Variable-Temperature X-ray Structural Investigation of $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (pz = Pyrazolyl Ring): Observation of a Thermally Induced Spin State Change from All High Spin to an Equal High Spin-Low Spin Mixture, Concomitant with the Onset of Nonmerohedral Twinning

Daniel L. Reger* and Christine A. Little

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

Victor G. Young, Jr.* and Maren Pink

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received January 16, 2001

The complex $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (pz = pyrazolyl ring) undergoes a phase transition that occurs concomitantly with a thermally induced spin conversion between the high-spin (HS, $S = 2$) and low-spin (LS, $S = 0$) states. Above 204 K the compound is completely HS with the structure in the $C2/c$ space group with $Z = 4$. A crystal structure determination of this phase was performed at 220 K yielding the cell constants $a = 20.338(2)$ Å, $b = 10.332(1)$ Å, $c = 19.644(2)$ Å, $\beta = 111.097(2)°$, and $V = 3851.5(6)$ Å^3. There is one unique iron(II) site at this temperature. Below 206 K the compound converts to a 50:50 mixture of HS and LS. The radical change in the coordination sphere for half of the iron(II) sites, most notably a shortening of the Fe−N bond distances by ca. 0.2 Å, that accompanies this magnetic transition causes a phase transition. The crystal system changes from C-centered monoclinic to primitive triclinic with $Z = 2$ with two half-molecules on independent inversion centers. A crystal structure determination was performed at 173 K in space group $P\bar{1}$ with $a = 10.287(2)$ Å, $b = 11.355(3)$ Å, $c = 18.949(4)$ Å, $\alpha = 90.852(4)°$, $\beta = 105.245(4)°$, $\gamma = 116.304(4)°$, and $V = 1892.3(8)$ Å^3. All specimens investigated below the phase transition temperature were determined to be nonmerohedral twins. Temperature cycling between these two forms does not appear to degrade crystal quality. Previous magnetic susceptibility measurements indicate a second, irreversible increase in the magnetic moment the first time the crystals are cooled below 85 K. A crystal structure determination at 220 K of a specimen precooled to 78 K was not significantly different from those not cooled below 220 K.

Introduction

The properties of octahedral iron(II) complexes that undergo thermal spin conversions between the high-spin (HS, $S = 2$) and low-spin (LS, $S = 0$) states have been widely investigated.[1] We have recently shown that $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (pz = pyrazolyl ring) displays a new type of this spin-crossover behavior.[2] At ambient temperature in the solid state, the compound is completely HS with X-ray crystallographic studies showing that there is one unique iron(II) site in the crystal lattice. As the temperature of the solid is lowered, the magnetic properties follow the Curie law with a μ_{eff} of 4.77 μ_B. As demonstrated by magnetic (Figure 1) and Mössbauer spectral studies, as the temperature is lowered below 206 K, the solid changes abruptly from all HS to a 50:50 mixture of HS and LS below 200 K. The unusual observation is that even though there is only the one iron(II) site observed at ambient temperature, the composition of this mixture does not continue to change as the temperature is lowered from 200 to 10 K. This behavior of $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ is new for a complex that contains one unique crystallographic iron site when fully HS. Clear crystals of the compound change from colorless above 206 K to purple below this temperature. These crystals, when warmed back above 206 K, become colorless with no apparent degradation of the crystal quality. The magnetic and Mössbauer behavior is also reversible, until the crystals are cooled below ca. 85 K.

The first time the crystals are cooled below 85 K there is an irreversible increase in the magnetic moment (Figure 1), changing from 3.49 to 3.55 μ_B, but after this slight change the magnetic moment is constant. Upon warming, the magnetic moment stays at 3.55 μ_B *all the way up to 200 K*, i.e., it does not show the slight change at ca. 85 K that was observed on cooling. Then a very abrupt increase is observed at ca. 200 K as the compound changes back to the completely HS form. After this abrupt change the μ_{eff} is 4.88 μ_B. During the second cooling, the magnetic properties superimpose upon *the initial warming plot* and show only one abrupt change starting at 204 K.

