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Remarkable Paramagnetically Shifted ^{1}H and ^{2}H NMR Spectra of Iron(II) Complexes of 2-Aza-21-carbaporphyrin: An Evidence for Agostic Interaction

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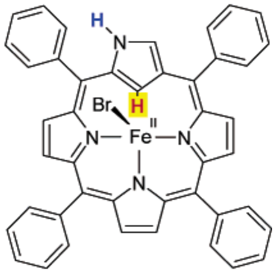
Iron(II) 2-aza-21-carbaporphyrins have been characterized by paramagnetically shifted ^{1}H and ^{2}H NMR spectra. The high-spin iron(II) complex (*H*CTPP*H*)Fe^{II}Br displays the β-H resonances which reflect the combination σ and π routes of spin density delocalization. The uniquely large isotropic shift of the inner H(21) hydrogen (812 ppm, 298 K) indicates an Fe^{II}–{C(21)–H} agostic interaction.

Chart 1. Iron(II) 2-Aza-21-carbaporphyrin



An uncommon type of a metal ion−inverted pyrrole ring interaction, detected in the solid-state structure of iron(II) 2-aza-21-carbaporphyrin (*H*CTPP*H*)Fe^{II}Br, Chart 1, has raised a question of its impact on the ^{1}H NMR spectroscopic features.[1,2]

The iron(II) inverted porphyrin (*H*CTPP*H*)Fe^{II}Br presents a conformation with the side on position of the iron with respect to the inverted pyrrole plane.[1] The inverted pyrrole ring is sharply bent from the porphyrin plane. The Fe···C(21) distance 2.361 Å is longer than the regular iron−carbon bonds but shorter than the sum of van der Waals radii.

Importantly, the solid-state geometry of the Fe^{II}···{C(21)−H(21)} fragment in (*H*CTPP*H*)Fe^{II}Br is within the bond distances of an agostic interaction (Fe···H(21), 1.971 Å).[1] An agostic interaction has also been suggested for dimeric iron(II) 2-aza-2-carbaporphyrin, [(CTPP*H*)Fe^{II}]$_2$,[3] and monomeric manganese 2-aza-2-carbaporphyrin complexes.[4]

The ^{1}H NMR spectrum of (*H*CTPP*H*)Fe^{II}Br bears substantial similarities to the spectra of high-spin iron(II) core modified porphyrins.[5−7] Five pyrrole resonances of (*H*CTPP*H*)Fe^{II}Br are spread out the low field region from 30 to 50 ppm with chemical shifts of 44.8, 43.7, 43.7, 31.7, and 31.7 ppm (298 K). Two other β-H resonances occur at 8.4 and 0.78 ppm. A resonance at −8.0 ppm (293 K) has been assigned to the 2-NH hydrogen. This resonance is absent in the ^{2}H NMR spectrum of (*H*CTPP*D-d$_7$*)Fe^{II}Br. The additional resonances, presented in Figure 1 in the 15−0 ppm range, come from the *meso* phenyl hydrogens.

The most characteristic ^{1}H NMR (^{2}H NMR) feature (*H*CTPP*H*)Fe^{II}Br, i.e., the unprecedently downfield shifted resonance at 812 ppm (line width 6200 Hz, at 293 K, dichloromethane-*d$_2$*), has been unambiguously assigned to the internal 21-H hydrogen. This resonance disappears in the ^{1}H NMR spectrum of (*H*CTPP*D-d$_7$*)Fe^{II}Br (carbaporphyrin deuterated at all pyrrole positions). The ^{2}H NMR spectrum of (*H*CTPP*D-d$_7$*)Fe^{II}Br, shown in the 900 ppm window, helps appreciate the remarkably large paramagnetic shift of 21-CD, as the ^{2}H NMR spectrum combines simultaneously all pyrrole resonances including the 21-CD one (Figure 2).

A Curie plot for the 21-CH resonance of (*H*CTPP*H*)Fe^{II}Br reveals the remarkable changes of the chemical shifts

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(2) We will use the symbol CTPP to denote the trianion obtained from the inverted porphyrin by abstraction of all pyrrolic NH proton and the C-bound H(21) hydrogen. The groups attached to the N(2) atom will be indicated by a prefix in italic and the group attached to C(21) will appear as a suffix in italic.

