Do sitting-atop metalloporphyrin complexes exist? Observation of N-H- -π bonding in arene solvates of a diprotonated porphyrin dication

Permalink
https://escholarship.org/uc/item/92r745zt

Journal
Inorganic Chemistry, 46(5)

ISSN
0020-1669

Authors
Gárate-Morales, JL
Tham, FS
Reed, CA

Publication Date
2007-03-05

DOI
10.1021/ic062213g

Peer reviewed
Do Sitting-Atop Metalloporphyrin Complexes Exist? Observation of N–H---π Bonding in Arene Solvates of a Diprotonated Porphyrin Dication

J. Luis Gárate-Morales, Fook S. Tham, and Christopher A. Reed*

Center for S and P Block Chemistry, Department of Chemistry, University of California, Riverside, California 92521-0403

Received November 20, 2006

The existence of sitting-atop metalloporphyrin complexes, the proposed intermediates in the metatation of free-base porphyrins, has been explored via the microscopic reverse reaction, i.e., protonation of metalloporphyrins with a strong acid. The reaction of M(Tp-TP) (M = Zn, Cu, Ni; Tp-TP = diamin of tetra-p-tolylporphyrin) with mesitylenium carborane salts produced only the demetalted porphyrin in its diprotonated form, [H$_4$Tp-TP$^2$](carborane)$^2$ (carborane = CH$_{11}$H$_5$Cl$_6^-$, CH$_{11}$H$_5$Br$_6^-$, CH$_{11}$Cl$_{11}^-$). In arene solvents, the H$_4$Tp-TP$^{2+}$ dication shows an unusually upfield shifted $^1$H NMR resonance at ca. -6 ppm, which X-ray crystallography reveals to arise from N–H---π hydrogen bonding of the acidic protons to arene solvent molecules.

The metalloporphyrin formation reaction is an important process related to the biosynthesis of heme. The mechanism by which a metal is inserted into a porphyrin has been extensively investigated via kinetic methods and a “sitting-atop” (SAT) reaction intermediate has been suggested by Fleisher and Wang.

Funahashi and co-workers have reported that long-lived SAT complexes can be observed and characterized spectroscopically when porphyrin free bases [H$_2$TPP, H$_2$T(p-CIP)P, H$_2$TMP, and H$_2$OEP] are treated with metal(II) triflates in aqueous acetonitrile (eq 1). However, Tsai et al., working on the same reaction but using a slightly different porphyrin (tetra-p-tolylporphyrin, H$_2$Tp-TP), in a less basic solvent (chloroform), were only able to observe metalated porphyrin and diprotonated free base (eq 2).

$$\text{H}_2(\text{Porph}) + \text{M}^{2+} \rightarrow \text{MH}_2(\text{Porph})^{2+}$$  \hspace{1cm} (1)

$$2\text{H}_2\text{Tp-TP} + \text{M}^{2+} \rightarrow \text{M(\text{Tp-TP})} + \text{H}_2\text{Tp-TP}^{2+}$$  \hspace{1cm} (2)

Metalloporphyrin and dication is a natural consequence of the liberation of 2 equiv of strong acid per 1 equiv of inserted metal. This suggests that Funahashi et al. might have misinterpreted mixtures of M(porph) and H$_4$(porph)$^{2+}$ as SAT complexes.

In an attempt to resolve this controversy, we decided to approach the SAT intermediate by investigating the microscopic reverse reaction, i.e., treating a metalloporphyrin with a strong acid. Demetatalation reactions are typically carried out with aqueous acid, which solvates M$^{2+}$ cations well, and to our knowledge, there are no reports of the observation of intermediates. We argued that the treatment of metalloporphyrins with anhydrous acids in low dielectric media might allow the observation of a SAT complex (or some other protonated metalloporphyrin) if the elimination of the metal salt was a high-energy process due to poor solvation of the metal ion. Carborane acids were chosen for this purpose because of their good solubility in low dielectric media and, more particularly, because of the nature of their conjugate base anions, CH$_{11}$R$_5$X$_4^-$ (R = H, Cl; X = Cl, Br). Carborane anions are large and very weakly nucleo-

* To whom correspondence should be addressed. E-mail: chris.reed@ucr.edu.


dichloromethane, or acetonitrile, the 1 H NMR spectrum of the reaction mixture showed a signal in the upfield region from the other 1 H NMR signals, the relative weighting was four solubility allowed reliable integration of this signal versus protons, consistent with the H 4 Tp-TP 2+ upfield signal (at 6.05 ppm) when solubility, dryness, and minimal basicity of the anion were optimized by use of the undecachlorocarborane anion, CHB 11 Cl 11− (Figure 1). This anion is known to be the weakest carborane anion base; its conjugate acid is the strongest known Brønsted acid.5b Because of poor solubility and the presence of unreacted starting material, it was not possible to obtain reliable integration of the −6.05 signal versus the other 1 H NMR signals. We entertained the possibility that the upfield signal arises from a SAT complex, but it turns out to be a “red herring”. As indicated by X-ray crystallography below, the origin of the upfield shift must be a ring-current effect of the arene solvent on the otherwise familiar H 4 Tp-TP 2+ dication.