Reported here are a series of X-ray crystallographic studies aimed at measuring the structural changes that accompany each of the changes noted in the magnetic and Mössbauer spectral

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[1] (a) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024 and references therein. (b) Kahn, O.; Krober, L.; Jay, C. *Adv. Mater.* **1992**, *4*, 718. (c) Cotton, F. A.; Wilkinson, J.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; pp 785−786.

[2] (a) Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, K.-C.; Concolino, T.; Mohan, A.; Long, G. J. *Inorg. Chem.* **2000**, *39*, 4674. (b) Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Liable-Sands, L. M.; Rhagitan, B.; Concolino, T.; Mohan, A.; Long, G. J.; Briois, V.; Grandjean, F. *Inorg. Chem.* **2001**, *40*, 1508.

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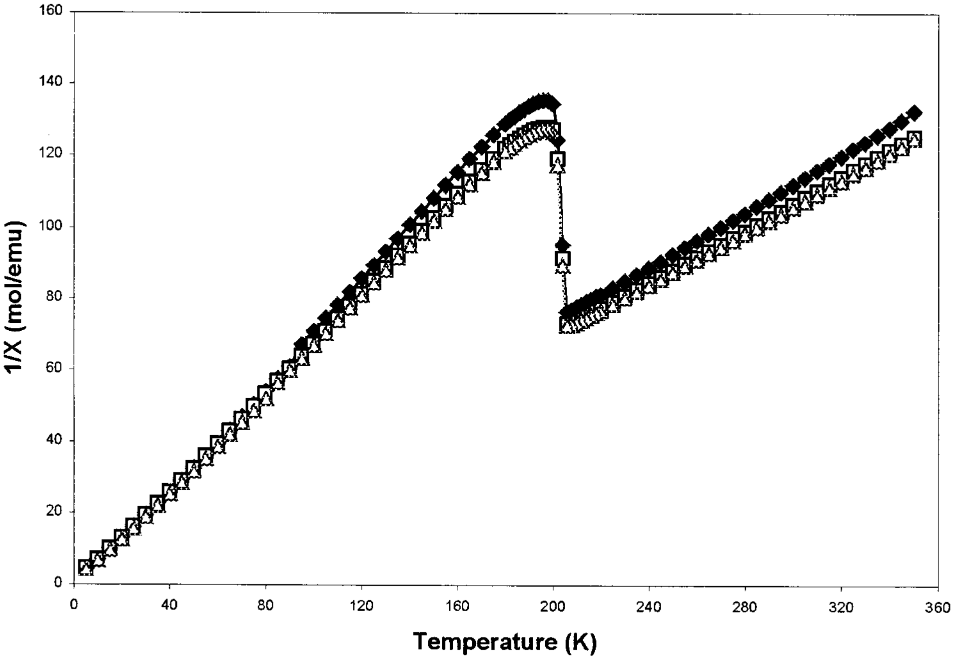

Figure 1. Magnetic data for $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$. Black diamonds (◆) mark the first cooling curve, squares (□) the first warming curve, and triangles (△) the second cooling curve. The latter two curves are superimposed, and all three curves are superimposed below 80 K.

studies. Specifically, we have carried out structural studies at 220 K on a crystal that had not been previously cooled, on the same crystal at 173 K, and on a crystal that was cooled to 173 K and heated back to 220 K. Another data collection at 220 K was carried out on a crystal that had been cooled to 77 K. In addition, we have collected data at 84 K to see if there are substantial differences in the structures below the phase transition. The most important result of this study is that in the 220 K, monoclinic structure there is one unique HS iron(II) site whereas in the 173 K, triclinic structure half the iron(II) cations remain HS while half become LS with reduced Fe−N bond distances of ca. 0.2 Å. This phase transition is reversible and accompanied by the 173 K phase being a nonmerohedral twin.

Experimental Section

The complex $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ was prepared as described elsewhere.[2] Large colorless crystals were grown by layering a saturated acetone solution with hexanes and allowing the two layers to slowly combine. The crystals were mounted on 0.1 mm glass fibers or capillaries. X-ray diffraction data were collected on a Bruker CCD with Mo Kα radiation ($\lambda = 0.71073$ Å) equipped with an Oxford Cryosystems cryostat. Intensity data were collected to a maximum resolution of either 0.84 or 0.77 Å with 0.30° frames. Please refer to Table 1 for all crystal and data collection parameters.

