149.11 (C), 147.53 (C), 132.46 (CH), 125.30 (CH), 121.71 (CH), 113.21 (CH), 79.01 (C), 48.83 (CH<sub>3</sub>), 43.52 (C), 33.81 ( $\text{CH}_3$ ), 24.50 (CH), 23.31 ( $\text{CH}_3$ ). MS (CI,  $\text{NH}_3$ ): 343 ( $\text{MH}^+$ ); Anal. Calcd for  $\text{C}_{18}\text{H}_{26}\text{N}_6\text{O}$  (342.45): C 63.13, H 7.65, N 24.54. Found: C 63.08, H 7.85, N 24.47.

**(3) Ligand (L).** NaH (60% in mineral oil, 175 mg, 4.4 mmol) was added under argon to a solution of carbinol **5** (1 g, 2.92 mmol) in anhydrous DMF (20 mL) cooled to 0 °C. After 30 min at 0 °C, MeI (540 mg, 3.8 mmol) was added to the mixture. After 6 h at 0 °C, the usual workup with  $\text{H}_2\text{O}$  and EtOAc gave a crude product which was washed 3 times with pentane resulting in analytically pure L as a colorless solid (977 mg, 94%). Mp (1:9 EtOAc/cyclohexane): 141–143 °C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.37 (s, 1 H), 6.91 (s, 2 H), 6.61 (s, 2 H), 6.33 (s, 1 H), 4.17 (m, 1 H), 3.09 (s, 3 H), 2.88 (s, 6 H), 1.88 (s, 6 H), 1.34 (d, 6 H,  $J$  6.7 Hz).  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 148.47 (C), 146.67 (C), 132.59 (CH), 125.92 (CH), 121.73 (CH), 114.72 (CH), 86.00 (C), 54.52 ( $\text{CH}_3$ ), 48.89 ( $\text{CH}_3$ ), 46.31 (C), 33.90 ( $\text{CH}_3$ ), 25.20 (CH),

- (14) Roach, P. L.; Clifton, I. J.; Hensgens, C. M. H.; Shibata, N.; Schofield, C. J.; Hajdu, J.; Baldwin, J. E. *Nature* **1997**, *387*, 827.  
 (15) Deisshofer, J.; Epp, E.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618.  
 (16) Place, C.; Zimmermann, J. L.; Mulliez, E.; Guillot, G.; Bois, C.; Chottard, J. C. *Inorg. Chem.* **1998**, *37*, 4030–4039.  
 (17) Breslow, R.; Hunt, J. T.; Smiley, R.; Tarnowski, T. *J. Am. Chem. Soc.* **1983**, *105*, 5337–5342.  
 (18) Wu, L. P.; Yamagiwa, Y.; Ino, I.; Sugimoto, K.; Kuroda-Sowa, T.; Kamikawa, T.; Munakata, M. *Polyhedron* **1999**, *18*, 2047–2053.  
 (19) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 4244.  
 (20) Goldberg, D. P.; Koulougliotis, D.; Brudvig, G. W.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 3134–3144.  
 (21) Toftlund, H. *Coord. Chem. Rev.* **1989**, *94*, 67–108.  
 (22) Mukherjee, R. *Coord. Chem. Rev.* **2000**, *203*, 151.  
 (23) Ogihara, T.; Hikichi, S.; Akita, M.; Uchida, T.; Kitagawa, T.; Morooka, Y. *Inorg. Chim. Acta* **2000**, *297*, 162.  
 (24) Siemer, C. J.; Meece, F. A.; Armstrong, W. H.; Eichhorn, D. M. *Polyhedron* **2001**, *20*, 2637–2646.  
 (25) Tromenko, S. *Scorpionates: The coordination Chemistry of Poly-pyrazolylborate Ligand*; Imperial College Press: London, 1999.

(26) Jönsson, A. *Acta Chem. Scand.* **1954**, *8*, 1389.

(27) Hodgkinson, J.; Jordan, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 763.

23.80 (CH<sub>3</sub>). MS (Cl, NH<sub>3</sub>): 357 (MH<sup>+</sup>). Anal. Calcd for C<sub>19</sub>H<sub>28</sub>N<sub>6</sub>O (356.47): C 64.02, H 7.92, N 23.58. Found: C 64.07, H 7.68, N 23.45.