From the reaction mixture of Zn(Tp-TP) and mesitylenium CHB 11 Cl 11− acid, we were able to grow two types of single crystals of the [H 4 Tp-TP][CHB 11 Cl 11−] 2 salt, one without solvate molecules and the other with two benzene solvate molecules. Evidently, as suggested by the 1 H NMR data, the relative weighting was four protons, consistent with the H 4 Tp-TP 2+ dication formulation. The chemical shift is somewhat dependent on the nature of the anion (Table 1), indicating ion-pairing effects. This is corroborated by X-ray crystallography (see below).

When the solvent was benzene or toluene, an additional signal was frequently observed. A color change to dark green is expected if a significant distortion of the planar ring of the porphyrin has occurred.7 It could arise from either a SAT complex or the H 4 Tp-TP 2+ dication.

The nature of the solvent is important. Using chloroform, dichloromethane, or acetonitrile, the 1 H NMR spectrum of the reaction mixture showed a signal in the upfield region (−3.96 to −4.45 ppm; Figure 1a), where the N−H protons of the H 4 Tp-TP 2+ dication are expected to resonate.8 When solubility allowed reliable integration of this signal versus the other 1 H NMR signals, the relative weighting was four protons, consistent with the H 4 Tp-TP 2+ dication formulation. The chemical shift is somewhat dependent on the nature of the anion (Table 1), indicating ion-pairing effects. This is corroborated by X-ray crystallography (see below).

When the solvent was benzene or toluene, an additional signal was seen in the range −4.88 to −6.05 ppm (Table 1). This unusually large upfield shift became essentially the only upfield signal (at −6.05 ppm) when solubility, dryness, and

### Table 1. Selected 1 H NMR Data

<table>
<thead>
<tr>
<th>compound</th>
<th>solvent</th>
<th>Hpyrrole</th>
<th>N−H</th>
</tr>
</thead>
<tbody>
<tr>
<td>H 4 Tp-TP</td>
<td>CDCl 3</td>
<td>8.87 (8H)</td>
<td>−2.75</td>
</tr>
<tr>
<td>ZnTp-TP</td>
<td>CDCl 3</td>
<td>8.98 (8H)</td>
<td>−4.10</td>
</tr>
<tr>
<td>[H 4 Tp-TP][CHB 11 H 5 Cl 6 ] 2</td>
<td>CDCl 3</td>
<td>8.46 (8H)</td>
<td>−3.96</td>
</tr>
<tr>
<td>[H 4 Tp-TP][CHB 11 Cl 11 ] 2</td>
<td>CDCl 3</td>
<td>9.06 (8H)</td>
<td>−4.45</td>
</tr>
<tr>
<td>[H 4 Tp-TP][CHB 11 H 5 Cl 6 ] 2 CD 2 C 6 H 6</td>
<td>CD 2 C 6 H 6</td>
<td>9.15 (8H)</td>
<td>−4.34 (4H)</td>
</tr>
<tr>
<td>[H 4 Tp-TP][CHB 11 H 5 Br 6 ] 2 CD 2 C 6 H 6</td>
<td>CD 2 C 6 H 6</td>
<td>9.16 (8H)</td>
<td>−4.15 (4H)</td>
</tr>
<tr>
<td>[H 4 Tp-TP][CHB 11 Cl 11 ] 2 CD 2 C 6 H 6</td>
<td>CD 2 C 6 H 6</td>
<td>9.05 (8H)</td>
<td>−5.17 (4H)</td>
</tr>
<tr>
<td>[H 4 Tp-TP][CHB 11 Cl 11 ] 2 CD 2 C 6 H 6</td>
<td>CD 2 C 6 H 6</td>
<td>9.06</td>
<td>−6.05</td>
</tr>
</tbody>
</table>

