

Notes

Crystal structure of $[\text{Fe}(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ having $\text{Fe}^{\text{II}}\text{N}_6$ coordination [$\text{L}^1 = 2,6$ -bis(pyrazol-1-ylmethyl)pyridine]

Samiran Mahapatra,^a Ray J Butcher^b
& Rabindranath Mukherjee^{a,*}

^aDepartment of Chemistry, Indian Institute of Technology,
Kanpur 208 016, India
E-mail: rnm@iitk.ac.in

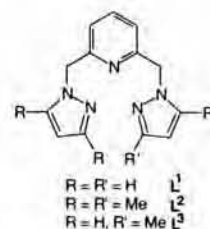
^bDepartment of Chemistry, Howard University,
Washington, DC 20059, USA

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The structure of the compound $[\text{Fe}(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) [$\text{L}^1 = 2,6$ -bis(pyrazol-1-ylmethyl)pyridine] has been determined by X-ray crystallography at ≈ 130 K. Temperature-dependent magnetic susceptibility and Mössbauer spectral studies reveal that the iron atom in **1** is in the high-spin state at room temperature and in the low-spin state at low temperature, whereas in $[\text{Fe}(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**2**) and $[\text{Fe}(\text{L}^3)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**3**) [$\text{L}^2 = 2,6$ -bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine and $\text{L}^3 = 2$ -(pyrazol-1-ylmethyl)-6-(3,5-dimethylpyrazol-1-ylmethyl)pyridine] the iron atom is in the high-spin state at both the temperatures [Mahapatra S, Mukherjee R, *Polyhedron* 12 (1993) 1603]. The metal-ligand bond distances in **1** have been compared with those of **3**, determined at ≈ 173 K [Mahapatra S, Butcher R J, Mukherjee, R, *J chem Soc, Dalton Trans* (1993) 3723]. The $\text{Fe}-\text{N}_{\text{pyridine}}$ and $\text{Fe}-\text{N}_{\text{pyrazole}}$ bond distances in **1** are shorter by ~ 0.23 Å and ~ 0.14 Å, respectively, than those for the high-spin complex **3**, revealing its low-spin character. Moreover, a noticeable variation of the N-Fe-N angles, leading to a more regular shape of the $\text{Fe}^{\text{II}}\text{N}_6$ octahedron in **1**, is observed.

The variation of spin-states among iron(II) complexes has been the subject of many studies¹⁻⁴. Six-coordinate iron(II) complexes may be diamagnetic, low-spin ($^1\text{A}_1$, LS), paramagnetic, high spin ($^5\text{T}_2$, HS), or exhibit a temperature-induced $\text{LS} \leftrightarrow \text{HS}$ transition that depends on the relative magnitude of crystal-field strength of the ligand and the mean electron-pairing energy. The present work stems from our continued research interest⁵⁻⁸ in the identification of the steric effect of methyl substituent(s) adjacent to donor atoms in a group of bis-chelates, $\text{M}^{\text{II}}\text{L}_2^{2+}$ ($\text{M} = \text{Mn}$, Fe, Co, Ni or Ru), using non-planar tridentate ligands, L^1 - L^3 . The temperature-dependence of the spin-state properties of iron(II) complexes using magnetic susceptibility and ^{57}Fe Mössbauer spectroscopy revealed⁶ that perchlorate salts of $[\text{Fe}(\text{L}^2)_2]^{2+}$ and

$[\text{Fe}(\text{L}^3)_2]^{2+}$ are uniformly high-spin at room temperature as well as at low-temperature, while that of $[\text{Fe}(\text{L}^1)_2]^{2+}$ is high-spin at room temperature and is low-spin at low temperature (gradual spin-crossover behaviour¹). Previously we carried out⁸ a single-crystal X-ray structural study at ≈ 173 K for yellow high-spin complex $[\text{Fe}(\text{L}^3)_2](\text{ClO}_4)_2$ (**3**). We present here the crystal structure of crimson-red low-spin form of complex $[\text{Fe}(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) by X-ray diffraction at ≈ 130 K. The $\text{Fe}-\text{N}_{\text{pyridine}}$ and $\text{Fe}-\text{N}_{\text{pyrazole}}$ bond distances have been compared between **1** and **3**.



Experimental

Preparation of the complex

The compound $[\text{Fe}(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) was synthesized as before^{6a}. The single crystals of **1** were grown from aqueous methanol over a period of 6-8 weeks. However, they were not stable in the absence of the mother liquor (losing their crystallinity in less than 1 min under the microscope).

