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Low-Spin Iron Complex

Dramatic Remote Substitutent Effects on the Electronic Spin State of Bis(scorpionate) Iron(II) Complexes**

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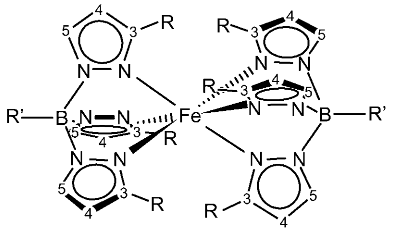
One of the most spectacular examples of bistability is the spin crossover (SCO) phenomenon in molecular coordination compounds.[1] SCO materials are increasingly investigated for their potential technological applications in molecular electronics[2] and memory devices,[3] and as contrast agents for magnetic resonance imaging.[4] Their bistable behavior results from a switching between the high-spin (HS) state and the low-spin (LS) state leading to distinctive changes in color, structure, and magnetism, which may be triggered by an external stimulus, such as temperature, pressure, magnetic field, or light irradiation.[1,5] Although SCO occurs in transition-metal ions with 3d^n ($n = 4$–7) electronic configuration, it is most common for iron complexes, especially those containing nitrogen donor atoms. Among the N ligands used, the versatile classes of anionic tris(pyrazolyl)borates[6] and their neutral isoelectronic tris(pyrazolyl)methane analogues[7] provide useful platforms for investigating electronic spin-state crossover properties of iron(II) in nitrogen-rich coordination environments.[8] In the solid state, the prototypical purple bis[hydrotris(pyrazolyl)borato]iron(II) derivative, $[\mathrm{Fe\{HB(pz)_3\}_2}]$ (pz = 1-pyrazolyl; Scheme 1, **A**), is LS at room temperature and undergoes a SCO transition to the colorless HS state above approximately 420 K.[9] In contrast, its colorless counterpart, bearing a methyl group at the 3-position of the pyrazolyl ring, $[\mathrm{Fe\{HB(3\text{-}Mepz)_3\}_2}]$ (Scheme 1, **B**), is HS at room temperature and undergoes a spin conversion into the purple LS state on cooling to 4.2 K.[10,11] This behavior is also detected in iron(II) species having a fourth substituent placed on the central boron, $[\mathrm{Fe\{R'B(pz)_3\}_2}]$ (Scheme 1, **C**),[12,13a,b] which are purple LS complexes, whereas the 3-methylated analogues, $[\mathrm{Fe\{R'B(3\text{-}Mepz)_3\}_2}]$ (Scheme 1, **D**),[13,14] are colorless HS species at room temperature. Such spin-state modification has been rationalized in terms of ligand field strength controlling the electronic state of the iron(II) ion through intra- and interligand contacts.[15,16] The 3-methyl groups in **D** bring about severe interligand steric clashes and thus **D** favors the HS state, which typically has Fe−N bond distances that are ca. 0.2 Å longer than those in the LS state.[17] Of note is the terminal dialkynylated derivative, $[\mathrm{Fe\{(\textit{p}\text{-}HC{\equiv}C\text{-}C_6H_4)B(3\text{-}Mepz)_3\}_2}]$, reported by Reger et al.,[13b] which partially contravenes the empirical rule of colorless HS complexes, in that it is pale purple in the crystalline phase at 294 K, as a result of two crystallographically independent molecules, one being fully HS and the second undergoing iron(II) HS/LS electronic spin-state relaxation. Thus, the metrical parameters of the latter component, the average Fe−N bond distance (2.101 Å) and the torsion angles of the pyrazolyl rings, are intermediate between those expected for fully LS and fully HS iron(II) ions.[17,18]



R' = H	R' = Me, *n*Bu, *i*Bu, pz 3-Mepz, p-C$_6$H$_4$X (X = I, C≡CH, C≡CPh)	R' = *t*Bu
R = H (purple) (**A**)	R = H (purple) (**C**)	R = H (pink) (**2**)
R = Me (colorless) (**B**)	R = Me (colorless) (**D**)	R = Me (purple) (**1**)

Scheme 1. Bis[tris(3-R-pyrazolyl)borato]iron(II) complexes with different fourth substituent R′ at boron.

Recently, we designed a series of novel scorpionate ligands bearing the bulky *tert*-butyl substituent on the hub boron atom.[19] We postulated that the steric requirement of this distal substituent can be used to alter the electronic spin-state properties of the resultant octahedral iron(II) complexes. Herein, we test this hypothesis for the case of the 3-methylated derivative $[\mathrm{Fe\{\textit{t}BuB(3\text{-}Mepz)_3\}_2}]$ (Scheme 1, **1**). To our knowledge, **1** is the first reported bis[poly(3-hydrocarbylpyrazolyl)borato]iron(II) complex to be fully low-spin at room temperature.[20] For the purpose of comparison, its expected LS unsubstituted counterpart **2** (Scheme 1) was also prepared.