**Synthesis of Complexes.** *Warning! Several compounds described here contain perchlorate anions. Although no accident has occurred, the use of perchlorate is hazardous because of the possibility of explosion, especially when the compounds are anhydrous.*

**[Fe(L)Cl<sub>3</sub>] (1).** L (285 mg, 0.80 mmol) was added under argon to a solution of FeCl<sub>3</sub> (130 mg, 0.80 mmol) in anhydrous CH<sub>3</sub>CN (5 mL). After 5 min at room temperature, an orange-yellow solid precipitated from the initial orange solution, and stirring was continued for an additional 20 min. The solid was filtered off, washed with cold CH<sub>3</sub>CN (3 × 3 mL), and dried under vacuum yielding complex **1** as an orange-yellow solid (257 mg, 62%). UV–vis (CH<sub>3</sub>CN): 330 nm ( $\epsilon = 4500 \text{ M}^{-1} \text{ cm}^{-1}$ ), 360 nm ( $\epsilon = 4200 \text{ M}^{-1} \text{ cm}^{-1}$ ). Anal. Calcd for C<sub>19</sub>H<sub>28</sub>N<sub>6</sub>OCl<sub>3</sub>Fe (518.68): C 44.00, H 5.44, N 16.20. Found: C 44.25, H 5.27, N 16.33.

Slow diffusion of <sup>t</sup>BuOME into a solution of the crude powder of **1** in CH<sub>3</sub>CN at 4 °C for 2 weeks allowed the isolation of **1** as orange-yellow single crystals suitable for X-ray diffraction.

**[Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (2).** L (50 mg, 0.14 mmol) was added under argon to a solution of [Fe(DMF)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> (54 mg, 0.07 mmol) in anhydrous CH<sub>3</sub>CN (2 mL). After 20 min at room temperature, Et<sub>2</sub>O was added. The solid was filtered off, washed with Et<sub>2</sub>O, and dried under vacuum yielding complex **2** as a dark brown crystalline powder (39 mg, 52%). UV–vis (CH<sub>3</sub>CN): 340 nm ( $\epsilon = 4750 \text{ M}^{-1} \text{ cm}^{-1}$ ), 380 nm ( $\epsilon = 3100 \text{ M}^{-1} \text{ cm}^{-1}$ ), 470 nm ( $\epsilon = 850 \text{ M}^{-1} \text{ cm}^{-1}$ ). Anal. Calcd for C<sub>38</sub>H<sub>56</sub>N<sub>12</sub>O<sub>14</sub>Cl<sub>3</sub>Fe (1067.15): C 42.77, H 5.29, N 15.75. Found: C 42.91, H 5.12, N 15.91.

Single crystals were obtained by slow diffusion of <sup>t</sup>BuOME into a solution of the crude powder of **2** in CH<sub>3</sub>CN at 25 °C for 3 weeks. Compound **2** was isolated as dark plates.

**Physical Measurements.** Melting points were determined with a Büchi SMP-20 apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded with a Bruker AM-250 spectrometer, and chemical shifts refer to an internal standard of Me<sub>4</sub>Si ( $\delta = 0.00$ ). High-resolution mass spectra (HRMS) and Chemical-ionization (CI) mass spectra were recorded at Ecole Normale Supérieure, Paris. Elemental analyses were performed by Service de Microanalyse, ICSN, Gif-sur-Yvette.

Voltammetric experiments were performed in a single-compartment cell with a potentiostat EGG-PAR model 173 and interface model 276. The electrode system consisted of a NaCl saturated calomel electrode as reference electrode, a platinum electrode as auxiliary electrode, and a glassy carbon electrode as working electrode. The voltammograms were recorded at room temperature in CH<sub>3</sub>CN solution with a 10 mM concentration of the complexes. The scanning rate was 50 mV·s<sup>-1</sup>. [<sup>10</sup>Bu<sub>4</sub>N](BF<sub>4</sub>) was used as supporting electrolyte (0.1 M).

UV–vis spectra were recorded with an Uvikon 820 spectrophotometer.

EPR spectra were obtained with a Bruker Elexsys 500 spectrometer equipped with a SHQ 001 cavity operating at X-band. The EPR measurements were performed at 4.2 K using an Oxford liquid helium continuous flow cryostat. Fitting of the EPR spectra was performed using Xepr & Xsophe suite (Bruker).

Variable-temperature magnetic data were collected with a Quantum Design MPMS SQUID susceptometer in the 4–300 K temperature range.

