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Lithium Complexes of N-Confused Porphyrin

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Presented herein are the first lithium complexes of the porphyrin isomer N-confused porphyrin and its 21-N-methylated variant. In both cases, the macrocycle acts as a monoanionic ligand, and the internal C−H bond is retained upon metalation. In the presence the coordinating solvent tetrahydrofuran, pseudo-five-coordinate complexes are generated; in the absence of solvent, the axial positions remain vacant.

The metal chemistry of N-confused porphyrin, also known as 2-aza-21-carbaporphyrin and inverted porphyrin, continues to grow.[1] Over the past 15 years, the metal complexes of N-confused porphyrin have been generated using main-group elements,[2] lanthanides,[3] and early-, middle-, and late-transition-metal ions.[1,4] Compared to normal porphyrins, the metal complexes of N-confused porphyrin exhibit an increased diversity in metal binding structures, charges (ranging from 1− to 3−), and highly variable UV−visible spectra. In this report, we extend the chemistry of N-confused porphyrin to the s-block elements with the synthesis and characterization of the first lithium complexes of this macrocycle. The lithium complexes of both unmodified N-confused porphyrin (**1**) and externally N-methylated N-confused porphyrin (**2**) are presented. Figure 1 shows the general reaction schemes by which lithium can be inserted into these rings. In both cases, the internal C−H bonds are retained and the macrocycles act as monoanions, in contrast to the lithium complexes of normal porphyrins.

Previously, we have reported that the lithium bis(trimethylsilyl)amide reagent readily inserts the cation into hemiporphyrazines,[5] which are isoindoline-substituted phthalocyanine analogues.[6] Similarly, exposure of free-base N-confused porphyrin to this lithium amide with heating results in readily observable changes to the UV−visible spectra of toluene, toluene/tetrahydrofuran (THF), and toluene/pyridine solutions of **1**. The spectrum of such a reaction in toluene/THF can be seen in Figure 2. The Soret band is red-shifted from 443 to 468 nm, as is the lowest-energy Q band, which appears at 739 nm. Previous studies of the deprotonation chemistry of N-confused porphyrins have observed similar shifts to the red in their UV−visible spectra.[7]

A bulk solid product of a lithium adduct of N-confused porphyrin can be made by refluxing the free-base macrocycle and excess lithium bis(trimethylsilyl)amide in toluene under dry anaerobic conditions for 4 h (Figure 1). The spectrum of this compound in solution is identical with that seen in Figure 2. Upon recrystallization of the initial metalation product by diffusing hexane, we were able to grow crystals suitable for X-ray structure elucidation.[8] The structure of Li(NCPP) (compound **Li1**) is shown in Figure 3. The alkali metal adopts an unusual coordination environment, unlike that observed in typical tetrahedral Li^+ cations. The metal ion adopts a pseudo-square-planar geometry, where the three internal nitrogen atoms of the N-confused porphyrin are bound to the lithium. The internal carbon position remains protonated, forming an agostic-like interaction with the

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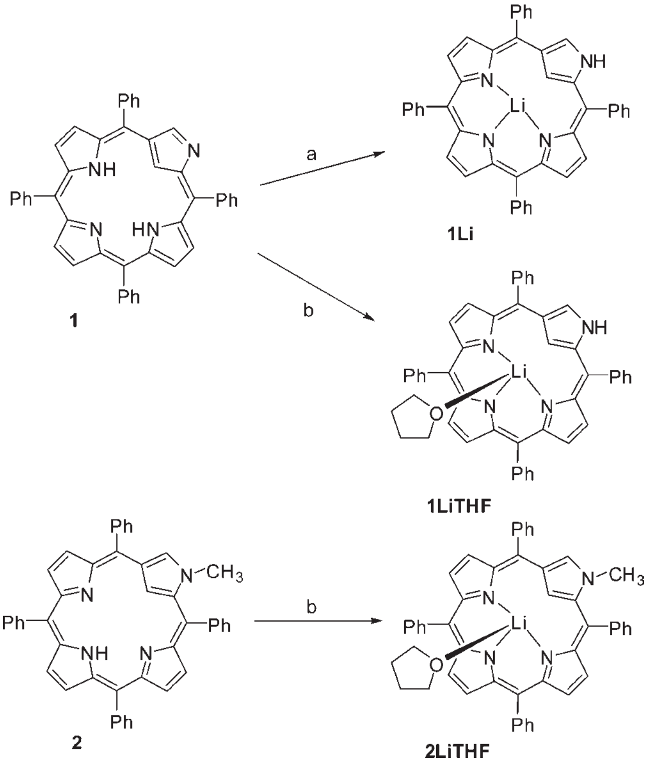

