Paramagnetic NMR Evidence for a Novel Tetrahydroboratoiron(III) Porphyrin Complex

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Complexes involving covalently bound tetrahydroborate ion have been reported for many transition. lanthanide. and actinide metals.[1] Tetrahydroborate complexes are generally prepared by reaction of an alkali tetrahydroborate with the corresponding metal halide. or by treatment of a solution of a metal alkoxide with diborane.[1] The chemical and physical nature of tetrahydroborate complexes has been investigated in terms of ligand activation and bond configuration in catalytic transformation such as polymerization,[2] oligomerization,[3] and hydrogenation of olefins.[4] Hence the structural. analytical, and chemical characteristics of the tetrahydroborate ligand are of great importance in organotransition metal chemistry.

To the best of our knowledge, no tetrahydroborate complexes are known for iron porhyrins. Here we describe evidence for generation and solution characterization of the tertahydroboration(III) porphyrin complexes as a product from reaction of tetrabutylammonium borohydride (Bu₄NBH₄) and chloroiron(III) tetraphenylporphyrin.

Experimental Section

Benzene, dichloromethane. and toluene were purchased as "distilled-in-glass" solvents and were purified as described elsewhere.[5] All solvents were degassed after or during purification either by an N_2 purge or by the freeze-pump-thaw method. Deuterated benzene-d_6. dichlorometane-d_2. and toluene-d_8 were purchased from Aldrich and deoxygenated by the freeze-pump-thaw method. Solvents were stored in an Ar or N_2 atmosphere of a dry box. Tetrabutyl-ammonium borohydride (Bu₄NBH₄) was obtained from Aldrich and recrystallized from ethyl acetate.

Preparation of tetrabutylammonium borodeuteride (Bu₄NBD₄) was from a published method.[6] Typically one mole of tetrabutylammonium hydrogen sulfate is dissolved in 100 mL of water. A volume of 125 mL of 5 M NaOH is added and the mixture is cooled to room temperature. A solution of 1.1 mole of NaBD₄ dissolved in 50 mL water is then added and the mixture is extracted two times with 500 mL of dichloromethane. The dichlorometane layers are combined and dried with anhydrous K₂CO₃. The solid salt is acquired by removing dichloromethane at room temperature and reduced pressure. The residue is then recrystallized from

ethyl acetate.

Porphyrin compounds were prepared by the standard pyrrole-aldehyde condensation reaction.[7] Specially pyrrole-deuterated iron(III) tetraarylporphyrins were prepared as previously described.[8] (F₂₀-TPP)Fe(III)Cl was purchased from Aldrich.

Proton and deuterium NMR spectra were recorded on a Bruker WM-360 FT spectrometer. Chemical shift values are reported with respect to internal tetramethylsilane and downfiled shifts are given positive sign. EPR spectra were recorded at X-band frequency with a Varian E-104A instrument. Solutions were approximately 3 mM in iron porphyrin complexes in toluene for measurement at 77 K. UV-Vis spectra were examined before and after NMR spectroscopic measurement to verify predominant solution species.

Results and Discussion

Addition of 1.0 equiv of Bu₄NBH₄ to a toluene solution of (TPP)Fe(III)Cl produced a high-spin (S=5/2) iron(III)porphyrin complex. In the deuterium NMR spectrum a pyrrole deuteron signal at 79.4 ppm for (d₈-TPP)Fe(III)Cl in toluene is converted to a pyrrole deuteron signal at 76.0 ppm at room temperature. This comound is so unstable that it may readily convert to the parent chloro compound.

$$(TPP)Fe(III)Cl + Bu_4NBH_4 \xrightarrow{\text{tol}} (TPP)Fe(III)(BH_4) + Bu_4NCl$$
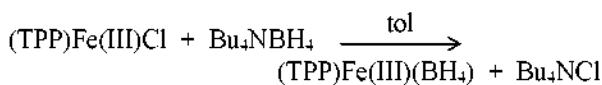
A benzene or toluene solvent is appropriate for this reaction. and solvent choice is critical in this reaction. No other solvents such as acetonitrile, dichloromethane. or THF, were suitable for generation of this complex. For example, in THF solvent. addition of Bu₄NBH₄ to (TPP)Fe(III)Cl produced TPPFe(II)(THF)₂ with a characteristic pyrrole resonance at 48.0 ppm. Even at low temperature reduction prevailed.