Mössbauer measurements were obtained on a constant-acceleration conventional spectrometer with a 50 mCi source of <sup>57</sup>Co (Rh matrix). Isomer shift values ( $\delta$ ) are given with respect to metallic

iron at room temperature. The absorber was a sample of 100 mg of microcrystalline powder enclosed in a 20 mm diameter cylindrical plastic sample-folder, the size of which had been determined to optimize the absorption. The spectra were obtained at 80 K, by using an MD 306 Oxford cryostat monitored by an Oxford ITC4 servocontrol device ( $\pm 0.1 \text{ K}$  accuracy). A least-squares computer program was used to fit the Mössbauer parameters and determine their standard deviations of statistical origin.<sup>28</sup>

**Crystallographic Data Collection and Structural Determination.** Crystal data were collected at 298 K (**1**) on a CAD4 Enraf-Nonius diffractometer and at 160 K (**2**) on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The final unit cell parameters were obtained by least-squares refinement of the setting angles of 25 well-centered reflections (**1**) and of a set of 5000 well-measured reflections (**2**). Two standard reflections (**1**) and 200 reflections per image (**2**) were monitored periodically showing no significant fluctuations during data collection. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs)<sup>29</sup> were applied (**1**). A secondary extinction correction was unnecessary. The structure of **1** was solved by direct methods (SHELXS)<sup>30</sup> and successive Fourier maps. Computations were performed by using the PC version of CRYSTALS.<sup>31</sup> Full-matrix least-squares refinements were carried out by minimizing the function  $\sum w(|F_o| - |F_c|)^2$  where  $F_o$  and  $F_c$  are the observed and calculated structure factors. Real and imaginary parts of anomalous dispersion were taken into account. The structure of **2** has been solved by direct methods using SIR92<sup>32</sup> and refined by least-squares procedures on  $F^2$  with SHELXL97<sup>33</sup> included in the package WINGX32.<sup>34</sup> Refinements have been performed by minimizing the function  $\sum w(F_o^2 - F_c^2)^2$ . Atomic scattering factors were taken from the International Tables for X-ray Crystallography.<sup>35</sup> All hydrogen atoms were located on difference Fourier maps; for **1**, they were given an overall isotropic thermal parameter; for **2**, they were introduced in the refinement process by using a riding model, with isotropic thermal parameters fixed at values 20% higher than those of riding atoms. Non-hydrogen atoms were refined anisotropically. Weighted  $R$ -factors  $R_w$  and goodness of fit  $S$  are based on  $F_o^2$ , conventional  $R$ -factors  $R$  are based on  $F_o$ , with  $F_o$  set to zero for negative  $F_o^2$ . Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviations being less than 0.1 and no significant features in the last Fourier-difference map. Drawings of the molecules were performed with the programs CAMERON<sup>36</sup>

(28) Varret, F. Proceedings of the International Conference on Mössbauer Effect Applications, Jaipur, India 1981; Indian National Science Academy: New Delhi 1982.

(29) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158.

(30) Sheldrick, G. M. *SHELXS: Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

(31) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *Crystals User Guide*; Chemical Crystallography Laboratory: Oxford, U.K., 1988.

(32) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. Sir 92: Program for Automatic Solution of Crystal Structures by Direct Methods. *J. Appl. Crystallogr.* **1994**, 27, 435.

(33) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(34) Farrugia, L. J. WinGX version 1.63: An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-ray Diffraction Data. *J. Appl. Crystallogr.* **1999**, 32, 837.

(35) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(36) Pearce, L. J.; Watkin, D. J. *CAMERON*; Chemical Crystallography Laboratory: Oxford, U.K., 1992.

**Table 1.** Crystal Data Collection and Refinement Parameters for [Fe(L)Cl<sub>3</sub>] (**1**) and [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**)

	<b>1</b>	<b>2</b>
formula	C <sub>19</sub> H <sub>28</sub> N <sub>6</sub> OCl <sub>3</sub> Fe	C <sub>38</sub> H <sub>56</sub> N <sub>12</sub> O <sub>14</sub> Cl <sub>3</sub> Fe
fw	518.68	1067.26
<i>a</i> (Å)	9.7406(5)	16.1057(15)
<i>b</i> (Å)	17.207(2)	11.1079(12)
<i>c</i> (Å)	14.615(2)	26.283(2)
$\beta$ (deg)	104.448(9)	102.062(10)
<i>V</i> , (Å <sup>3</sup> )	2372.1(4)	4598.2(8)
<i>Z</i>	4	4
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
$\lambda$ (Å)	0.71069	0.71073
$\rho$ (g·cm <sup>-3</sup> )	1.45	1.542
$\mu$ (cm <sup>-1</sup> )	10	5.24
<i>T</i> (K)	298	160
no. data collected	6296	31585
no. unique data collected	5713	6575
no. reflns used in refinement	2491	6575
GOF	0.970	0.920
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.044	0.0465
$R_w^{*a}$	0.055	0.0902
$\Delta\rho$ min (e, Å <sup>-3</sup> )	-0.37	-0.323
$\Delta\rho$ max (e, Å <sup>-3</sup> )	0.47	0.523

