CrystEngComm, **1999, 4**
DOI: 10.1039/a907126a

Spin crossover behavior of $[Fe^{II}(isoxazole)_6][BF_4]_2$—a structural study

Paper

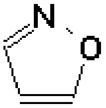
Wendy Hibbs, Atta M. Arif, Petra J. van Koningsbruggen and Joel S. Miller*

Department of Chemistry, University of Utah, 315 S. 1400 E. RM Dock, Salt Lake City, UT 84112-0850, USA. E-mail: jsmiller@chemistry.utah.edu

Received 31st August 1999, Accepted 17th September 1999, Published 15th October 1999

$[Fe^{II}(isoxazole)_6][BF_4]_2$
undergoes two reversible spin crossover transitions at 91 and 192 K and the single crystal structure determination reveals two different iron sites, Fe1 and Fe2, in a 1 : 2 ratio, with Fe1 attributed to the 91 K transition, and Fe2 attributed to the 192 K transition. This is the first such assignment for a material undergoing a two-step spin transition.

Some hexacoordinate Fe(II) complexes exhibit a transition from a low $S = 0$ (LS) and high spin $S = 2$ (HS) with increasing temperature. Several spin crossover materials have a two-step spin transition attributed to more than one type of spin crossover site, each undergoing a transition at different temperatures.[1] Assignments of the LS and HS sites have yet to be made. We have revisited the homoleptic Fe(II) isoxazole complexes[2] with the goal of developing new Fe(II) spin crossover materials with transition temperatures near room temperature. Isoxazole (**1**) is a monodentate ligand able to coordinate to a metal *via* either N or O. $[Fe^{II}\mathbf{1}_6][BF_4]_2$ was reported to exhibit an unusual temperature dependence of the magnetic moment, $\mu_{eff}(T)$, with the 5.25 μ_B moment at room temperature as expected for HS Fe(II), but with the 1.90 μ_B below 70 K representing 60% of LS Fe(II) and 40% HS Fe(II); hence, indicating incomplete conversion to the LS state.[2] Unexpectedly, however, an intermediate moment of 3.20 μ_B was found between 110 to 150 K. This anomaly was initially attributed to an impurity, but proved to be reproducible. Herein, we report the structure and magnetic properties of $[Fe^{II}\mathbf{1}_6][BF_4]_2$[†] and identify transition temperatures associated with each site.



The unit cell of $[Fe\mathbf{1}_6][BF_4]_2$ (Table 1) contains two unique iron sites; Fe1 resides on $\bar{3}$ while Fe2 sits on a three-fold symmetry with Fe1 : Fe2 being in a 1 : 2 ratio, Fig. 1.

Table 1 Crystal data for $C_{18}H_{18}B_2F_8FeN_6O_6$[a]

