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The Doubly Oxidized, Antiaromatic Tetraphenylporphyrin Complex $[Li(TPP)][BF_4]$

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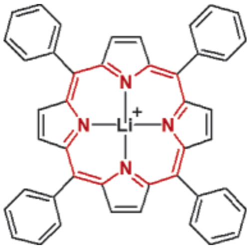
ABSTRACT



Oxidation of dilithium tetraphenylporphyrin, $Li_2(TPP)$, yields the doubly oxidized porphyrin complex $[Li(TPP)][BF_4]$. Free TPP appears to be unstable. The crystal structure of $[Li(TPP)][BF_4]$ reveals that the 16-atom C–N inner ring of the porphyrin consists of alternating single and double bonds. NMR spectroscopy and nucleus-independent chemical shift (NICS) calculations, in addition to the distortion from planarity observed in the crystal structure, indicate that the 16 π-electron inner C–N ring of the porphyrin is antiaromatic.

In the vast majority of known porphyrin complexes the oxidation state of the porphyrin ring system is 2−. We recently reported the first crystallographic characterization of a porphyrin complex with a ring system in the 3− oxidation state, the aluminum tetraphenylporphyrin radical, $Al(TPP)(THF)_2$.[1] In another recent communication we described the antiaromatic $Si(TPP)(THF)_2$, a porphyrin complex with a ring system in the 4− oxidation state.[2] The one reported example of a neutral porphyrin complex with a ring system in the 1− oxidation state is Li(TPP),[3] and there are several examples of porphyrin radical cations with ring systems in the 1− oxidation state.[4] The existence of stable porphyrin complexes with ring systems in the 4−, 3−, 2−, and 1− oxidation states led us to explore the possibility of isolating a porphyrin with a ring system in the zero oxidation state. We were encouraged by the fact that many porphyrin complexes can be reversibly oxidized by two electrons in cyclic voltammetry experiments.[5] Our interest has been in neutrally charged, oxidized or reduced molecules as isostructural dopants for molecular semiconductors,[6] and in the case of tetraphenylporphyrin the doubly oxidized, neutral species would be simply "TPP", which contains no central metal atom or hydrogens.

Li(TPP) was synthesized by the oxidation of $Li_2(TPP)$ with ferrocenium hexafluorophosphate.[3] Cyclic voltammetry of Li(TPP) in CH_2Cl_2 showed that it is reversibly oxidized at

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+0.12 V vs ferrocene$^{0/+}$, indicating that oxidation of the ring system to the zero oxidation state is possible but requires an oxidizing agent stronger than ferrocenium. Oxidation of Li(TPP) with thianthrenium tetrafluoroborate ($Thn^+BF_4^-$) in CH_2Cl_2 did not produce free TPP, but instead yielded a complex that spectroscopic evidence indicated was [Li(TPP)]-[BF_4]. In [Li(TPP)][BF_4] the porphyrin ring is in the desired zero oxidation state, but TPP is acting as a neutral complexing ligand for Li^+. We attempted to remove the Li^+ cation by treating [Li(TPP)][BF_4] with $NBu_4^+Cl^-$ in CH_2Cl_2, but no free TPP could be isolated. The cation K^+ is significantly larger than Li^+, so while Li typically sits in the N_4 plane in porphyrin[7] and phthalocyanine[8] complexes, K^+ sits far outside the N_4 plane.[7,9] We therefore thought that oxidation of K_2(TPP) might yield free TPP. Oxidation of K_2(TPP) with 2 equiv of $Thn^+BF_4^-$ in CH_2Cl_2 yielded a product mixture that contained some doubly oxidized porphyrin species (as indicated by ^{1}H NMR), but TPP could not be isolated from this mixture. Similar reactions in 1,2-dichlorobenzene, fluorobenzene, and acetonitrile did not yield TPP. We concluded that TPP is probably not stable as a free molecule but is stabilized when coordinated to Li^+.

When we had reached this point in our study, the first isolation of doubly oxidized porphyrins, the oxidized forms of octaethyltetraphenylporphyrin (OETPP) and octaisobutyltetraphenylporphyrin were reported.[10] OETPP was synthesized unintentionally by the reaction of Li_2(OETPP) and $SOCl_2$. (We therefore carried out the reaction of Li_2(TPP) and $SOCl_2$, but it did not yield TPP.) It appears that the steric protection of the eight alkyl groups on the β-carbons of these oxidized porphyrins stabilizes them enough for isolation, although OETPP reportedly slowly decomposes in solution at room temperature.