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Addition of one equivalent of cobaltocene to THF solutions of PF_6^- salts[19] of $\mathbf{1}^+$ and $\mathbf{2}^+$ [Eq. (1)] caused the immediate formation of colored precipitates. These materials

$$\begin{gathered}\{Fe[tBuB(3\text{-}Rpz)_3]_2\}^+ PF_6^- + Cp_2Co \\ \downarrow \text{THF/20° C} \\ Fe[tBuB(3\text{-}Rpz)_3]_2 + [Cp_2Co]^+ PF_6^- \end{gathered} \quad (1)$$

$1^+PF_6^-$: R=Me, purple, 98%; $2^+PF_6^-$: R=H, pink, 98%

were isolated by filtration and were analytically pure (see the Supporting Information). For **1**, high-resolution ESI mass spectrometry gave an exact mass of m/z 678.3665 for $[M^+]$ in accordance with the calculated value of m/z 678.3660 and the expected isotopic distribution of peaks (see Figure S1 in the Supporting Information). The two new compounds were isolated as thermally stable, purple (**1**) and pink (**2**) solids in quantitative yields. Crystals of these compounds were stable in air for short periods without apparent signs of decomposition. The solids are poorly soluble in common solvents, preventing reliable solution characterization. The diffuse-reflectance optical spectrum of **1** recorded at 293 K is dominated by a very intense charge-transfer band in the UV region centered at 28600 cm^{-1}, and also shows a less intense band centered at 18900 cm^{-1} (Figure 1), accounting for its purple color. This spectrum is essentially identical to that of **2** and to those of LS $[Fe\{R'B(pz)_3\}_2]$ (R' = H, Ph, pz).[9,12a]

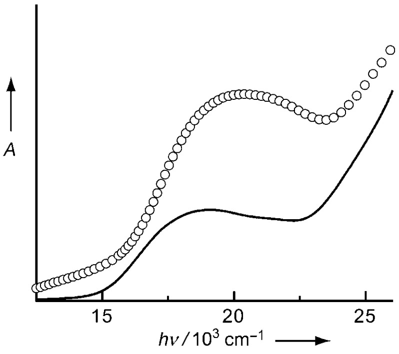

Figure 1. Room-temperature diffuse-reflection optical absorption spectra of **1** (line) and of **2** (circles).

The LS state of **1** was confirmed by its room-temperature ^{13}C CPMAS NMR spectrum (CPMAS = cross-polarization magic angle spinning) with all the expected resonances showing up in the diamagnetic region (Figure 2).[21] Moreover, the spectrum is consistent with the six pyrazolyl arms being equivalent and unrearranged, with all the methyl substituents located in the 3-position. The three characteristic resonances of the pyrazolyl rings appear at $\delta_{C4} = 128$, $\delta_{C5} = 162$, and $\delta_{C3} = 190$ ppm, in accordance with those reported for $Li[tBuB(3\text{-}iPrpz)_3]_2$.[19] Each resonance can be split into three equal components (see Figure S2 in the Supporting Information) that are attributable to the three crystallographically independent pyrazolyl fragments (see below).

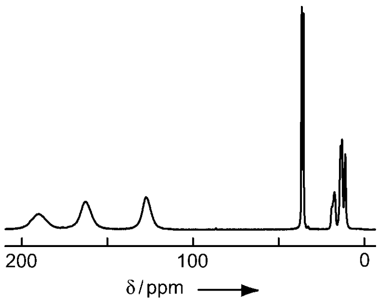

Figure 2. Room-temperature ^{13}C CPMAS (12 kHz) NMR spectrum of **1**.

Complex **1** was crystallized as purple hexagonal platelets, which were subjected to X-ray crystallographic analysis at 293 K.[22] The ORTEP representation in Figure 3 indicates that iron(II) is sandwiched by two N_3 planes defined by the nitrogen donors of the two negatively charged *tert*-butyl-[tris(3-methylpyrazolyl)]borato ligands bound in a tridentate fashion, that is κ^3-N,N',N''-tBuB(3-Mepz)$_3$. The ferrous ion, which is situated on a center of inversion, adopts a quasi-perfect octahedral coordination geometry with three intra-ligand N-Fe-N bond angles averaging 89.50(9)°. More importantly, the short Fe–N bond lengths (1.975(2)–1.993(2) Å) establish that, despite the steric hindrance brought about by