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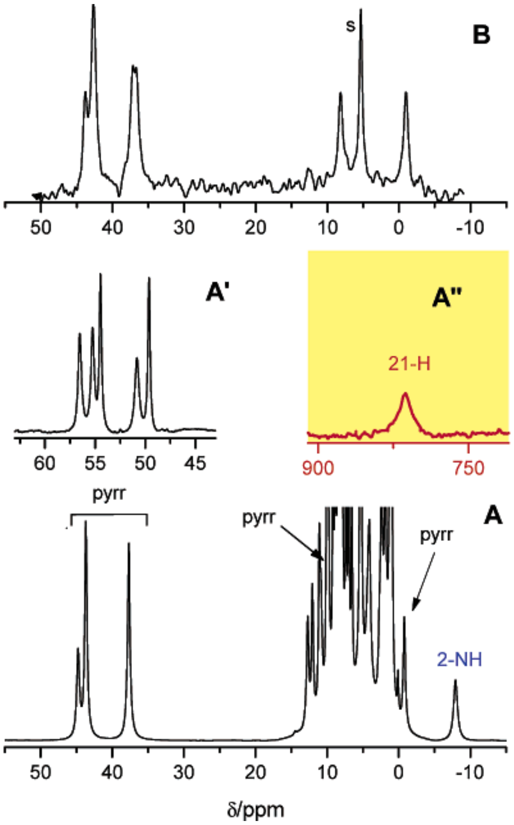

Figure 1. NMR spectra of iron(II) inverted porphyrins: (A) (*H*CTPP*H*)-Fe$^{\mathrm{II}}$Br, **1** (^{1}H NMR, dichloromethane-d_2, 298 K), (B) (*H*CTPP*D*-d_7)Fe$^{\mathrm{II}}$Br (^{2}H NMR, dichloromethane, 298 K). Inset A′ presents the downfield pyrrole region measured at 223 K, and the 21-H resonance is shown in inset A″ (both insets present ^{1}H NMR spectra). In this and in the following figure, peak labels follow systematic numbering of the porphyrin ring or denote proton groups: pyrr, regular pyrrole ring protons; s, solvent.

reaching 1244 ppm at 208 K. While the experimental data for 21-H and all β-H resonances (Supporting Information) are consistent with a linear behavior over the investigated temperature range, the extrapolated intercepts are outside the normal diamagnetic positions, which have been estimated from the data for diamagnetic Zn(II) complex.[8]

Addition of 2-methylimidazole to a dichloromethane-d_2 solution of (*H*CTPP*H*)Fe$^{\mathrm{II}}$Br results in formation of a high-spin five-coordinate species [(*H*CTPP*H*)Fe$^{\mathrm{II}}$(2-MeIm)]$^{+}$. The titration produces marked changes in the position of resonances, but the overall ^{1}H NMR features of high-spin iron(II) inverted porphyrin are preserved. In particular, a dramatic relocation of the 21-CH resonance to 1090 ppm has been noticed. Actually, the position of this resonance varies in the 1020−1090 ppm range (298 K) depending on the nitrogen base concentration.

The ^{1}H NMR titration of (*H*CTPP*H*)Fe$^{\mathrm{II}}$Br with pyridine-d_5 or 1-methylimidazole provided direct evidence for the coordination of these ligands. The severe broadening of the downfield β-H resonances is consistent with an exchange between five-coordinate species, which contain a nitrogen base or bromide as the apical ligand. Clearly, the coordination changed positions of the 21-CH resonance once compared to (*H*CTPP*H*)Fe$^{\mathrm{II}}$Br: ([(*H*CTPP*H*)Fe$^{\mathrm{II}}$(py-d_5)]$^{+}$, 762 ppm; ([(*H*CTPP*H*)Fe$^{\mathrm{II}}$(1-MeIm)]$^{+}$, 828 ppm.

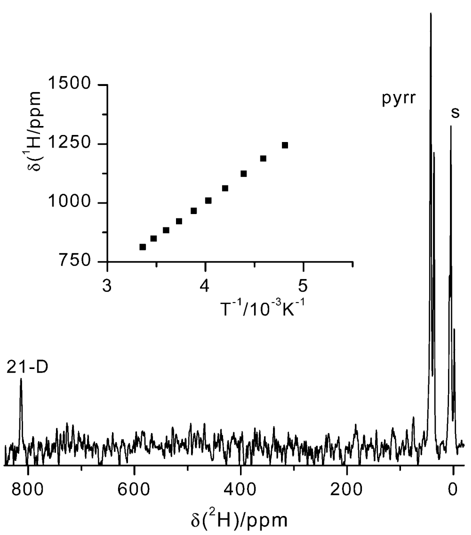

Figure 2. ^{2}H NMR spectrum of (*H*CTPP*D*-d_7)Fe$^{\mathrm{II}}$Br (dichloromethane, 298 K). Peak labels follow systematic numbering of the porphyrin ring. Inset presents the Curie plot for 21-H as determined by ^{1}H NMR.

