

## Do Sitting-Atop Metalloporphyrin Complexes Exist? Observation of N–H- $\pi$ Bonding in Arene Solvates of a Diprotonated Porphyrin Dication

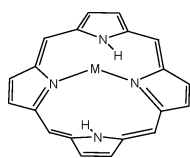
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The existence of sitting-atop metalloporphyrin complexes, the proposed intermediates in the metalation of free-base porphyrins, has been explored via the microscopic reverse reaction, i.e., protonation of metalloporphyrins with a strong acid. The reaction of M(Tp-TP) (M = Zn, Cu, Ni; Tp-TP = dianion of tetra-*p*-tolylporphyrin) with mesitylenium carborane salts produced only the demetalated porphyrin in its diprotonated form, [H<sub>4</sub>Tp-TP]-[carborane]<sub>2</sub> (carborane = CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub><sup>-</sup>, CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub><sup>-</sup>, CHB<sub>11</sub>Cl<sub>11</sub><sup>-</sup>). In arene solvents, the H<sub>4</sub>Tp-TP<sup>2+</sup> dication shows an unusually upfield shifted <sup>1</sup>H NMR resonance at ca. –6 ppm, which X-ray crystallography reveals to arise from N–H- $\pi$  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<sup>1</sup> and a “sitting-atop” (SAT) reaction intermediate has been suggested by Fleisher and Wang.<sup>2</sup>



Funahashi and co-workers<sup>3</sup> have reported that long-lived SAT complexes can be observed and characterized spectro-

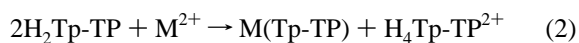
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 (2) Fleisher, E. B.; Wang, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 3498.  
 (3) (a) Inamo, M.; Kamiya, N.; Inada, Y.; Nomura, M.; Funahashi, S. *Inorg. Chem.* **2001**, *40*, 5636. (b) Inada, Y.; Nakamoto, Y.; Inamo, M.; Nomomura, M.; Funahashi, S. *Inorg. Chem.* **2000**, *39*, 4793. (c) Inada, Y.; Sugimoto, Y.; Itoh, Y.; Funahashi, S. *Inorg. Chem.* **1998**, *37*, 5519. The following abbreviations are used in this paper: H<sub>2</sub>TPP = 5,10,15,20-tetraphenylporphyrin, H<sub>2</sub>T(*p*-CIP)P = (4-chlorophenyl)-porphyrin, H<sub>2</sub>TMP = 5,10,15,20-tetramesitylporphyrin, H<sub>2</sub>OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin, and H<sub>2</sub>Tp-TP = *meso*-tetra-*p*-tolylporphyrin.

scopically when porphyrin free bases [H<sub>2</sub>TPP, H<sub>2</sub>T(*p*-CIP)P, H<sub>2</sub>TMP, and H<sub>2</sub>OEP] are treated with metal(II) triflates in aqueous acetonitrile (eq 1). However, Tsai et al.,<sup>4</sup> working



on the same reaction but using a slightly different porphyrin (tetra-*p*-tolylporphyrin, H<sub>2</sub>Tp-TP), in a less basic solvent (chloroform), were only able to observe metalated porphyrin and diprotonated free base (eq 2). The 1:1 mixture of

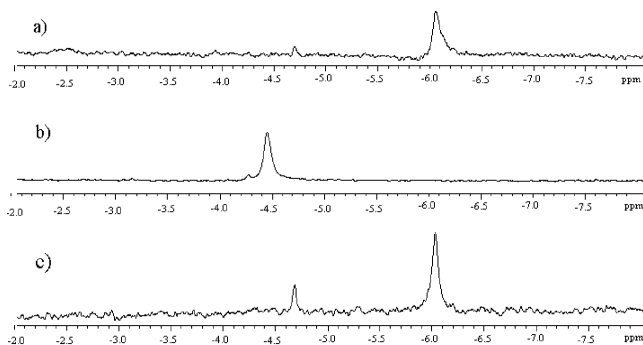


metalloporphyrin and dication is a natural consequence of the liberation of 2 equiv of strong acid per 1 equiv of inserted metal. This suggests that Funahashi et al.<sup>3</sup> might have misinterpreted mixtures of M(porph) and H<sub>4</sub>(porph)<sup>+2</sup> as SAT complexes.

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. Demetalation reactions are typically carried out with aqueous acid, which solvates M<sup>2+</sup> 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<sup>5</sup> 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, CHB<sub>11</sub>R<sub>5</sub>X<sub>6</sub><sup>-</sup> (R = H, Cl; X = Cl, Br). Carborane anions are large and very weakly nucleo-

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**Figure 1.**  $^1\text{H}$  NMR spectrum in the upfield region of  $\text{H}_4\text{Tp-TP}^{2+}$  in (a) benzene- $d_6$ , (b) chloroform- $d_1$ , and (c) a benzene- $d_6$ /chloroform- $d_1$  mixture.