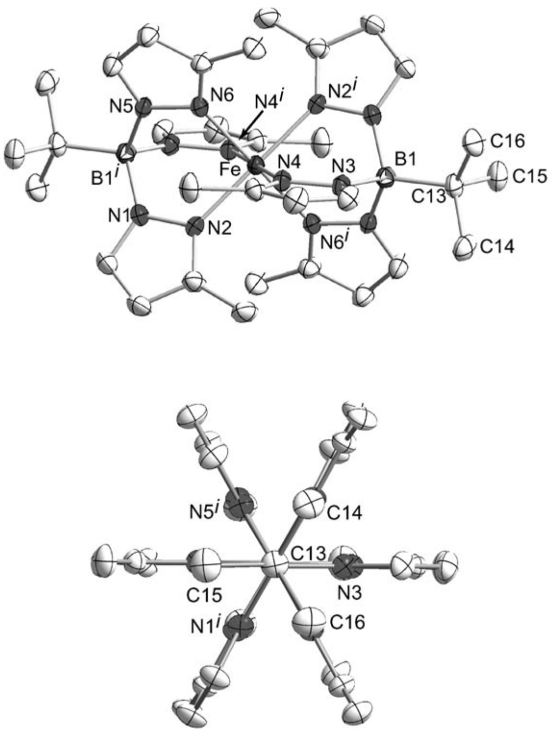

Figure 3. Top: ORTEP representation of **1**. Bottom: A view oriented down the C–B···Fe axis, showing the ideal C_{3v}-type arrangement in the ligand. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Fe–N2 1.988(2), Fe–N4 1.993(2), Fe–N6 1.975(2), B–N1 1.578(4), B–N3 1.564(4), B–N5 1.564(4), B–C13 1.652(4); N2-Fe-N4 90 67(10), N2-Fe-N6 89.61(9), N4-Fe-N6 90.45(9).

Table 1: Selected room-temperature geometrical parameters for **1**, **2**, and related [Fe{R′B(3-Rpz)$_3$}$_2$] compounds (R = H, Me).

Scorpionate	Spin state	Bond lengths [Å][a] Fe–N	Fe–B	V(FeN$_6$) [Å^3]	Torsion angles [°][a] Fe-N-N-B	Fe-N-N-C	Reference
[tBuB(3-Mepz)$_3$]$^-$ (**1**)	LS	1.985	3.13	10.428	2.0(3)	178.1(2)	This work
[tBuB(pz)$_3$]$^-$ (**2**)	LS	1.955(2)	3.17	9.972	4.38(18)	177.02(12)	This work
[HB(3-Mepz)$_3$]$^-$[b]	HS	2.204	3.22	14.192	2.0	177.5	[10]
[HB(pz)$_3$]$^-$[b]	LS	1.972	3.08	10.210	1.9	178.3	[17]
[PhB(3-Mepz)$_3$]$^-$	HS	2.188	3.23	13.847	11.8	162.9	[13c]
[PhB(pz)$_3$]$^-$	LS	1.987	3.15	10.141	5.3	171.3	[15]
[(p-IC$_6$H$_4$)B(3-Mepz)$_3$]$^-$	HS	2.175	3.23	13.619	8.6	166.1	[13a]
[(p-IC$_6$H$_4$)B(pz)$_3$]$^-$[c]	LS	1.963	3.12	10.078	5.1	172.6	[13a]

[a] Average values. [b] Average values for two crystallographically independent molecules in the unit cell. [c] X-ray crystallographic data obtained at 150 K.

the six methyl groups in the equatorial belt of the complex, [Fe{tBuB(3-Mepz)$_3$}$_2$] is fully LS at room temperature. The mean interligand separation between the 3-Me substituents (3.67 Å) is consistent with such congestion.[23] LS complexes usually have shorter Fe–N bond lengths of approximately 1.98 Å (Table 1 and Tables S2 and S3 in the Supporting Information), whereas HS complexes have longer Fe–N bond lengths of approximately 2.18 Å (Table 1 and Table S1 in the Supporting Information), as a result of the antibonding character of the partially filled e_g* orbitals. As expected for the LS state, the mean values of the torsion angles of the pyrazolyl rings (2.0(2)° for Fe-N-N-B and 178.1(2)° for Fe-N-N-C) are in good agreement with the ideal ring-twisting and ring-tilting values of 0° and 180°, respectively, expected for a metal-bonded ligand fragment with D_{3d} symmetry (Figure 3).[18] Notably, these values are similar to those measured for the prototypical unsubstituted LS derivative [Fe{HB(pz)$_3$}$_2$] (Table 1).