To the best of our knowledge, these are the largest chemical shifts reported thus far for iron porphyrins or iron porphyrin derivatives.[9−11] Actually, these values are even larger than the extreme chemical shifts determined for paramagnetic compounds, including σ-aryl complexes of nickel(II) heteroporphyrins (e.g., ortho-H 568 ppm at 203 K).[12−15]

The extreme contact shifts were reported for β-CH$_2$ hydrogens of cysteines that ligate iron in oxidized rubredoxin (300−900 ppm, 303 K),[16] and copper(II) in azurin (800, 850 ppm at 278 K).[17]

^{1}H NMR spectroscopy has been shown to be a definitive method for detecting and characterizing iron(n) porphyrins ($n = 1-4$),[10,18] and lower symmetry derivatives modified at the coordination core: iron(n) N-substituted porphyrins ($n = 2-4$),[5,10,19−22] iron(II) 21-thiaporphyrin,[6] and iron(n) 21-

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oxaporphyrin ($n = 1-3$).[7] The hyperfine shift patterns, that were recorded for iron porphyrins, are sensitive to iron oxidation and spin and ligation states.[10,23] The fundamental spectroscopic features are preserved in iron core modified porphyrins ($N-CH_3$, O, S, N−C−Fe) providing that spin/electronic states were identical.[5−7,10,19−22,24]

The ^{1}H NMR spectra of iron(II) 2-aza-21-carbaporphyrins display characteristics that reveal the lowering of symmetry. Thus, the spread of regular β-H resonances are markedly larger than for more symmetrical counterparts.[6,21,24] The paramagnetic shifts of (HCTPPH)Fe^{II}Br can be explained by a model typically applied to high-spin iron(II) porphyrins and iron(II) N-substituted porphyrins. In the case of a high-spin iron(II) center, $(d_{xy})^2(d_{xz}d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$, both σ and π routes of spin density delocalization can operate. The contact shift predominates for the regular pyrrole resonances yielding their downfield positions.[5,7,10] The typical delocalization pathways involve the delocalization through a σ-framework by way of a σ-donation to the half occupied $d_{x^2-y^2}$ iron(II) orbital.[5] Actually, the variation of the β-H positions in the ^{1}H NMR spectrum may be accounted for by specific π-delocalization mechanisms discussed in detail for iron(III) porphyrins.[25,26]

The distinctive feature of the iron(II) complex (HCTPPH)Fe^{II}Br is the localized effect of the N-confused pyrrole ring. For (HCTPPH)Fe^{II}Br, one pyrrole and 2-NH resonances are evidently different from the other six and show upfield shifts. The logical conclusion that follows is that the side on location of the iron(II) with respect to the pyrrole ring primarily affects spin transfer to the modified pyrrole ring. The analogous effect has been observed for paramagnetic nickel(II) 2-aza-21-carbaporphyrin, and metalloheteroporphyrins.[15,27]

Significantly, the peculiar metal ion−inverted pyrrole ring interaction detected in the solid-state structure of (HCTPPH)Fe^{II}Br has been clearly reflected by an unprecedented isotropic shift of the engaged H(21) atom (Figures 1 and 2).

In conclusion, the hyperfine shift patterns for the high-spin iron(II) inverted porphyrin present a potentially unique probe for detecting an agostic interaction Fe^{II}−{C(21)−H} in solution. In particular, the enormous downfield H(21) paramagnetic shift provides a distinct resonance in a unique window (700−1100 ppm) for a range of axial ligands which can be considered as a diagnostic sign of such interaction. The generalization of such a spectroscopic approach to other paramagnetic carbaporphyrinoids can be suggested.

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Supporting Information Available: Synthetic and sample preparation procedures and Curie plots for (HCTPPH)Fe^{II}Br. This material is available free of charge via the Internet at http://pubs.acs.org.

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