Because it was not possible to isolate free TPP, we continued our study on its stabilized form in [Li(TPP)][BF_4]. [Li(TPP)][BF_4] was most efficiently synthesized by the reaction of $Li_2(TPP)(OEt_2)_2$[11] with 2 equiv of $Thn^+BF_4^-$ in CH_2Cl_2. The orange-brown solution was filtered to remove 1 equiv of $LiBF_4$. The product was crystallized by the addition of toluene and isolated by filtration. After remaining under vacuum for 1 h, orange-brown [Li(TPP)][BF_4]·1.5-(toluene) was collected in 84% yield. The compound is stable at room temperature in the solid state and in CH_2Cl_2 solution in the absence of water, with which it reacts slowly. [Li(TPP)][BF_4] does not react with O_2. It slowly decomposes in CH_3CN to yield the Li(TPP) radical.

Crystals suitable for X-ray diffraction were grown by heating a solution of [Li(TPP)][BF_4] in CH_2Cl_2/heptane and slowly cooling to room temperature. An ORTEP representation of the structure of [Li(TPP)][BF_4] in crystals of [Li(TPP)][BF_4]·CH_2Cl_2 is given in Figure 1. The lithium cation is displaced toward the BF_4^- anion by 0.440 Å from the mean plane of the four nitrogen atoms. The ring system is moderately distorted from planarity by both a ruffle and a saddle distortion.[12] OETPP exhibits the same combination of ruffle and saddle distortions,[10] but its deviation from planarity is significantly larger than that of [Li(TPP)][BF_4].

Figure 1. Solid-state structure of [Li(TPP)][BF_4].

Figure 2 depicts the valence-bond structure that best represents the bonding in [Li(TPP)][BF_4], with each bond labeled with its appropriate bond length from the crystal structure. Also shown in Figure 2 are the bond lengths calculated for Li(porphine)$^+$ [Li(TPP)$^+$ with the phenyl groups replaced by hydrogen atoms] in a density functional theory (DFT) calculation (Gaussian 03,[13] B3LYP/6-31G*). The calculated structure for Li(porphine)$^+$ is perfectly planar,

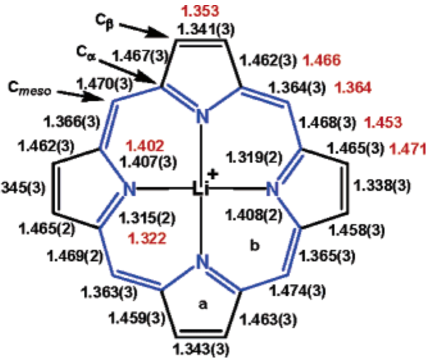

Figure 2. Valence-bond structure of Li(TPP)$^+$ with bond distances (Å) from the crystal structure of [Li(TPP)][BF_4] (black) and calculated (B3LYP/6-31G*) for Li(porphine)$^+$ (red). C−C distances are outside of the ring, and C−N distances are inside the ring. The letters "a" and "b" indicate where NICS calculations were performed. The blue outline indicates the 16 π-electron system.

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in constrast to the observed crystal structure of Li(TPP)$^+$. Nevertheless, the calculated bond lengths agree quite well with those observed in the crystal structure. The C$-$C and C$-$N bond lengths clearly correspond to those expected from the most reasonable valence-bond depiction of TPP, and neutral TPP is simply acting as a donor ligand to the Li$^+$ cation. The doubly oxidized porphyrin OETPP has similar C$-$C and C$-$N bond lengths throughout its porphine core.[10]

The aromaticity of a normal-valent porphyrin is generally understood to be a consequence of an 18 π-electron circuit that is present in its ring system. The doubly oxidized Li(TPP)$^+$ would therefore be expected to have an antiaromatic 16 π-electron circuit, and exactly such a circuit is evident in Li(TPP)$^+$—it is highlighted in blue in Figure 2. Evidence from ^{1}H NMR and calculated nucleus-independent chemical shifts (NICS)[14] both agree with the picture of an antiaromatic 16-membered C$-$N inner ring with four appended ethene groups. The ^{1}H NMR spectrum of [Li(TPP)]-[BF$_4$] in CD$_2$Cl$_2$ contains a singlet due to the C$_\beta$ protons (see Figure 2 for atom-type labels) at 5.94 ppm (a chemical shift typical of alkene protons), far upfield from the typical resonance of about 9 ppm for the C$_\beta$ protons of an aromatic porphyrin. NICS values were calculated (Gaussian 03, B3LYP/6-31G*) for Li(porphine)$^+$ at the centroid of a pyrrole ring (labeled “a” in Figure 2) and at the centroid of two C$-$N bonds (labeled “b” in Figure 2). The NICS value at “a” is -0.6 and that at “b” is $+36.5$, indicating a strong paratropic ring current along the outlined 16-atom circuit with the appended ethene groups excluded. Paratropic ring currents are characteristic of antiaromatic systems,[15] as opposed to the diatropic ring currents of aromatic molecules. An optimized structure of neutral “porphine” (TPP with the phenyl groups replaced by hydrogen atoms) was calculated (B3LYP/6-31G*), and in contrast to the planar structure of Li(porphine)$^+$ it is moderately saddled and slightly ruffled. NICS values calculated at the center of the ring system of porphine and at positions “a” and “b” (analogous to those in Figure 2) were $+13.5$, -4.8, and $+20.2$ ppm, respectively. The structure of porphine was minimized with an enforced planar (C_{4h}) geometry, and the calculated NICS values at the center, “a”, and “b” were $+20.0$, -6.8, and $+30.4$, respectively. All of those values are consistent with a paratropic ring current in the central 16-atom C$-$N circuit of porphine. The lower NICS value at “b” in the saddled geometry of porphine (relative to either planar porphine or Li(porphine)$^+$) indicates that Li$^+$ increases the paratropic ring current, at least in part, by maintaining planarity in the ring system. NICS calculations in the vicinity of a bare Li$^+$ cation show that it has negligible influence on NICS values.