Compared to the general trend for [Fe{R′B(3-Mepz)$_3$}$_2$] (see Table 1; R′ = H, Ph, p-IC$_6$H$_4$), the unique LS situation encountered in **1** can be ascribed to the steric demand of the bulky tBu substituent. Steric interactions with the hydrogen atoms at the 5-position of the pyrazolyl rings (H_{tBu}···H5 ≈ 2.06 Å) prevent the pyramidal deformation at boron (average C-B-N and N-B-N bond angles are 112.7(2)° and 106.1(2)°, respectively), distortions of the pyrazolyl rings and opening up of the ligand.[11,15,16] As a consequence of the steric requirements of the distal tBu group on the conformational flexibility of the [B(3-Mepz)$_3$] fragment, the Fe–N bond length decreases and the tripod lengthens along the B···Fe axis, highlighting the structurally adaptive nature of scorpionate ligands. The Fe–N and Fe···B distances are, indeed, the shortest and the longest, respectively, ever measured for this class of LS [Fe{R′B(3-Mepz)$_3$}$_2$] complex (see Table S2 in the Supporting Information).These effects (shortest Fe–N length, and longest Fe···B distance) also occur in **2** (see Table 1 and Figure S3 and Tables S2 and S3 in the Supporting Information).

At room temperature, for a powdered sample of **1**, $\chi_M T$ has a value of 0.130 cm^{3}Kmol^{-1}, fully consistent with a LS state.[24] On cooling, this value does not change noticeably, in agreement with Mössbauer spectral studies (see the Supporting Information). In contrast, on heating, $\chi_M T$ increases smoothly but inexorably to reach 2.53 cm^{3}Kmol^{-1} at 460 K (Figure 4), which highlights the SCO transition to the HS state. The SCO can be thermally cycled but no thermal hysteresis takes place. The lack of cooperativity is related to the absence in the crystal structure of significant close contacts between molecules. The spin-state conversion can also be monitored by reversible color change, from purple to white on heating from 300 K to the decomposition temperature (≈325 °C).

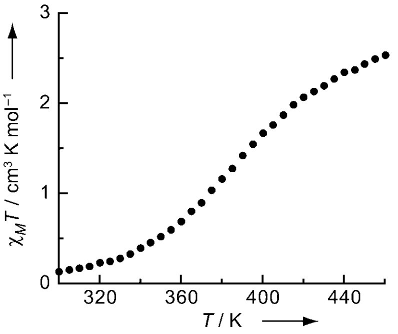

Figure 4. Temperature dependence of $\chi_M T$ measured for a powdered sample of **1** in the temperature range 300–460 K.

Preliminary density functional calculations[25–27] on **1** and **2** in D_{3d} symmetry, confirm their diamagnetic nature with a LS ($S = 0$) ground state computed to be significantly more stable than the lowest HS ($S = 2$) state, by 0.83 eV and 1.28 eV, respectively. These LS/HS energy gaps are likely to be overestimated.[28] As is often the case at this level of calculations and as reported for related complexes,[29] the optimized bond distances are systematically longer by approximately 1% than their experimental counterparts. Assuming correction for this slight expansion, the optimized metrical data match very well with the X-ray structures. The LS computed Fe–N bond lengths are 1.998 Å and 1.963 Å for **1** and **2**, respectively, whereas in the HS state they increase to 2.191 Å and 2.154 Å, respectively. The computed intraligand N-Fe-N bond angles (89° and 88° in the LS state for **1** and **2**, respectively) are not significantly different from the experimental values. These angles are approximately 84° in the HS state for both compounds.

In conclusion, we have described the isolation and structural characterization of the first bis(scorpionate) iron(II) complex with 3-hydrocarbyl-substituted pyrazolyl rings to be fully low-spin at room temperature. This complex features κ^3-bound *tert*-butyl[tris(3-methylpyrazolyl)]borate ligands. Owing to its stereoelectronic effect, the remote *tert*-butyl substituent on boron forces the tripod body to lengthen, thus increasing the ligand field strength and favoring LS complex formation with a small ferrous ion. In this way, the *tert*-butyl group seems to act like the locking screw of a molecular vise. In addition, [Fe{*t*BuB(3-Mepz)$_3$}$_2$] undergoes a spin-state crossover at about 400 K and, therefore, represents one of only a few LS iron(II) complexes known to exhibit SCO phenomena above room temperature. Further studies aimed at characterizing this transition, as well as the high-temperature structure and behavior of **1**, are currently underway.

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temperatures up to 800 K. The experimental data were corrected for the diamagnetism of the sample holder and the intrinsic diamagnetism of the materials evaluated with Pascal's tables.

[25] DFT calculations were performed with the Amsterdam Density Functional package (ADF2005.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com),[26] with the BP84 gradient-corrected functional.[27] Triple-ζ-quality Slater-type orbital basis sets including polarization functions (TZVP) were employed for all atoms to describe valence electrons. Inner shells were kept frozen up to 3p for Fe, and 1s for B, C and N.

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