Data collection, structure solution and refinement

When a pale yellow-green crystal of **1** ($0.5 \times 0.3 \times 0.01$ mm) was transferred into the cold N_2 gas stream on the Siemens P4 diffractometer, the crystal became crimson-red. Data collection was performed at ≈ 130 K with $\text{Mo K}\alpha$ radiation. However, the crystal had badly split peaks and a poor mosaicity; but data collection was still done with such a crystal, as it was the best we could have. A total of 2294 reflections were collected, of which 2133 reflections were independent ($R_{\text{int}} = 0.0494$). 2129 reflections ($I = 2\sigma(I)$) were used in the refinement. The structure was solved by direct methods with the SHELXTL PLUS program⁹, followed by successive difference Fourier syntheses and refined using full-matrix least-squares methods. The Cl and O atoms of one perchlorate ion

were disordered over two positions. Due to bad data set, anisotropic refinements of the thermal parameters were performed only for the following selected non-hydrogen atoms: Fe, non-disordered Cl and three O atoms associated with it, N(21a), N(11b), N(12b), N(22b), all C atoms from ring a, C(1b), C(3b), C(4b), C(6b), C(11b), C(21b), C(22b), C(23b).

Crystal data

The cell constants and crystallographic data for the complex (**1**) are: Formula $C_{26}H_{28}Cl_2FeN_{10}O_6$; mol. wt. 751.33; monoclinic $P2_1$; $a = 8.710(2)$ Å, $b = 10.020(2)$ Å, $c = 17.540(4)$ Å, $\beta = 92.49(3)^\circ$; $V = 1529.3(6)$ Å³; $Z = 2$; $F(000) = 772$; $\rho_{\text{calc}} = 1.632$ mgm⁻³.

Results and discussion

The synthesis and characterization of $[Fe(L^1)_2](ClO_4)_2 \cdot H_2O$ (**1**) were achieved by microanalysis, spectroscopic and magnetic studies, as described previously⁶.

Description of the structure

Figure 1 shows a perspective drawing of the cationic part of the complex $[Fe(L^1)_2](ClO_4)_2 \cdot H_2O$ (**1**) together with the atom-numbering scheme. Selected bond lengths and angles are given in Table 1. For comparison of metric parameters, the data for high-spin complex $[Fe(L^3)_2](ClO_4)_2$ (**3**)⁸ are also included in Table 1. The octahedron defined by the six nitrogen

atoms around the iron atom in **1** is more regular than that in **3** (Table 1). Whereas average Fe-N_{pyrazole} (2.035 Å) and Fe-N_{pyridine} (2.04 Å) distances are closely similar for the complex **1**, the corresponding values for high-spin complex **3** are 2.173 Å and 2.274 Å, respectively. The metal-ligand bond distances in **1** are reminiscent of the existence of a low-spin iron(II) state¹⁻⁴. The average N_{terminal}-Fe-N_{central} bite angles for two ligands are 89.25° and 89.45° for complex **1** and 85.25° and 84.7° for high-spin complex **3**⁸. This

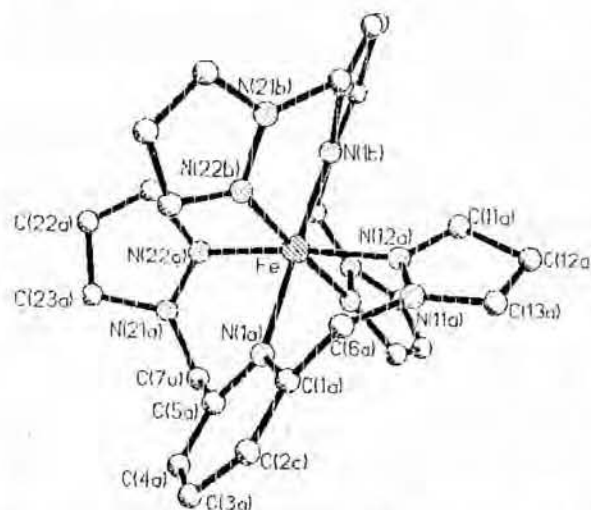


Fig. 1—Perspective view of the cationic part of $[Fe(L^1)_2](ClO_4)_2 \cdot H_2O$ (**1**), showing the atom numbering scheme (for clarity, not all atoms are shown with labelling). Hydrogen atoms are also omitted for clarity.

Table 1—Selected bond lengths (Å) and angles (°) for $[Fe(L^1)_2](ClO_4)_2 \cdot H_2O$ (**1**) (at = 135 K) and $[Fe(L^3)_2](ClO_4)_2 \cdot H_2O$ (**2**) (at = 173 K)