Many porhyrin radical cations, in which the oxidation state of the ring system is 1$-$, undergo a distortion that is often described as a bond-length alternation along the 16-membered C$-$N inner ring.[4] The distortion is the same as that observed in Li(TPP)$^+$, except that the magnitude of the distortions in the radical cations is smaller than that in Li(TPP)$^+$, and is at most half of that observed in Li(TPP)$^+$. A normal-valent porphyrin has nearly degenerate a$_{1u}$ and a$_{2u}$ HOMOs, and the bond-length changes in the radical cations are due to a pseudo-Jahn$-$Teller distortion caused by the unequal occupancy of the (former) a$_{1u}$ and a$_{2u}$ molecular orbitals.[4] The bond-length alternation in Li(TPP)$^+$ could be considered to be a consequence of a similar pseudo-Jahn$-$Teller distortion, but of a magnitude twice as large as that in the porphyrin radical cations because two electrons have been removed instead of one. The calculated HOMO of C_{4h} Li(porphine)$^+$ (Figure 3) has the same a$_u$ symmetry as the SOMO of the porphyrin radical cations.[4] The image of the HOMO of Li(porphine)$^+$ in Figure 3 is in the same orientation as the valence-bond structure of Figure 2, and the alternating bonding and antibonding π-interactions around the 16-membered inner ring further clarify the cause of the bond-length alternation. An alternative explanation of the bond-length alternation in Li(TPP)$^+$ is simply that it adopts the valence-bond structure of Figure 2. The situation is quite similar to that in the singly reduced Al(TPP)[1] and the doubly reduced Si(TPP),[2] which both have alternating lengthened and shortened C$-$C bonds along the 20-atom periphery of their porphine core. The bond-length changes in Al(TPP) are due to a Jahn$-$Teller distortion caused by the single electron in one of its formerly degenerate e$_g$ LUMOs. The distortion in Si(TPP) is approximately twice as large, and can be viewed either as a larger Jahn$-$Teller distortion (caused by two electrons instead of one) or simply as Si(TPP) adopting a new valence-bond structure.

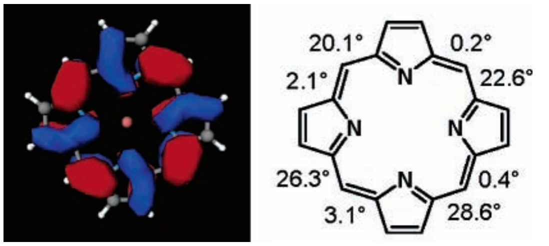

Figure 3. The HOMO of Li(porphine)$^+$ (left) and N$-$C$_\alpha$$-C_{meso}$$-C_\alpha$ and C$_\alpha$$-C_{meso}$$-C_\alpha$$-$N dihedral angles (right).

The deviations from planarity in the porphine core of Li(TPP)$^+$ can be understood in relation to its a$_u$ HOMO, and those deviations support the assertion that the 16-atom inner ring is antiaromatic. For each pyrrole ring, the five atoms of its ring and the two C$_{meso}$ to which it is attached are very nearly coplanar. However, the combined ruffling and saddling of Li(TPP)$^+$ lead to the N$-$C$_\alpha$$-C_{meso}$$-C_\alpha$ and C$_\alpha$$-C_{meso}$$-C_\alpha$$-$N dihedral angles indicated in Figure 3. The average dihedral angle across a C$-$C double bond (where there is a π-bonding interaction in the a$_u$ HOMO) is 1.5° and that across a C$-$C single bond (where there is a π-antibonding interaction in the a$_u$ HOMO) is 24.4°. In a normal conjugated system such as 1,3-butadiene, which is neither aromatic nor antiaromatic, the lowest energy conformation is planar s-trans,[16] which maximizes the interaction