Table 1. Crystallographic Data for the 220 K Structure before Cooling (220a) and the 173 K Structure

	220 K	173 K
empirical Formula	$FeN_{12}C_{32}H_{44}B_2F_8$	$FeN_{12}C_{32}H_{44}B_2F_8$
fw	826.26	826.26
space group	*C*2/*c*	$P\bar{1}$
a, Å	20.338(2)	10.287(2)
b, Å	10.332(1)	11.355(3)
c, Å	19.644(2)	18.949(4)
α, deg		90.852(4)
β, deg	111.079(2)	105.245(4)
γ, deg		116.304(4)
V, $Å^3$	3851.5(6)	1892.3(8)
Z	4	2
λ, Å	0.71073	0.71073
ρ(calcd), g cm^{-1}	1.425	1.450
μ, cm^{-1}	4.72	4.80
R1, wR2 $[I > 2\sigma(I)]^a$	0.0453, 0.0994	0.0454, 0.0957

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2 + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$, and *a* and *b* are constants given in the Supporting Information.

The previous magnetometry study[2] indicated a phase transition starting below 206 K. In order to study the structures above and below this phase change, data were collected at 220 K on a crystal that had not been cooled (220a); 173 K; 84 K; 220 K on a crystal cooled to 173 K and heated back to 220 K (220b); and 220 K on a crystal cooled to 77 K and heated back to 220 K (220c). Upon cooling, the colorless specimen was observed to undergo an abrupt color change to purple at 204.0(2) K on the diffractometer. The 173 K structure of this phase appeared to be a nonmerohedral twin. The Gemini[3] suite of programs was used to index both twin components and determine the twin law.[4] The twin components indexed to a pair of triclinic unit cells that correspond to a distortion of the reduced cell of the C-centered monoclinic cell of the HS phase. The twinning persisted at 84 K and is assumed to continue down to at least 10 K based on magnetometry data.[2] The twin law determined at 84 K[5] is essentially the same as that found at 173 K. The intensity data were integrated with SAINT 6.1 based on the respective, major twin components only.[6] The intensity

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(3) Gemini 2.0: Bruker-AXS, Madison, WI.

(4) The nonmerohedral twin at 173 K: The major twin component indexed with a random set of 972/999 reflections to cell constants $a = 10.278$ Å, $b = 11.335$ Å, $c = 18.944$ Å, $\alpha = 90.837°$. $\beta = 105.217°$, and $\gamma = 116.279°$. The minor twin component indexed with 17 of the remaining 27 reflections to the cell constants $a = 10.275$ Å, $b = 11.336$ Å, $c = 18.967$ Å, $\alpha = 90.673°$, $\beta = 104.975°$, and $\gamma = 116.091°$. The twin law (by rows) is [1 0 0 /−0.9781 −1 0/−0.9748 0 −1]. This twin law corresponds to a 180° rotation about the (1 0 0) axis in direct space. The difference between the masses of the twin components mandated the integration of only the major twin and applying a correction for the minor twin component with ROTWIN.

(5) The nonmerohedral twin at 84 K: The major twin component indexed with 295/341 reflections with cell constants $a = 10.220$ Å, $b = 11.284$ Å, $c = 18.799$ Å, $\alpha = 91.011°$, $\beta = 105.136°$, and $\gamma = 116.072°$. The minor twin component indexed with 45 of the remaining 46 reflections to the cell constants $a = 10.223$ Å, $b = 11.297$ Å, $c = 18.791$ Å, $\alpha = 90.938°$, $\beta = 105.070°$, $\gamma = 116.111°$. The twin law (by rows) is rounded to [1 0 0/−0.9741 −1 0/−0.9608 0 −1]. This twin law corresponds to a 180° rotation about the (1 0 0) axis in direct space. The difference between the masses of the twin components mandated the integration of only the major twin and applying a correction for the minor twin component with ROTWIN.