$$^a R_w^* = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for [Fe(L)Cl<sub>3</sub>] (**1**)

Fe–Cl(1)	2.330(1)	Fe–N(1)	2.126(4)
Fe–Cl(2)	2.324(1)	Fe–N(3)	2.111(4)
Fe–Cl(3)	2.320(1)	Fe–N(5)	2.210(4)
Cl(1)–Fe–Cl(2)	93.77(5)	Cl(1)–Fe–N(5)	172.2(1)
Cl(2)–Fe–Cl(3)	95.03(6)	Cl(2)–Fe–N(1)	171.5(1)
Cl(1)–Fe–Cl(3)	96.43(5)	Cl(2)–Fe–N(3)	93.0(1)
N(1)–Fe–N(3)	80.4(1)	Cl(2)–Fe–N(5)	90.4(1)
N(1)–Fe–N(5)	83.3(1)	Cl(3)–Fe–N(1)	90.7(1)
N(3)–Fe–N(5)	82.1(1)	Cl(3)–Fe–N(3)	168.5(1)
Cl(1)–Fe–N(1)	91.8(1)	Cl(3)–Fe–N(5)	89.7(1)
Cl(1)–Fe–N(3)	91.1(1)		

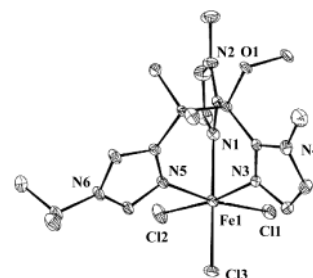
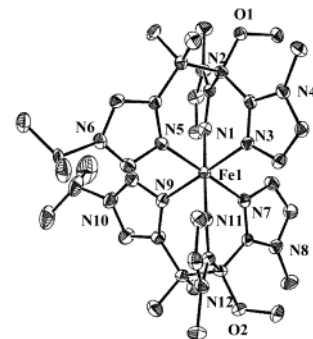
**Table 3.** Selected Bond Distances (Å) and Angles (deg) for [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**)

Fe(1)–N(1)	1.927(3)	Fe(1)–N(3)	1.928(3)
Fe(1)–N(5)	1.982(3)	Fe(1)–N(7)	1.920(3)
Fe(1)–N(9)	1.984(3)	Fe(1)–N(11)	1.936(3)
N(1)–Fe(1)–N(3)	87.17(14)	N(1)–Fe(1)–N(5)	89.56(14)
N(1)–Fe(1)–N(7)	91.70(14)	N(1)–Fe(1)–N(9)	91.36(14)
N(1)–Fe(1)–N(11)	178.56(14)	N(3)–Fe(1)–N(5)	90.00(13)
N(3)–Fe(1)–N(7)	90.28(13)	N(3)–Fe(1)–N(9)	178.54(14)
N(3)–Fe(1)–N(11)	91.71(14)	N(5)–Fe(1)–N(7)	178.72(14)
N(5)–Fe(1)–N(9)	89.91(13)	N(5)–Fe(1)–N(11)	91.35(14)
N(7)–Fe(1)–N(9)	89.84(13)	N(7)–Fe(1)–N(11)	87.38(14)
N(9)–Fe(1)–N(11)	89.75(14)		

(**1**) and ZORTEP<sup>37</sup> (**2**) with, respectively, 30% and 50% of probability displacement ellipsoids for non-hydrogen atoms. Crystal data collection and refinement parameters are gathered in Table 1, and selected bond distances and angles in Tables 2 and 3.