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of the π-orbitals across the single bond. In contrast, Li(TPP)$^+$ is clearly distorting from planarity to minimize the π-antibonding interactions of the HOMO across the C−C single bonds, indicating that the 16-atom inner ring is antiaromatic, rather than simply conjugated. It is unlikely that the Li$^+$ is contributing to the distortion from planarity because the ionic radius of Li$^+$ is appropriate for a planar porphyrin ring—both aromatic Li(porphyrin)$^-$ anions[7] and the Li(TPP) radical[3] are planar. In fact, the Li$^+$ of Li(TPP)$^+$ may be limiting the porphyrin's distortion from planarity and stabilizing it in that way.

The valence-bond picture of Li(TPP)$^+$ indicates that it has two inequivalent sets of C_α, two inequivalent sets of C_β, and two inequivalent sets of hydrogens bound to the C_β atoms. The calculated [B3LYP/6-31G*, Li(porphine)$^+$ model] chemical shift difference between those two types of C_α is 14.3 ppm, that between the two types of C_β is 7.32 ppm, and that between the two types of C_β hydrogens is 0.35 ppm. However, room temperature ^{1}H and ^{13}C NMR spectra contain only one resonance for each of those types of nuclei. The averaging of the NMR resonances is due to a very fast automerization that interconverts the double and single bonds in the 16-atom C−N inner ring of Li(TPP)$^+$. Even when a solution of [Li(TPP)][BF$_4$] in a 3:1 mixture of $CD_2Cl_2/CDCl_3$ was cooled to −100 °C the resonances were still averaged. This rapid interconversion at −100 °C is perhaps not surprising in light of the fact that cyclobutadiene undergoes a similar automerization quickly at 25 K.[17] Nevertheless, the interconversion is clearly stopped in crystals of [Li(TPP)][BF$_4$]·CH_2Cl_2 at 120 K, the temperature at which the crystal structure was determined.

The UV−vis spectrum of [Li(TPP)][BF$_4$] in CH_2Cl_2 consists of two high-absorptivity bands at 332 and 394 nm and a broad, lower intensity shoulder that extends to about 575 nm (see the Supporting Information). The spectrum is similar to that of OETPP, with the two major absorptions of OETPP blue-shifted to 275 and 339 nm.[10] The blue shift of the OETPP absorptions is due to its greater distortion from planarity (the average of its dihedral angles of the type shown in Figure 3 are 10.7° and 54.0°). Interestingly, that is the opposite of the effect observed in normal-valent aromatic porphyrins, where distortions from planarity cause a red shift of the absorption bands. The red shift in distorted normal-valent porphyrins is due mainly to a rise in the HOMO energy caused by the distortion.[18] In the doubly oxidized porphyrins, distortions from planarity (of the type observed for the three known compounds) will cause a lowering of the HOMO energy as it decreases the π-antibonding interactions of the HOMO (see Figure 3). Hence the more-distorted OETPP has a UV−vis spectrum that is blue-shifted relative to Li(TPP)$^+$.

[Li(TPP)][BF$_4$] is an oxidizing agent and undergoes a variety of chemical reactions in which TPP oxidizes a metal and the LiBF$_4$ is replaced by the oxidized metal ion. The yields are essentially quantitative and the reaction rates appear to be limited mainly by the surface area of the solid metals available for reaction. For example, the reaction of [Li(TPP)][BF$_4$] and copper powder in THF at 22 °C to form CuTPP is complete in an hour, while the reaction with finer Zn dust to form ZnTPP is complete in 10 min. Similarly, the reaction of [Li(TPP)][BF$_4$] and Mg turnings in THF yields MgTPP after a few hours. The reaction of [Li(TPP)][BF$_4$] with SnCl$_2$ yields Sn(TPP)Cl$_2$, oxidizing the Sn(II) to Sn(IV). Finally, the reaction of [Li(TPP)][BF$_4$] and hydroquinone yields H$_2$TPP and benzoquinone.

In summary, we have isolated the doubly oxidized porphyrin complex [Li(TPP)][BF$_4$], which is TPP stabilized by coordination to LiBF$_4$. It was not possible to isolate free TPP, but analogous oxidized porphyrins with eight alkyl substituents on the β-carbons are stable enough to be isolated.[10] The best description of the electronic structure of Li(TPP)$^+$ is an antiaromatic 16 π-electron core with four appended ethene groups. [Li(TPP)][BF$_4$] acts as an oxidizing agent in reactions with elemental metals and compounds to yield metalloporphyrins.

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Supporting Information Available: Experimental procedures of all synthesized compounds, including their characterization and crystalligraphic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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