The ^2H NMR spectra were recorded from 205 K to 298 K. A plot of chemical shift *vs.* 1/T followed linearity and confirmed that the 76.0 ppm signal is for a single species and not a dynamically averaged resonance. The optical spectrum with an iron porphyrin concentration of 2.6×10^{-5} M in toluene solution at 25 °C is indicative of a high-spin iron(III) complex with bands at 416 and 508 nm. The toluene glass EPR spectrum collected at 77 K exhibits a signal at g = 5.68

which is indicative of a high-spin (S = 5/2, d^5) iron(III) porphyrin complex.

Reaction of Bu_4NBH_4 with the very electron-deficient $(F_{20}$-TPP)Fe(III)Cl is similar to reaction with (TPP)Fe(III)Cl. Addition of 1.0 equiv Bu_4NBH_4 to $(F_{20}$-TPP)Fe(III)Cl generated a very broad pyrrole proton signal at 71.0 ppm and new four resonances in the upfield region. these four upfield peaks can be attributable to paramagnetically shifted signals of the Bu_4N^- counter ion.

$$(F_{20}\text{-TPP})Fe(III)Cl \ + \ Bu_4NBH_4 \ \xrightarrow{\text{tol}} \ [(F_{20}\text{-TPP})Fe(III)(Cl)(BH_4)]^-[Bu_4N]^-$$
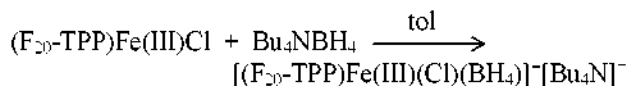
Based on this proton NMR evidence, the eletron-deficient $(F_{20}$-TPP)Fe(III)Cl can accomodate BH_4^- as a sixth ligand.[7-9] The proposition is supported by addition of a slight excess of Bu_4NBH_4 to $(F_{20}$-TPP)Fe(III)Cl(BH_4)^-$. The excess Bu_4NBH_4 produced $(F_{20}$-TPP)Fe(III)Cl^-$.[9] This six-coordination was also supported by the appearance of a precipitated salt. In the case of (TPP)Fe(III)BH_4, Bu_4NCl was precipitated, but not in the case of $[(F_{20}$-TPP)Fe(III)(Cl)(BH_4)]^-[Bu_4N]^+$.

The BD_4^- coordination is evident since when the BD_4^- ion was replaced with BH_4^-, a signal at 51 ppm disappeared. The bonding mode between iron and BD_4 was not clearly resolved due to broadness. However the intensity ratio (8 : 2) between the pyrrole deuteron and coordinated BD_4 signals in
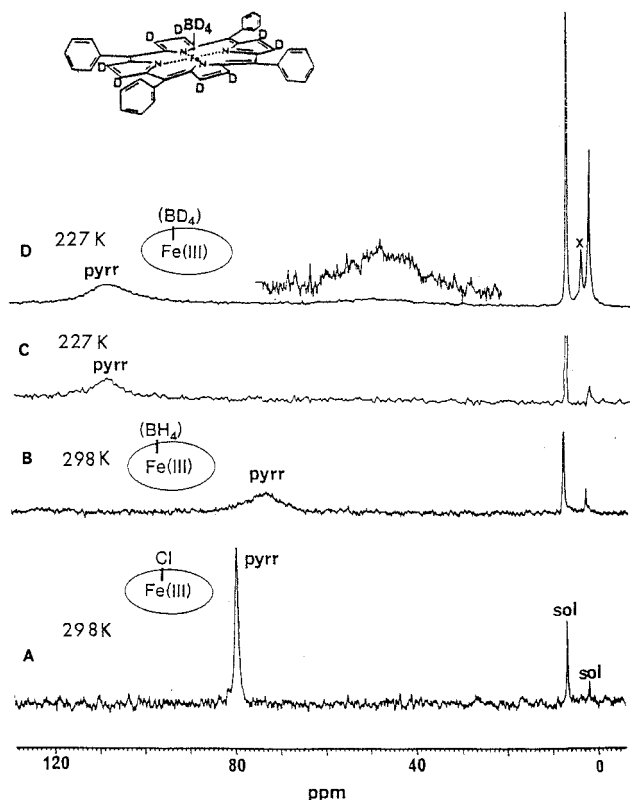