## Results

**Description of the Structures. [Fe(L)Cl<sub>3</sub>] (**1**).** A CAMERON view is shown in Figure 1, and selected interatomic bond lengths and angles are listed in Table 2. The unit cell

**Figure 1.** CAMERON representation (ellipsoid at 30% probability level) of [Fe(L)Cl<sub>3</sub>] (**1**). H atoms are omitted for clarity.**Figure 2.** ZORTEP representation (ellipsoid at 50% probability level) of [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**). H atoms are omitted for clarity.

includes four mononuclear complex molecules. The iron is hexacoordinated in a N<sub>3</sub>Cl<sub>3</sub> environment with a distorted octahedral geometry. The three nitrogen donors originating from L are in a *fac* arrangement, and the coordination sphere is completed with three chloride anions. N(1) and N(3) belong to the two MeIm groups, while N(5) belongs to the third <sup>i</sup>PrIm ligand. The Fe–N(1) and Fe–N(3) bond lengths (2.126(4) and 2.111(4) Å, respectively) are significantly shorter than the Fe–N(5) bond distance (2.210(5) Å). The latter is close to the Fe–N<sub>pyridine</sub> bond length (2.208 Å) found in trichloro[di(2-pyridyl)methylamine]iron(III), namely [Fe<sup>III</sup>(DPMA)Cl<sub>3</sub>] complex.<sup>38</sup> The Fe–Cl bond lengths (2.320(1)–2.330(1) Å) are in the usual range.<sup>38,39</sup> The significant departure of the FeN<sub>3</sub>Cl<sub>3</sub> core from octahedral geometry is also evidenced by the bond angles: Cl(1)–Fe–Cl(2), Cl(2)–Fe–Cl(3), and Cl(1)–Fe–Cl(3) = 93.77(5)°, 95.03(6)°, and 96.43(5)°, respectively, while N(1)–Fe–N(3), N(1)–Fe–N(5), and N(3)–Fe–N(5) = 80.4(1)°, 83.3(1)°, and 82.1(1)°, respectively.

**[Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**).** A ZORTEP view of the [Fe(L)<sub>2</sub>]<sup>3+</sup> cation of **2** is shown in Figure 2, and selected interatomic bond lengths and angles are listed in Table 3. The unit cell includes four mononuclear complex molecules. The iron is hexacoordinated in a slightly distorted N<sub>6</sub> environment. The six nitrogen donors originate from two L molecules with the same *fac* arrangement as in complex **1**. Moreover, the two <sup>i</sup>PrIm moieties are *cis* to each other. The Fe–N distances are shorter than in complex **1**, with Fe–N(1) = 1.927(3) Å, Fe–N(3) = 1.928(3) Å, Fe–N(5) = 1.982(3) Å, Fe–N(7) = 1.920(3) Å, Fe–N(9) = 1.984(3) Å, and Fe–N(11) =

(38) Renz, M.; Hammert, C.; Gornitzka, H.; Meunier, B. *New J. Chem.* **1999**, *23*, 773–776.

(39) Fukui, H.; Ito, M.; Moro-oka, Y.; Kitajima, N. *Inorg. Chem.* **1990**, *29*, 2868.

(37) Zolnai, L. *ZORTEP, Graphical Program for X-ray Structures Analysis*; University of Heilderberg: Germany, 1998.

1.936(3) Å. This suggests a stronger coordination of the imidazoles to the iron in **2** compared to **1**. As in **1**, the <sup>1</sup>PrIm groups via N(5) and N(9) bind less tightly than the MeIm analogues via N(1), N(3), N(7), and N(11). The N–Fe–N angles are close to 90°.

**Magnetic Susceptibility.** The thermal dependence of the magnetic susceptibility was measured in the 2–300 K (**1**) and 5–300 K (**2**) temperature ranges. The effective magnetic moment per iron of **1** at 300 K (5.81 μ<sub>B</sub>), close to the spin-only value for  $S = 5/2$ , remains constant when the temperature is lowered down to 80 K (5.80 μ<sub>B</sub>). A decrease in μ<sub>B</sub> is observed on further lowering the temperature down to 2 K (4.85 μ<sub>B</sub>), indicating the presence of zero-field splitting of the high-spin iron(III) ground state. The effective magnetic moment per iron of **2** at 300 K (2.12 μ<sub>B</sub>), close to the spin-only value for  $S = 1/2$ , slightly decreases upon lowering the temperature down to 5 K (1.92 μ<sub>B</sub>).