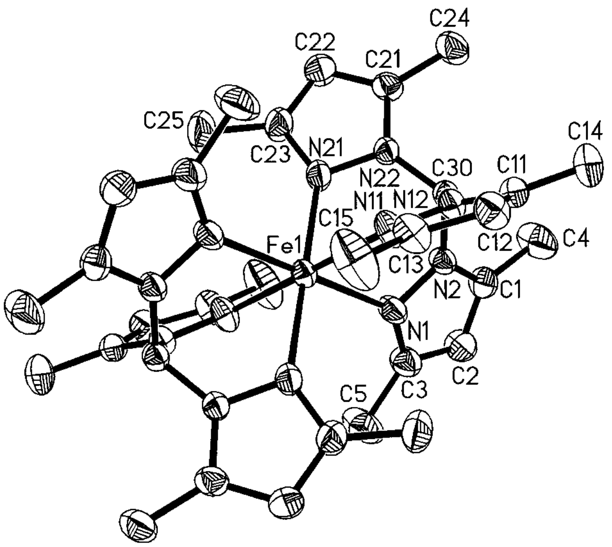

Figure 2. Thermal ellipsoid drawing at 50% probability of the cation in $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ at 220 K. Hydrogen atoms have been omitted for clarity.

data for both the 173 and 84 K data were corrected for the effects of nonmerohedral twinning by correcting it with UNTWIN 2.0.[7]

All structures were solved by direct methods and refined with SHELXTL V5.1.[8] All 220 K structures were found in the *C*2/*c* space group and determined to be the same as previously determined at room temperature.[2] The crystal structures determined at 173 and 84 K are reported for the first time within.

Results and Discussion

220 K Structures. Figure 2 shows a thermal ellipsoid drawing of the cation in $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ with the data collected at 220 K on a crystal that had not been previously cooled. Table 2 lists important bond distances and angles. The crystal is in the monoclinic space group *C*2/*c*. The complex has a unique iron site, which lies on an inversion center, with a N_6 coordination arrangement. The chelate rings restrict the intraligand N−Fe−N angles to an average of 84.40°, making the structure a trigonally distorted octahedron. The average Fe−N bond distance of 2.164 Å clearly demonstrates that the iron is HS; average distances of ca. 1.97 Å are observed in LS octahedral FeN_6 complexes.[9]

Figure 3a shows the arrangement of six of the cations. They are arranged in alternate rows, with the pseudo-3-fold axis (defined by the line connecting the two central methine carbon atoms and the iron(II)) oriented perpendicular. In the *C*2/*c* space group, the cations in the two rows are related by a 2-fold axis.

A crystal was cooled to 173 K and heated back to 220 K and a second data set collected at 220 K. The results of this crystallographic study are shown in the second column of Table S1 in the Supporting Information. The metrical parameters of this structure are not significantly different from the first 220 K structure. Thus, cooling the crystal below the spin-crossover temperature of 206−200 K, where it changes color to purple, leads to no significant structural changes when it is heated back above the spin-crossover temperature.

Table 2. Selected Bond Distances and Angles for $\{[HC(3,5\text{-}Me_2pz)_3]_2Fe\}(BF_4)_2$ for Data Collected at 220 K (220a) before Cooling and at 173 K (Both HS and LS Forms)