**Table 1.** Selected  $^1\text{H}$  NMR Data

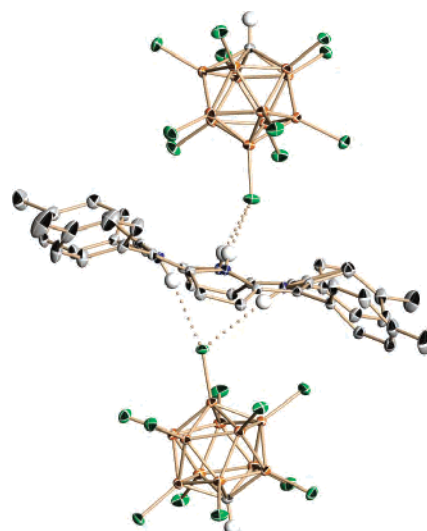
compound	solvent	$\text{H}_{\text{pyrrole}}$	N–H
$\text{H}_2\text{Tp-TP}$	$\text{CDCl}_3$	8.87 (8H)	–2.75
$\text{ZnTp-TP}$	$\text{CDCl}_3$	8.98 (8H)	
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Br}_6]_2$	$\text{CDCl}_3$	8.87 (8H)	–4.10
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]_2$	$\text{CDCl}_3$	8.46 (8H)	–3.96
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2$	$\text{CDCl}_3$	9.06 (8H)	–4.45
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Br}_6]_2$	$\text{C}_6\text{D}_6$	9.15 (8H)	–4.34 (4H)
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Br}_6]_2 \cdot 2\text{C}_6\text{H}_6$		9.05 (8H)	–4.88 (4H)
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]_2$	$\text{C}_6\text{D}_6$	9.16 (8H)	–4.15 (4H)
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]_2 \cdot 2\text{C}_6\text{H}_6$		9.05 (8H)	–5.17 (4H)
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2 \cdot 2\text{C}_6\text{H}_6$	$\text{C}_6\text{D}_6$	9.06	–6.05

philic. Their active participation in the extraction of a metal from a metalloporphyrin is anticipated to be low, potentially adding a kinetic barrier to the collapse of the putative SAT complex.

Treatment of solutions of  $\text{M}(\text{Tp-TP})$  ( $\text{M} = \text{Ni}, \text{Cu}, \text{Zn}$ ) with a  $[\text{H}(\text{mesitylene})][\text{carborane}]$  salt, a convenient source of carborane acid,<sup>6</sup> caused a color change from purple to dark green. Depending upon solubility, a dark-green precipitate was frequently observed. A color change to dark green is expected if a significant distortion of the planar ring of the porphyrin has occurred.<sup>7</sup> It could arise from either a SAT complex or the  $\text{H}_4\text{Tp-TP}^{2+}$  dication.

The nature of the solvent is important. Using chloroform, dichloromethane, or acetonitrile, the  $^1\text{H}$  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  $\text{H}_4\text{Tp-TP}^{2+}$  dication are expected to resonate.<sup>8</sup> When solubility allowed reliable integration of this signal versus the other  $^1\text{H}$  NMR signals, the relative weighting was four protons, consistent with the  $\text{H}_4\text{Tp-TP}^{2+}$  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



**Figure 2.** Crystal structure (50% thermal ellipsoids) of unsolvated  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2$ . Color code: green = Cl, brown = B, blue = N, black = C, white = H. The NH...Cl hydrogen-bonding interactions in the ion pair are shown as dotted lines. For clarity, H atoms from the phenyl and pyrrole groups are not shown.

minimal basicity of the anion were optimized by use of the undecachlorocarborane anion,  $\text{CHB}_{11}\text{Cl}_{11}^-$  (Figure 1). This anion is known to be the weakest carborane anion base; its conjugate acid is the strongest known Brønsted acid.<sup>5b</sup> 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  $^1\text{H}$  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  $\text{H}_4\text{Tp-TP}^{2+}$  dication.

From the reaction mixture of  $\text{Zn}(\text{Tp-TP})$  and mesitylenium  $\text{CHB}_{11}\text{Cl}_{11}^-$  acid, we were able to grow two types of single crystals of the  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2$  salt, one without solvate molecules and the other with two benzene solvate molecules. Evidently, as suggested by the  $^1\text{H}$  NMR data, there is a competition between the anion and the arene solvent for interaction with the porphyrin dication. Arene solvation competes favorably with ion pairing with the undecachlorocarborane anion because it is the least basic of those used.