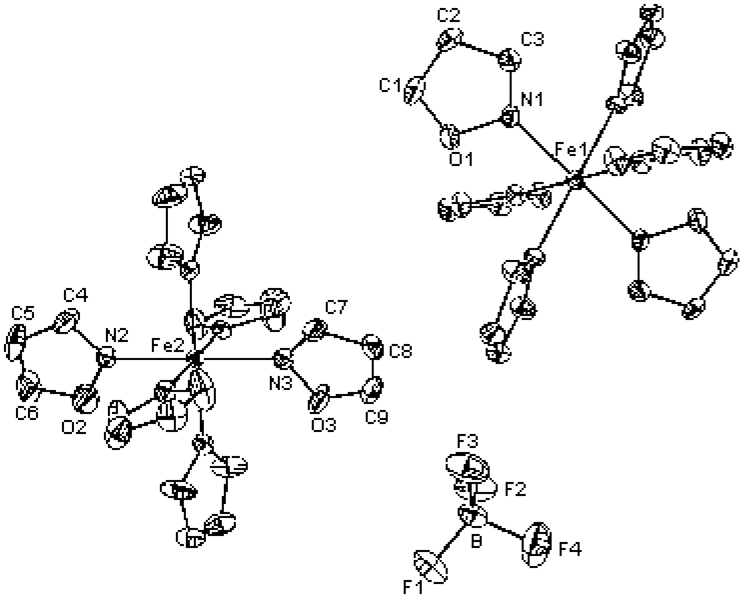
Property	Value

Formula weight, M/g mol^{-1}	643.85
Crystal system	trigonal $P\bar{3}$
a/Å	7.376(6)
c/Å	7.661(2)
Unit cell volume, U/Å^3	2003.2(10)
Z	3
D_c/Mg m^{-3}	1.601
μ(Mo-Kα)/mm^{-1}	0.666
T/K	230(1)
$R_1(F_0)$	0.0997
$wR_2(F_0)$	0.281
GOF	1.131
No. parameters	
measured	2601
used	2003

[a] The data were collected on a CAD4 diffractometer. The structure was solved by standard heavy-atom techniques with a MOLEN/VAX package and nonhydrogen atoms were refined with anisotropic thermal parameters using SHELXL-93.[3] The hydrogen atoms were included using the riding model where the H atoms coordinates are reidealized before each refinement cycle and 'ride' on the atoms to which they are attached. There is no crystallographic symmetry imposed on the anions. Attempt to determine the structure at 106, 127, 136, and 163 K failed because the crystals disintegrated. Click here for full crystallographic data (CCDC no. 1350/4).

All Fe(II)s are octahedrally coordinated by *N*-bound **1**. Fe1 has a center of inversion, such that looking down the three-fold axis all oxygen atoms would point along the same rotation direction, Fig. 2, with the Fe1–N distance 2.179 (7) Å. The shortest O···O separation is 4.09 Å. The Fe2s do not possess a center of inversion; thus, looking down the three-fold axis the oxygen atom of one ligand points directly at the oxygen atom on the neighboring ligand, Fig. 2, and have an average O···O separation of 3.315 Å, 0.77 Å shorter than that for Fe1. The Fe2–N distances are 2.167(8) and 2.160(8) Å; hence, the Fe–N distances are chemically equivalent and average 2.169 Å.

(a)



(b)

Spacefill Spin the molecule

Fig. 1 (a) ORTEP[4] drawing of $[Fe\mathbf{1}_6][BF_4]_2$ (20% electron density). The crystallographically unique atoms are labeled. H atoms have been omitted for clarity. (b) A 3D view of the structure.

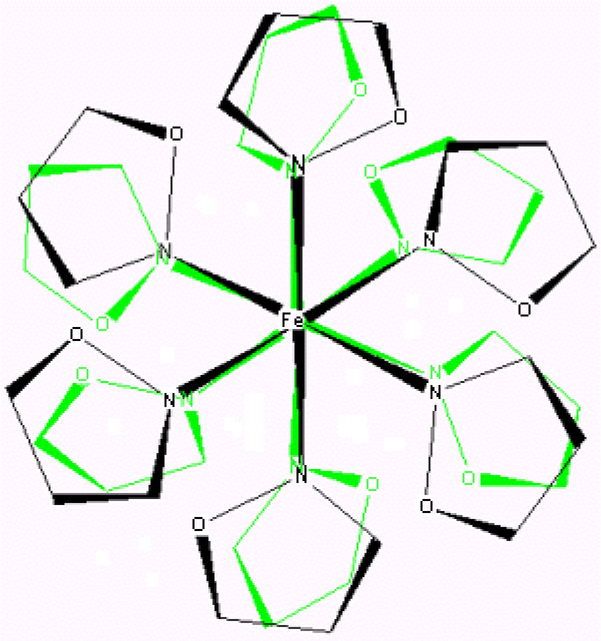


Fig. 2 Comparison between the hexacoordinate structures of Fe1 (black) and Fe2 (green) sites present in a 1 : 2 ratio in [Fe**1**$_6$][BF$_4$]$_2$.