		173	
	220	HS	LS
Bond Distances (Å)			
Fe(1, 2)−N(1, 31)	2.175(3)	2.184(3)	1.982(3)
Fe(1, 2)−N(11, 41)	2.147(3)	2.150(3)	1.982(3)
Fe(1, 2)−N(21, 51)	2.169(3)	2.179(3)	1.987(3)
C(30, 60)−N(2, 32)	1.448(4)	1.451(4)	1.458(4)
C(30, 60)−N(12, 42)	1.441(4)	1.435(4)	1.440(4)
C(30, 60)− N(22, 52)	1.446(4)	1.445(4)	1.443(4)
N(1, 31)−N(2, 32)	1.374(3)	1.384(4)	1.376(4)
N(11, 41−N(12, 42)	1.376(3)	1.381(4)	1.380(4)
N(21, 51)−N(22, 52)	1.372(3)	1.371(4)	1.377(4)
distance Fe out of N_3 donor plane	1.3675	1.3648	1.1772
Bond and Torsion Angles (deg)			
N(1, 31)−Fe(1,2)−N(11,41)	84.7(1)	85.0(1)	88.5(1)
N(1,31)−Fe(1,2)−N(21,51)	84.7(1)	84.9(1)	88.3(1)
N(11,41)−Fe(1,2)−N(21,51)	83.9(1)	84.1(1)	88.4(1)
N(1,31)−Fe(1,2)−N(11A,41A)	95.3(1)	95.0(1)	91.5(1)
N(1,31)−Fe(1,2)−N(21A,51A)	95.4(1)	95.1(1)	91.7(1)
N(11,41)−Fe(1,2)−N(21A,51A)	96.1(1)	95.9(1)	91.6(1)
N(1,31)−N(2,32)−C(30,60)	120.0(2)	119.3(3)	117.8(3)
N(11,41)−N(12,42)−C(30,60)	119.4(2)	119.3(3)	118.4(3)
N(21,51)−N(22,52)−C(30,60)	119.6(3)	119.6(3)	118.2(3)
N(2,32)−C(30,60)−N(12,42)	111.3(2)	111.3(3)	109.6(3)
N(2,32)−C(30,60)−N(22,52)	110.9(2)	110.9(3)	110.0(3)
N(12,42)−C(30,60)−N(22,52)	111.9(2)	112.0(3)	111.2(3)
Fe(1,2)N(1,31)−N(2,32)C(1,31)	168.2(2)	161.8(2)	178.9(2)
Fe(1,2)N(11,41)−N(12,42)C(11,41)	165.4(2)	157.6(2)	178.5(2)
Fe(1,2)N(21,51)−N(22,52)C(21,51)	170.4(2)	165.7(2)	179.6(2)

In order to attempt to measure a structural change associated with the small increase in magnetic moment the first time a crystalline sample is cooled below 85 K, a third crystallographic study was conducted at 220 K on a specimen precooled to 77 K. The results of this structural determination (Table S1) are not significantly different from either of the above 220 K structures. Thus, the small changes noted by both magnetic and Mössbauer studies[2] are not observable by X-ray crystallography.

173 K Structure. Below 204 K the crystal turns purple. From data collected at 173 K, the system is triclinic in the space group $P\bar{1}$ that is a nonmerohedral twin. Data collected at 84 K (Table S1) are similar to these 173 K data. There is a drastic change in the structure where half of the cations have an average Fe−N distance that is greatly reduced to 1.984 Å, the distance expected for LS iron(II), whereas half remain essentially constant at 2.171 Å. The second column in Table 2 shows the metrical parameters for the HS cations (the numbering scheme is the same as in Figure 2). While there are clearly changes from the 220 K structures, the changes are small. The average Fe−N bond distances increase by 0.007 Å, and the spread of the longest to shortest distance is just slightly larger. The average intraligand N−Fe−N bond angles increase by only 0.37° in going to the 173 K structure, and the interligand angles are also very similar. Even though half of the cations have changed their metrical parameters substantially, the cations that remain HS show only minor structural changes.

The third column of Table 2 shows the metrical parameters for the LS cations, and Figure 4 shows a thermal ellipsoid drawing with the numbering scheme. As expected, these parameters are very different from those in the first two columns and are similar to those reported elsewhere for the ambient-

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(6) SAINT 6.1: Bruker-AXS, Inc., Madison, WI, 2000.

(7) ROTWIN: Young, V. G., Jr., and Pink, M. Unpublished work, 2000. The metric tensor, the twin law, and an algorithm for partially overlapped reflections were used to output a corrected HKLF 5 SHELX reflection file. For the 173 K data the partially overlapped reflections were grouped in separate batches in ascending 0.003 $Å^{-1}$ sets in the range 0.0−0.015 $Å^{-1}$. For the 84 K data the partially overlapped reflections were grouped in separate batches in ascending 0.0015 $Å^{-1}$ sets in the range 0.0−0.0075 $Å^{-1}$.

(8) SHELXTL V5.1: Bruker-AXS, Inc., Madison, WI, 2000.

(9) (a) König, E. *Struct. Bonding (Berlin)* **1991**, *76*, 51. (b) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527.