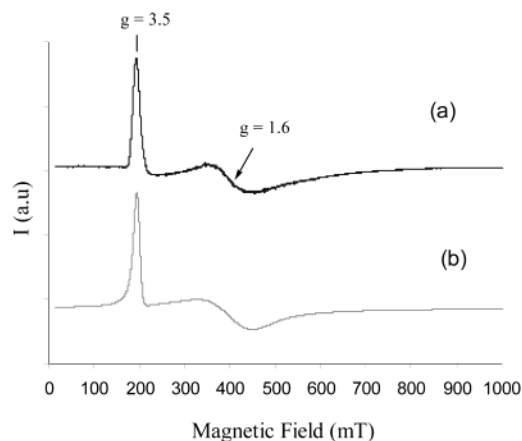
The previously reported<sup>40</sup> high-spin complex [Fe(terty)-Cl<sub>3</sub>] (5.75 μ<sub>B</sub> at 290 K) and the low-spin complex [Fe(terpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (2.16 μ<sub>B</sub> at 286.5 K and 1.91 μ<sub>B</sub> at 78.5 K) have magnetic data similar to those of **1** and **2**, respectively.

**Mössbauer Spectroscopy.** Mössbauer spectra of complexes **1** and **2** collected in the 80–200 K temperature range consist of a single quadrupole split doublet. They were least-squares fitted with Lorentzian lines. The resulting isomer shift (δ, mm·s<sup>-1</sup>) and quadrupole splitting (ΔE<sub>Q</sub>, mm·s<sup>-1</sup>) parameters indicate the ferric nature of their unique iron site and confirm the difference in spin state between **1** and **2**. At 80 K, the Mössbauer parameters of **1** (δ = 0.473(8), ΔE<sub>Q</sub> = 0.469(4) mm·s<sup>-1</sup>) are typical of high-spin Fe<sup>III</sup> while those of **2** (δ = 0.14(1), ΔE<sub>Q</sub> = 1.60(2) mm·s<sup>-1</sup>) are consistent with low-spin Fe<sup>III</sup>, in agreement with the magnetic data.

In the literature,<sup>40</sup> while the high-spin complex [Fe(terpy)-Cl<sub>3</sub>] (δ = 0.46, ΔE<sub>Q</sub> = 0.54 mm·s<sup>-1</sup> at 77 K) has data comparable to those of **1**, the low-spin complex [Fe(terpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> displays a low value of the isomer shift (δ = 0.07 mm·s<sup>-1</sup> at 77 K) and an unexpectedly large quadrupole splitting (ΔE<sub>Q</sub> = 3.43 mm·s<sup>-1</sup> at 77 K). The authors have explained these data by an additive effect of a valence contribution from the “hole” in the t<sub>2g</sub> subshell and a lattice contribution due to the asymmetry of the ligands. It is noteworthy that neither [Fe(terpy)Cl<sub>3</sub>] nor [Fe(terpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> was characterized by X-ray diffraction.

**EPR Spectroscopy.** The EPR spectrum of [Fe(L)Cl<sub>3</sub>] (**1**) recorded at 4 K in CH<sub>3</sub>CN is typical of rhombic high-spin Fe<sup>III</sup> ( $g = 4.3$ ).

The experimental and computed EPR spectra of [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**) at 4.5 K in CH<sub>3</sub>CN are shown in Figure 3a,b, respectively. Typical low-spin Fe<sup>III</sup> species have  $g$  values around 2.<sup>3</sup> The spectrum in Figure 3a displays a sharp signal at  $g = 3.5$  and a broad one at about  $g = 1.6$ ; no other feature can be observed from 0 to 1 T. Fitting of the spectrum in Figure 3a gave  $g_z = 3.40$ ,  $g_y = 1.67$ ,  $g_x = 0.87$ . According to Duelund and Toftlund,<sup>41</sup> this type of spectrum can be



**Figure 3.** EPR spectrum of [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**) at 4.5 K in CH<sub>3</sub>CN: (a) experimental, (b) fit.

attributed to a highly anisotropic low-spin Fe<sup>III</sup> species. The crystal field parameters were calculated following the convention used by Thomson et al.,<sup>42</sup> with  $g_z > g_y > g_x > 0$ . Applying Taylor’s formulas<sup>43</sup> (eqs 1 and 2) for t<sub>2g</sub><sup>5</sup> hole model to low-spin complexes in acetonitrile yielded  $V/\lambda = 0.831$ ,  $\Delta/\lambda = 4.006$ ,  $V/\Delta = 0.207$ . The calculated<sup>44</sup>  $g_{av}$  value (2.14) is consistent with the magnetic data (vide supra). The large splitting of the ground state,  $\Delta/\lambda = 4.006$ , may be understood<sup>45</sup> as arising from the anisotropy resulting from the *cis* arrangement of the longer Fe–N(5) and Fe–N(9) bonds (~1.99 Å) compared to the shorter Fe–N(1), Fe–N(3), Fe–N(7), and Fe–N(11) ones (~1.92 Å).