	1		2
Fe-N(1a)	2.09(2)	Fe-N(1a)	2.259(2)
Fe-N(12a)	2.01(3)	Fe-N(12a)	2.156(2)
Fe-N(22a)	2.02(2)	Fe-N(22a)	2.160(2)
Fe-N(1b)	1.99(3)	Fe-N(1b)	2.289(2)
Fe-N(12b)	2.09(3)	Fe-N(12b)	2.199(3)
Fe-N(22b)	2.02(2)	Fe-N(22b)	2.178(3)
N(1a)-Fe-N(1b)	179.0(11)	N(1a)-Fe-N(1b)	174.9(1)
N(1a)-Fe-N(12a)	90.5(9)	N(1a)-Fe-N(12a)	85.2(1)
N(1a)-Fe-N(22a)	88.0(9)	N(1a)-Fe-N(22a)	84.2(1)
N(1a)-Fe-N(12b)	93.0(9)	N(1a)-Fe-N(12b)	96.9(1)
N(1a)-Fe-N(22b)	88.2(9)	N(1a)-Fe-N(22b)	92.7(1)
N(1b)-Fe-N(12b)	86.1(10)	N(1b)-Fe-N(12b)	86.2(1)
N(1b)-Fe-N(22b)	92.8(10)	N(1b)-Fe-N(22b)	84.3(1)
N(1b)-Fe-N(12a)	89.7(10)	N(1b)-Fe-N(12a)	98.6(1)
N(1b)-Fe-N(22a)	91.7(10)	N(1b)-Fe-N(22a)	91.9(1)
N(12a)-Fe-N(22a)	178.3(11)	N(12a)-Fe-N(22a)	169.4(1)
N(12a)-Fe-N(12b)	85.5(11)	N(12a)-Fe-N(12b)	94.2(1)
N(12a)-Fe-N(22b)	93.3(9)	N(12a)-Fe-N(22b)	86.2(1)
N(12b)-Fe-N(22a)	93.8(9)	N(12b)-Fe-N(22a)	86.4(1)
N(12b)-Fe-N(22b)	178.3(11)	N(12b)-Fe-N(22b)	170.4(1)
N(22a)-Fe-N(22b)	87.5(10)	N(22a)-Fe-N(22b)	94.9(1)

reveals that for two closely similar six-coordinate $\text{Fe}^{\text{II}}\text{N}_6$ complexes, on passing from a high-spin complex **3** to a low-spin complex **1**, the coordination geometry of the iron atom approximates more regular octahedral. The degree of distortion from the ideal geometry is small, as assessed by the average N-Fe-N angles between opposite vertices is 178.65° for **1** and 172.15° for **3**. Average Fe-N_{pyridine} and Fe-N_{pyrazole} bond lengths for **1** are shorter than those observed for **3**; shortening of 0.234 Å and 0.138 Å were observed. Similar variations of structural parameters as a function of spin-state change have been reported for six-coordinate bis-ligand or tris-ligand iron(II) complexes¹⁻⁴, having FeN_6 coordination. Therefore, all of the metric parameters are consistent with the adoption of the low-spin configuration of the iron(II) atom in **1**. Compared to the Fe-N bond distances in low-spin complex **1**, the longer distances in **3** (Table 1) lead to a weakening of the crystal field, consistent with the failure of $[\text{Fe}(\text{L}^2)_2]^{2+}$ or $[\text{Fe}(\text{L}^3)_2]^{2+}$ to undergo $\text{HS} \rightarrow \text{LS}$ transition down to 8 K^{6b}.

In each ligand, the pyridine and pyrazole rings are planar. The two pyridine ring mean planes are tilted to each other at an angle of $\sim 30^\circ$. The two pyrazole mean planes of each ligand make an angle of $\sim 65^\circ$ and $\sim 66^\circ$ to each other. The pyridine mean plane is tilted to adjacent pyrazole rings within a ligand at angles of $\sim 47^\circ$ and $\sim 62^\circ$ and $\sim 39^\circ$ and $\sim 66^\circ$. Closely similar behaviour of the angles between the planes of the heterocyclic rings was observed in the case of **3**⁸. It should be noted that the structural changes, which occur in the course of a spin-state change, are concentrated in the central region of the molecule and these changes are considerably larger than any modification encountered in peripheral areas (*vide supra*). The central part of the molecule is directly influenced by electronic changes on the metal atom and thus the changes of molecular structure are directly related to the rearrangement of t_{2g} and e_g electrons of the metal^{1f}.

To the best of our knowledge, six-coordinate $\text{Fe}^{\text{II}}\text{N}_6$ systems with general formula $[\text{FeL}_2]^{2+}$ (L = neutral tridentate ligands) in which both high-spin and low-spin states exist in thermal equilibrium, as in **1**, are rare^{1,3,4}. Our strategy has been to incorporate sterically demanding substituents [methyl group(s)] close to the donor atoms such that the metal-donor atom distances could be lengthened, reducing the ligand field and making the high-spin configuration more favourable. This has been realized in the X-ray structure of yellow

high-spin complex **3** at ≈ 173 K, than with the unsubstituted parent ligand, as in the crystal structure of crimson-red low-spin complex **1** at ≈ 130 K. Moreover, to our knowledge, there is no report on studies devoted to the homologous species with non-planar tridentate ligands having two different heterocyclic rings, as in the present group of ligands ($\text{L}^1\text{-L}^3$).

Supplementary data

Tables containing listings of positional parameters, thermal parameters, all distances and angles, and plane calculations for the complex (**1**) are available from the authors.

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