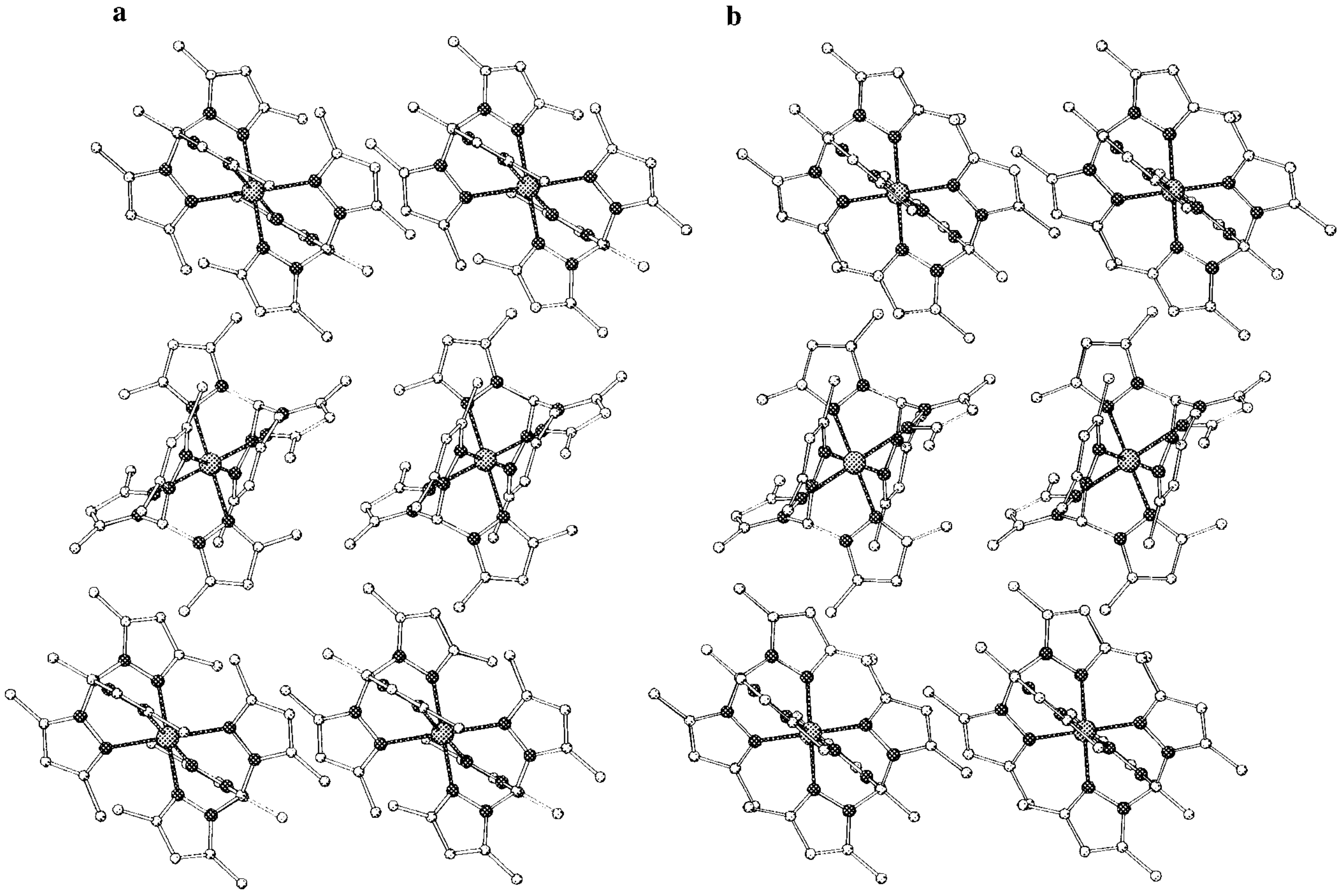

Figure 3. Packing drawings showing the arrangement of six of the cations. (a) The all-high-spin structure at 220 K. (b) The 50:50 mixture, high spin−low spin structure at 173 K. The top and bottom rows of panel b show the low-spin form, the middle row the high-spin form.