$$V/\lambda = g_x/(g_z + g_y) + g_y/(g_z - g_x) \quad (1)$$

$$\Delta/\lambda = g_x/(g_z + g_y) + g_z/(g_y - g_x) - V/2\lambda \quad (2)$$

## Discussion

**Synthesis of L.** The synthetic route chosen for the preparation of carbinol **5** allows the simultaneous incorporation of two MeIm moieties<sup>46</sup> (Scheme 1).

*N*-Isopropylation of the known imidazole derivative **3**<sup>26</sup> with sodium hydride and <sup>1</sup>PrI in anhydrous DMF yielded quantitatively the corresponding <sup>1</sup>PrIm **4**. It is noteworthy that the 1,4-disubstituted product was exclusively formed; no 1,5-disubstituted derivative was detected by <sup>1</sup>H NMR. This rather unusual situation is ascribed to the steric hindrance resulting from the presence of isopropyl and methyl groups at the α positions of the imidazole in **4**, thus preventing formation of the 1,5-disubstituted derivative. The anion of MeIm (2 equiv), generated in situ by *n*-BuLi in anhydrous THF at –78 °C, was then added to **4**, yielding the carbinol **5** in high yield. *O*-Methylation of **5** with sodium hydride and MeI in anhydrous DMF yielded L quantitatively.

**Complexes.** Previous work has shown that Fe<sup>3+</sup> and tripod tris(pyrazolyl)borate (Tpz) ligands, such as K[HB(Pz)<sub>3</sub>] or

(42) Gasby, P. M. A.; Thomson, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5003–5011.

(43) Taylor, C. P. S. *Biochim. Biophys. Acta* **1977**, *491*, 137.

(44) Aasa, R.; Vängard, T. *J. Magn. Reson.* **1975**, *19*, 308.

(45) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135–136*, 203.

(46) Kesicki, E. A.; DeRosch, M. A.; Freeman, L. H.; Walton, C. L.; Harvey, D. F.; Trogler, W. C. *Inorg. Chem.* **1993**, *32*, 5851.

(40) Reiff, W. M.; Baker, W. A.; Erickson, N. E. *J. Am. Chem. Soc.* **1968**, *90*, 4794–4800.

(41) Duelund, L.; Toftlund, H. *Spectrochim. Acta, Part A* **2000**, *56*, 331.

K[HB(3,5-Me<sub>2</sub>Pz)<sub>3</sub>], tend to form a mixture of “full-sandwich” Fe<sup>III</sup>(TPz)<sub>2</sub> and Fe<sup>II</sup>(TPz)<sub>2</sub> complexes, the latter resulting from Fe<sup>3+</sup> reduction. However, a few examples of “half-sandwich” [Fe<sup>III</sup>(TPz)Cl<sub>3</sub>]<sup>-</sup> complexes could be prepared using (Et<sub>4</sub>N)<sub>2</sub>[Fe<sub>2</sub>OCl<sub>6</sub>] as iron(III) source.<sup>39</sup> Reaction of the N<sub>3</sub> ligand L with FeCl<sub>3</sub> in anhydrous CH<sub>3</sub>CN yielded the stable monomeric complex [Fe<sup>III</sup>(L)Cl<sub>3</sub>] (**1**) quantitatively. Compound **1** is soluble in common solvents (CH<sub>3</sub>CN, DMF) yielding an orange-yellow solution.

The magnetic data and Mössbauer spectra clearly indicate that the iron of **1** is in the high-spin ferric state. The frozen solution (CH<sub>3</sub>CN) EPR spectrum of **1** at 4.2 K ( $g = 4.3$ ) is typical of rhombic high-spin Fe<sup>III</sup>, in agreement with the magnetic and Mössbauer data. The voltammogram of **1** shows a reversible reduction with  $E_{1/2} = +0.125$  V versus SCE in CH<sub>3</sub>CN (Figure S1, Supporting Information).