The 5 and 300 K magnetic susceptibility of [Fe**1**$_6$][BF$_4$]$_2$, measured on heating, does not exhibit linear $\mu(T)$ data (Fig. 2); hence, it does not obey the Curie–Weiss law. Below 65 K the moment is relatively constant at 2.0 μ_B (Fig. 2). Between ~65 and ~110 K the moment rises to ~3.3 μ_B at 115 to 155 K, and upon warming between ~170 and ~205 K $\mu_{eff}(T)$ rises rapidly reaching a second plateau at 5.0 μ_B above 270 K (Fig. 2) in agreement with an earlier report.[2] The abrupt drops in $\mu_{eff}(T)$ have maxima in d$\mu_{eff}(T)$/dT or spin crossover transition temperatures of 192 and 91 K. Upon recooling, the $\mu_{eff}(T)$ dependence is reversible, except with a hysteresis of $\leqslant$1 K. The calculated high temperature moment is as expected for high spin Fe^{II}.

The 3.3 μ_B moment at the higher temperature plateau is consistent with 1/3 of the Fe(II)s transitioned at 192 K to a low spin state (*i.e.*, 3.3 μ_B). Hence, 2/3 of the Fe(II)s are in a high spin state in this temperature regime and therefore this transition is assigned to Fe1 as it is present in a 1 : 2 ratio with respect to Fe2. The moment of 2.0 μ_B is reproducible,[2]
and consistent with 40% of the material maintaining a high spin state and is ascribed to dislocations and defects within the lattice.[1a]
Consistent with the change from high spin to low spin associated with a decrease in temperature, the color of the crystal changes from very pale purple to very dark purple. In contrast, the second lower temperature spin crossover transition temperature for [Fe**1**$_6$][BF$_4$]$_2$ (91 K) is attributed to Fe2 (Fig. 2), which occupies 2/3 of the iron sites. Hence, the subtle structural differences between the orientational isomers Fe1 and Fe2, Fig. 2, lead to slight differences in the crystal field stabilization energy and hence to different spin crossover transition temperatures, with Fe2 having a lower crystal field stabilization energy.

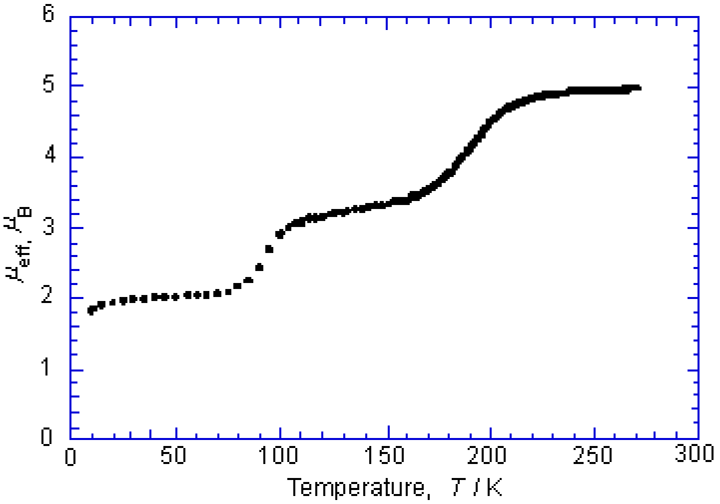


Fig. 3 $\mu(T)$ for [Fe$\mathbf{1}_6$][BF$_4$]$_2$ on heating showing spin transitions at 91 and 192 K.

Acknowledgement

The authors gratefully acknowledge support in part from the US Department of Energy Grant No. DE FG 03-93ER45504.

Footnote

† [Fe$\mathbf{1}_6$][BF$_4$]$_2$ was prepared according to the literature[2] using 69.0 mg (1.0 mmol) isoxazole, 42.2 mg (0.125 mmol) of the Fe^{II} salt, 3 ml nitromethane, and 2 ml acetic anhydride. Ascorbic acid, *ca.* 10 mg, was added to inhibit oxidation. Crystallization occurred at low temperature –20 °C, which was achieved by placing the flask in a constant temperature freezer. After 6 months undisturbed, crystals continue to grow into mm-sized prisms.

References

1 (*a*) P. Gütlich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2024; (*b*) E. König, *Prog. Inorg. Chem.* 1987, **35**, 527.
2 W. L. Driessen and P. H. van der Voort, *Inorg. Chim. Acta*, 1977, **21**, 217.
3 G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Determination, University of Göttingen, 1993.
4 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.