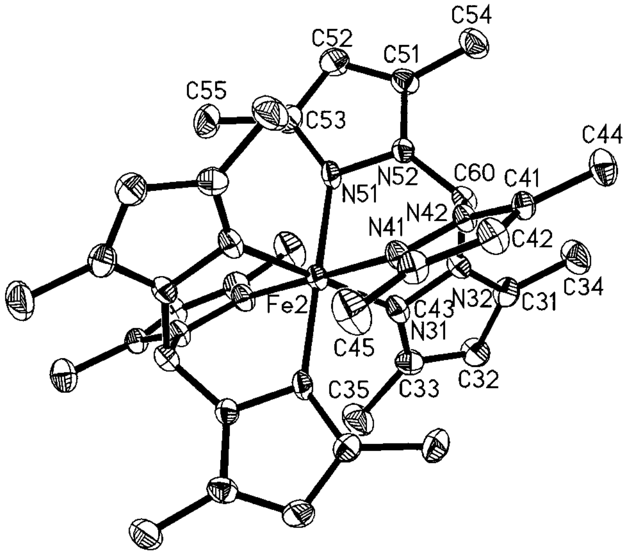

Figure 4. Thermal ellipsoid drawing at 50% probability of the cation in the low-spin form of $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$ at 173 K. Hydrogen atoms have been omitted for clarity.

temperature structure of $\{Fe[HC(pz)_3]_2\}(BF_4)_2$,[2b] a compound known to be fully LS at that temperature. The bond distances shorten by ca. 0.2 Å, causing the intraligand bond angles to increase to an average value of 88.4°. An interesting change is that the iron(II) moves from 1.37 Å out of the intraligand donor atom N_3 planes in the HS form to 1.18 Å out of these planes in the LS form. A consequence of this change is to lower the C···C nonbonding distances between adjacent interligand 3-methyl groups from an average of 3.75 Å in the HS form to an average of 3.65 Å in the LS form. The sum of the van der Waals radii of two methyl groups is 4.0 Å. We have argued previously[2b] that these contacts cause $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$ to be HS at ambient temperature whereas $\{Fe[HC(pz)_3]_2\}(BF_4)_2$, a compound that lacks these unfavorable interactions, is LS. The change from HS to LS at lower temperatures for $\{Fe[HC(3,5-Me_2pz)_3]_2\}(BF_4)_2$ increases these unfavorable contacts.

The most striking difference in the HS and LS structures at 173 K can be seen in Figures 5 and 6, where the two forms are pictured down the pseudo-3-fold axis. The degree of tilting the pyrazolyl rings make away from an ideal C_{3v} type arrangement is much larger in the HS form than in the LS form. In the absence of tilting, the FeN(n1)−N(n2)C(n1) torsion angles, where n denotes the ring number, would be 180° and the metal atom would reside in the planes defined by the pyrazolyl rings. In the HS complex, Figure 5, this angle averages 161.7°, whereas in the LS form, Figure 6, it averages a nearly ideal 179.0°. Clearly, the 1.984 Å bond distances in the LS form are nearly exactly suited for the intrinsic bite angle of the $HC(3,5-Me_2pz)_3$ ligand. Increasing the Fe−N distances by ca. 0.2 Å forces the rings to distort (Figure 5) such that the lone pairs on the donor nitrogen atoms are not pointing directly at the metal. As we have pointed out before,[10] the ability of tris(pyrazolyl)-methane and tris(pyrazolyl)-borate ligands to distort by this twisting action allows them to form stable complexes with metals of very different ionic radii. An interesting difference between the 220 K structure and the HS form of the 173 K

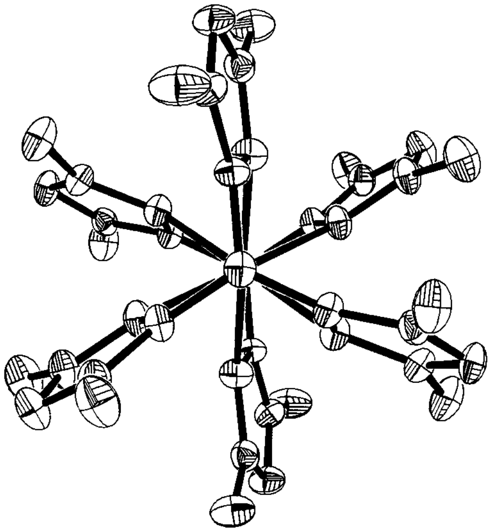

Figure 5. View down the pseudo-3-fold axis of the cation in the high-spin form of $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ at 173 K.