With the purpose of evaluating the ability of L to stabilize [Fe<sup>III</sup>N<sub>6</sub>] species, another iron(III) complex was prepared by addition of 2 equiv of L to [Fe(DMF)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub><sup>27</sup> in anhydrous CH<sub>3</sub>CN yielding cleanly [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**). The iron(III) center of **2** has a N<sub>6</sub> coordination sphere, with imidazolyl nitrogen donors. This situation is quite unusual, as direct addition of aromatic N ligands such as terpy, bipy, or phen to iron(III) salts usually results in spontaneous iron reduction with formation of [Fe<sup>II</sup>N<sub>6</sub>] complexes. The corresponding iron(III) complexes could only be obtained by oxidation of the [Fe<sup>II</sup>N<sub>6</sub>] complexes with PbO<sub>2</sub> in ~1 M H<sub>2</sub>SO<sub>4</sub> followed by addition of a suitable noncoordinating anion such as ClO<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>,<sup>47</sup> or by nitric acid in the presence of excess ligand. Two complexes were thus isolated and structurally characterized by X-ray diffraction,<sup>48,49</sup> but no spectroscopic data were reported probably because of their instability in solution. The previously mentioned [Fe(terpy)Cl<sub>3</sub>] and [Fe(terpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> complexes have been prepared using PbO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>.<sup>40</sup> A {[Fe<sup>III</sup>N<sub>6</sub>][Fe<sup>III</sup>Cl<sub>4</sub>]<sub>2</sub>Cl} complex with a tripod imidazole ligand as N donor set has recently been prepared by air oxidation of the corresponding [Fe<sup>II</sup>N<sub>6</sub>] species.<sup>18</sup>

(47) De Simone, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 2343.

(48) Baker, J.; Engelherdt, L. M.; Figgis, B. N.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 530.

(49) Figgis, B. N.; Skelton, B. N.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 57.

In the present case, the [Fe<sup>III</sup>N<sub>6</sub>] complex was obtained directly from [Fe<sup>III</sup>(DMF)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>, and no reduction was detected. [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**) was isolated in high yield. Compound **2** is soluble in common solvents (CH<sub>3</sub>CN, DMF) yielding a brown solution. As mentioned earlier, the Fe–N bond lengths, magnetic data, and Mössbauer and EPR spectroscopy clearly indicate an  $S = 1/2$  ferric state of the iron center in complex **2**. The voltammogram of **2** shows a reversible reduction with  $E_{1/2} = +0.24$  V versus SCE in CH<sub>3</sub>CN (Figure S2, Supporting Information). The stability of [Fe(L)<sub>2</sub>]<sup>3+</sup> (**2**) is tentatively assigned to the stronger  $\sigma$ -donor character of the imidazolyl N donors of L compared to that of the usual aromatic N ligands such as pyridine or pyrazole derivatives, suggesting that these aromatic N ligands stabilize the Fe<sup>II</sup> state. Comparing the  $E_{1/2}$  value of +0.24 V (vs SCE) for the [Fe(L)<sub>2</sub>]<sup>3+/2+</sup> couple to values<sup>50</sup> of +1.03 and +1.17 V (vs SCE), respectively, for the [Fe(phen)<sub>3</sub>]<sup>3+/2+</sup> and [Fe(bipy)<sub>3</sub>]<sup>3+/2+</sup> couples in CH<sub>3</sub>CN, indicates that the L ligand stabilizes the Fe<sup>III</sup> state.

## Conclusion

In this study, a new tripod imidazolyl ligand L, soluble in organic solvents, has been synthesized in a highly efficient way. Two monomeric Fe<sup>III</sup> complexes, [Fe(L)Cl<sub>3</sub>] (**1**) and [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**), have been isolated and fully characterized by X-ray diffraction and various spectroscopic measurements. In agreement with the magnetic and Mössbauer data, the rather unusual EPR spectrum of **2** has been interpreted as the signature of a highly anisotropic low-spin Fe<sup>III</sup>. Compared to the phen and bipy ligands, L stabilizes the Fe<sup>III</sup> oxidation state. The reactivity of the complexes of L is under investigation.

**Acknowledgment.** We thank Eckard Bill and Clotilde Policar for helpful discussions, and Eric Rivière for the magnetic susceptibility measurements of **2**.

**Supporting Information Available:** X-ray crystallographic files of [Fe(L)Cl<sub>3</sub>] (**1**) and [Fe(L)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**) in CIF format, and cyclic voltammograms of **1** (S1) and **2** (S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC020401A

(50) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.