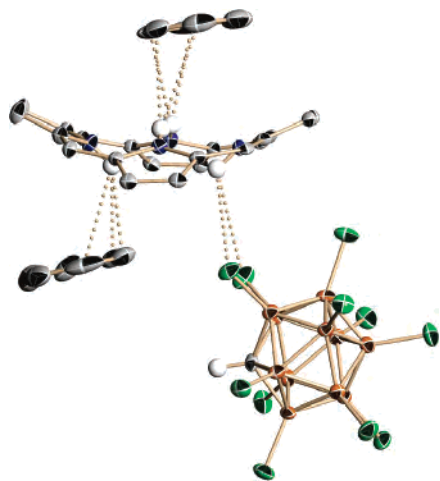
The crystal structure of the unsolvated form of  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2$  is shown in Figure 2. One Cl substituent of each anion acts as hydrogen-bond acceptor for two acidic protons of the porphyrin. The H...Cl distances lie in the range 2.47–2.67 Å. This ion pairing explains the dependence of the upfield  $^1\text{H}$  NMR signal on the nature of the carborane anion (Table 1). The B–Cl bond lengths of the hydrogen-bonded Cl atoms [1.786(2) Å] are elongated relative to the range of the other 10 B–Cl bonds [1.758(2)–1.776(2) Å]. The structure of the  $\text{H}_4\text{Tp-TP}^{2+}$  dication is highly distorted from planarity, similar to that seen with other counterions.<sup>4,9</sup>

The crystal structure of the dibenzene solvate  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2 \cdot 2\text{C}_6\text{H}_6$  is shown in Figure 3. Compared to the

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**Figure 3.** Portion of the crystal structure (50% thermal ellipsoids) of the dibenzene solvate  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2 \cdot 2\text{C}_6\text{H}_6$ . Color code: green = Cl, brown = B, blue = N, black = C, white = H. The 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.

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 ( $\text{H}\cdots\text{Cl} = 3.36$  and  $3.58 \text{ \AA}$ ), but it is very much weaker than those seen in the unsolvated form ( $\text{H}\cdots\text{Cl} = 2.47$ – $2.67 \text{ \AA}$ ). The N–H... $\pi$  interactions with the two benzene molecules involve seven close C atom contacts with  $\text{H}\cdots\text{C}$  distances in the range  $2.53$ – $3.12 \text{ \AA}$ . The N–H...C bond angles lie in the range  $120$ – $152^\circ$ . These dimensions are similar to a growing class of X–H... $\pi$  hydrogen-bonding interactions observed in crystal structures.<sup>10,11</sup> An analogous arene-solvated material is obtained when  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2$  is recrystallized from toluene.  $[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2 \cdot 2\text{toluene}$  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 ( $\text{NH}\cdots\text{Cl} = 3.26$  and  $3.62 \text{ \AA}$ ) and seven close N–H... $\pi$  interactions with ring C atoms of toluene ( $\text{NH}\cdots\text{C} = 2.57$ – $3.05 \text{ \AA}$ ).

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

compound	$\nu_{\text{NH}}$ ( $\text{cm}^{-1}$ )
$[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2 \cdot 2\text{C}_6\text{H}_6$	3384, 3365, 3334
$[\text{H}_4\text{Tp-TP}][[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{Cl}_{11}]_2]$	3379, 3357, 3332
$[\text{H}_4\text{Tp-TP}][[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Cl}_6]_2]$	3348 (br), 3290
$[\text{H}_4\text{Tp-TP}][[\text{H}_4\text{Tp-TP}][\text{CHB}_{11}\text{H}_5\text{Br}_6]_2]$	3346, 3325, 3269

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  $^1\text{H}$  NMR spectrum of the  $[\text{H}_4\text{Tp-TP}]^{2+}$  cation. The ring-current effect from the  $\pi$ -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- $\pi$ -benzene solvation of the  $\text{H}_3\text{O}^+$  ion, which experiences ca. 5 ppm upfield  $^1\text{H}$  NMR shift in benzene relative to a non-arene solution because of OH... $\pi$  hydrogen bonding.<sup>11</sup>

The relative strength of the hydrogen-bonding interaction of the  $[\text{H}_4\text{Tp-TP}]^{2+}$  cation with arenes or anions is reflected in the  $\nu_{\text{NH}}$  frequencies of its IR spectrum. As shown in Table 2, the highest  $\nu_{\text{NH}}$  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  $\text{CHB}_{11}\text{Cl}_{11}^- < \text{CHB}_{11}\text{H}_5\text{Cl}_6^- < \text{CHB}_{11}\text{H}_5\text{Br}_6^-$ . This explains why the arene-solvated crystals were obtained when the  $\text{CHB}_{11}\text{Cl}_{11}^-$  anion was used. The basicity ranking of anions is the same as that deduced from contact ion pairs in trioctylammonium salts.<sup>5d</sup>

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 metalloporphyrin and its demetalated dication,  $\text{H}_4\text{Porph}^{2+}$ , 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  $^1\text{H}$  NMR spectrum by an unusually upfield shifted resonance for the N–H protons in arene solvents, is instead an arene solvate of the  $\text{H}_4\text{Porph}^{2+}$  dication with previously unobserved N–H... $\pi$  hydrogen bonding.

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**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>.

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