Figure 1. Deuterium NMR spectra for reaction of 3.0 mM (d_8-TPP)Fe(III)Cl with Bu_4NBH_4 in toluene solution (A) (d_8-TPP)Fe(III)Cl in toluene, (B) addition of 1.0 equiv. Bu_4NBH_4 at 298 K, (C) solution (B) at 227 K, and (D) use of 1.0 equiv. Bu_4NBD_4 and acquired at 227 K.
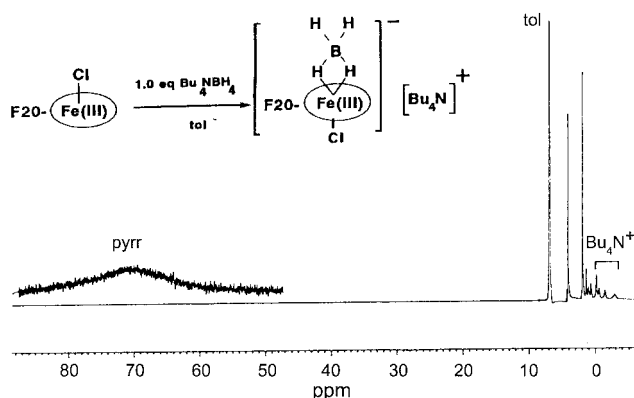

Figure 2. ^{1}H NMR spectrum for reaction of 4.0 mM $(F_{20}$-TPP)Fe(III)Cl with 1.0 equiv. of Bu_4NBH_4 in d_8-toluene solution at 298 K.

the (d_8-TPP)Fe(III)BD_4 complex indicated a possible bidentate coordination. The bridged deuteron signal will not be seen due to the large linewidth. The coordinated terminal deuteron signals of (d_8-TPP)Fe(III)BD_4 were presumably detected in the low temperature region (213 K to 241 K) in the deuterium NMR spectroscopy as shown in Figure 1.

The large pyrrole deuteron NMR linewidth (ca. 405 Hz) compared with (d_8-TPP)Fe(III)Cl (ca. 75 Hz) can be explained by a small zero-field splitting (ZFS).[8] A broad pyrrole resonance was observed for the bidentate peroxoiron (III) porphyrin anion complex, (TPP)Fe(III)O_2^-.[8] Coordination by peroxo ligand induces the samll ZFS associated with severe NMR line broadening. It is assumed that a coordinated BD_4 ligand undergoes fluxional behavior,[1] because a coordinated BD_4 signal is better resolved at lower temperature. while the pyrrole deuteron signal has no significant linewidth change.

The corresponding ^{1}H NMR spectrum (Figure 2) did not show a coordinated BH_4 signal even at the low temperature. In the limiting case of electron-nuclear dipolar relaxation the NMR linewidth is proportional to the square of the gyromagnetic ratio of the nucleus. Hence. the NMR linewidth for a proton signal can be as much as 42 times greater than that of the corresponding deuterium signal.

For classical organotransition metal chemistry. the BH_4^- ligation is almost always bidentate or tridentate[10-13] through bridging hydrogen atoms. It is reasoned that detection of a coordinated deuteron signal might be attributable to a slower fluxional behavior at low temperature.

Conclusions

The first NMR spectroscopic evidence of hydride-bonded porphyrin complexes of BH_4^- has been presented. Although the bonding configuration for the iron(III)BH_4 is not clear at present due to its extreme instability, the formation of monomeric iron(III)(BH_4) was evident by paramagnetic NMR results. The ligand underwent a fast fluxional behavior. This evidence could become a good initiation for search of noble hydride species in porphyrins.

Notes

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