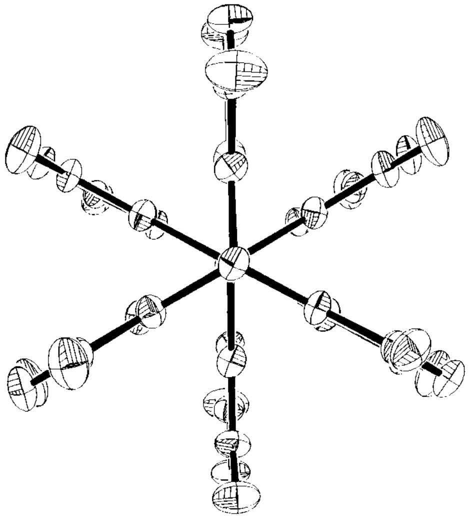

Figure 6. View down the pseudo-3-fold axis of the cation in the low-spin form of $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ at 173 K.

structure is that there is less tilting observed in the 220 K structure where this torsion angle averages 168.0°.

Figure 3b shows six of the cations in this 173 K structure that match as closely as possible the orientations in Figure 3a of the 220 K structure. In this case the top and bottom pairs of cations are LS whereas the central two cations are HS. What has happened in going from the 220 K structure to the 173 K structure is that every other row of cations in the 220 K structure has changed from HS to LS, leaving the other rows unchanged. The change is best seen by comparing the tilting of the pyrazolyl rings that are oriented perpendicular to the page (the central rings in the drawings of each cation) in the top and bottom rows. In the 220 K, high-spin structure (Figure 3a) the rings are tilted with the two central pyrazolyl rings not in alignment. In the low-spin rows of the 173 K structure (top and bottom rows of Figure 3b) these rings are not tilted with the two central pyrazolyl rings in perfect alignment. Although not readily seen in the angle of the view in Figure 3b, the pyrazolyl rings in the middle row, where the iron(II) sites are high spin, remain tilted. *The selectivity of the change is remarkable, as is the fact that the crystals can sustain these major structural changes without degradation.*

A number of systems have been reported previously that undergo the changeover of only half of the iron(II) centers or show a two-step changeover where as the temperature is lowered half of the iron(II) centers change to LS followed by the other half at lower temperatures.[1,11] For $\{Fe(4,4'\text{-bis-}1,2,4\text{-triazole})_3\}(ClO_4)_2$, structures measured at 260, 190, and 150 K show respectively two nonequivalent iron(II) sites, an equal mixture of HS and LS iron(II) sites, and two nonequivalent LS iron(II) sites.[11] The major difference between these structural studies and the results reported here is that in $\{Fe(4,4'\text{-bis-}1,2,4\text{-triazole})_3\}(ClO_4)_2$ at 260 K there are two nonequivalent HS iron(II) sites, whereas in $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ *all the sites are equivalent.* As observed with $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$, with the compound [Fe(1-methyl-1*H*-tetrazole)$_6$](BF$_4$)$_2$ only 50% of the iron(II) is converted to the LS state upon cooling.[12] However, in this complex there are also two crystallographically different iron(II) sites, and one site changes completely from HS to LS and the other remains HS.

Conclusion

We have been able to observe through crystallography that $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ is fully in the HS state at 220 K, but in the structure measured at 173 K half of the cations change over from the HS state to the LS state. Half of the Fe−N bond distances shorten by ca. 0.2 Å at the lower temperature. Even though at the higher temperature only one type of iron(II) site is observed, when the reversible changeover occurs below 206 K, half of the molecules change spin state with an accompanying lowering of the symmetry in a very organized way. The fact that the changeover takes place as the temperature is varied over only a few degrees indicates that cooperative effects are operational during the change. The surprising and unique result is that after half of the cations change to LS, the other half of the cations remain HS, even down to 10 K. The small changes noted by both magnetic and Mössbauer studies that take place the first time crystals are cooled below 85 K are not observable by X-ray crystallography.

Acknowledgment. The authors thank the National Science Foundation (CHE-9727325 to D.L.R.) for support.

Supporting Information Available: Table S1 showing selected bond distances and angles for three 220 K structures, the 173 K structure, and the 85 K structure. Five X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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