unsolvated form, benzene solvate molecules have displaced the carborane anions laterally such that the predominant hydrogen bonding of the acidic N–H protons is now with benzene rather than the anion. One N–H⋯Cl interaction with an anion remains (H⋯Cl = 3.36 and 3.58 Å), but it is very much weaker than those seen in the unsolvated form (H⋯Cl = 2.47–2.67 Å). The N–H⋯-π interactions with the two benzene molecules involve seven close C atom contacts with H⋯C distances in the range 2.53–3.12 Å. The N–H⋯C bond angles lie in the range 120–152°. These dimensions are similar to a growing class of X–H⋯-π hydrogen-bonding interactions observed in crystal structures.10,11 An analogous arene-solvated material is obtained when [H₄TP-TP][CHB₁₁Cl₁₁] is recrystallized from toluene. [H₄TP-TP]-[CHB₁₁Cl₁₁]·2toluene crystallizes in the same space group as the dibenzene solvate, and the molecular dimensions of the cations in the two structures are very similar (see the Supporting Information). Again, there is one weak ion-pairing interaction with the anion (NH⋯Cl = 3.26 and 3.62 Å) and seven close N–H⋯-π interactions with ring C atoms of toluene (NH⋯C = 2.57–3.05 Å).


With the reasonable assumption that the arene interaction seen in the crystal structures persists in an arene solution, an explanation is provided for the unusually upfield shifted N–H signals observed in the ¹H NMR spectrum of the H₄TP-TP⁺ cation. The ring-current effect from the π-bound arene moves the signal of the NH groups from their familiar position at ca. 4.2 ppm to the new position at ca. 6.0 ppm. This is conceptually related to the tri-π-benzene solvation of the H₂O⁺ ion, which experiences ca. 5 ppm upfield ¹H NMR shift in benzene relative to a non-arene solution because of OH⋯-π hydrogen bonding.11

The relative strength of the hydrogen-bonding interaction of the [H₄TP-TP]⁺ cation with anions or arenes is reflected in the υNH frequencies of its IR spectrum. As shown in Table 2, the highest υNH frequencies occur in the benzene solvate, suggesting a somewhat weaker overall interaction than that with a carborane anion. The increasing interaction ranking of anions is CHB₁₁Cl₁₁ < CHB₁₁H₃Cl₆ < CHB₁₁H₃Br₆. This explains why the arene-solvated crystals were obtained when the CHB₁₁Cl₁₁ anion was used. The basicity ranking of anions is the same as that deduced from contact ion pairs in trioctylammonium salts.5d

In summary, from the experimental evidence accumulated so far, we are unable to find evidence for a long-lived SAT complex. Rather, the competition between a metalloporphrin and its demetalated dication, H₂Porph²⁺, is fast on the synthetic time scale, even when conditions are chosen that might be expected to slow down the process. A potential candidate for a SAT complex, identified in the ¹H NMR spectrum by an unusually upfield shifted resonance for the N–H protons in arene solvents, is instead an arene solvate of the H₂Porph²⁺ dication with previously unobserved N–H⋯-π hydrogen bonding.

**Acknowledgment.** J.L.G.-M. thanks the UC-MEXUS-CONACYT program for a postdoctoral research fellowship. This work was supported by NIH Grant GM 23851.

**Supporting Information Available:** Synthetic details and crystallographic data including CIF files. This material is available free of charge via Internet at http://pubs.acs.org.

**Table 2.** Selected IR Data (KBr)

<table>
<thead>
<tr>
<th>Compound</th>
<th>υNH (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₄TP-TP][CHB₁₁Cl₁₁]·2C₆H₆</td>
<td>3384, 3365, 3334</td>
</tr>
<tr>
<td>[H₄TP-TP][CHB₁₁Cl₁₁]</td>
<td>3379, 3357, 3332</td>
</tr>
<tr>
<td>[H₄TP-TP][CHB₁₁H₃Cl₆]</td>
<td>3348 (br), 3290</td>
</tr>
<tr>
<td>[H₄TP-TP][CHB₁₁H₃Br₆]</td>
<td>3346, 3325, 3269</td>
</tr>
</tbody>
</table>

**Figure 3.** Portion of the crystal structure (50% thermal ellipsoids) of the dibenzene solvate [H₄TP-TP][CHB₁₁Cl₁₁]·2C₆H₆. Color code: green = Cl, brown = B, blue = N, black = C, white = H. The NH⋯-π and NH⋯-Cl hydrogen-bonding interactions are shown as dotted lines. For clarity, phenyl groups on the porphyrin and H atoms from the pyrrole and benzene rings are not shown.

Selected IR Data (KBr)