Figure 1. Insertion of lithium into N-confused porphyrin: (a) lithium bis(trimethylsilyl)amide in refluxing anhydrous toluene, 4 h; (b) lithium bis(trimethylsilyl)amide in refluxing toluene, followed by recrystallization from anhydrous THF, 4 h.

metal center. The Li−N bond opposite that of the inverted pyrrole is appreciably shorter [1.916(6) Å] than those immediately adjacent to the internal carbon position [2.067(6) and 2.085(6) Å]. The Li−C distance is 2.363(6) Å, which is slightly longer than a typical Li−C monomeric organometallic σ bond but typical for aggregates.[9]

The Li−C distance is also shorter than similar interactions observed in carbahemiporphyrazines, phthalocyanine analogues with carbon atoms at internal positions.[5] The inverted pyrrole ring is tilted away from the plane of the macrocycle by ~38° versus the plane defined by the three internal nitrogen atoms. As a result, in compound **1Li**, the lithium ion lies close to the plane of the three internal nitrogen atoms displaced by only ~0.20 Å. The tilt of the inverted pyrrole is less than that observed in other metal complexes of N-confused porphyrins. This factor, plus the presence of a proton on the external pyrrole nitrogen position (observable in the ^{1}H NMR spectrum at 9.06 ppm), results in the observed lack of dimerization, which has been seen in a number of metal complexes of N-confused porphyrin.[1,4] The internal C−H hydrogen atom appears at the expected −4.88 ppm.

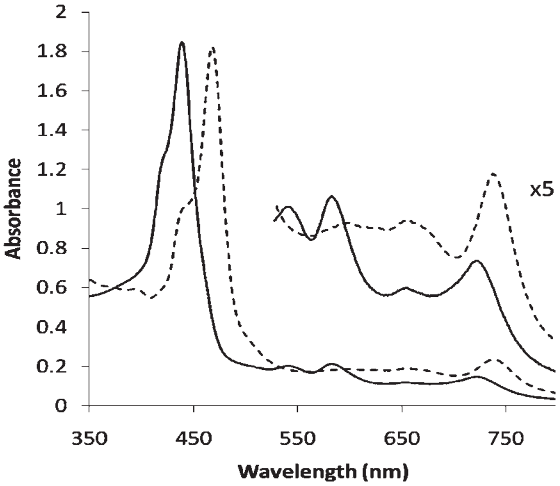

Figure 2. UV−visible spectra of N-confused porphyrin free base in anhydrous 5% THF in toluene (solid line) and the lithium adduct **1LiTHF** (dashed line) in the same solvent.

When the product from the initial metalation reaction is recrystallized from the coordinating solvent THF under anhydrous conditions, a solvent-bound form of the lithium complex is produced. We elucidated the structure of **Li1THF**, which is shown in Figure 3, by single-crystal X-ray methods. The solvent occupies the axial position in the complex, resulting in a pseudo-square-pyramidal structure. As in the **Li1** structure, the internal C−H bond remains intact, and the lithium ion is strongly coordinated by the three nitrogen atoms of the ring as well as the axial oxygen atom from the THF molecule. The Li−macrocycle bonds are lengthened upon axial coordination: the Li−N bonds are 1.938(4), 2.149(4), and 2.156(4) Å, and the Li−C distance is 2.482(4) Å. The lithium atom is also pulled out of the plane of the macrocycle; the distance between the metal and the plane defined by the three internal nitrogen atoms is ~0.56 Å. The angle formed between the plane of the inverted pyrrole and the plane defined by the three internal nitrogen atoms is considerably less than that in **1Li**, ~24°.

In both **1Li** and **1LiTHF**, the macrocycle is monoanionic, with only one of the ionizable protons removed upon lithium insertion. Therefore, we surmised that the externally N-methylated N-confused porphyrin macrocycle would bind lithium in a directly analogous fashion.[11] We were able to readily synthesize (2-*N*-methyl N-confused porphyrinato)(tetrahydrofuran)lithium (**2LiTHF**) by using the same methods as the synthesis of **1LiTHF**. This complex was structurally characterized by single-crystal X-ray diffraction, and the structure

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(8) **1Li**: monoclinic, $P2(1)/n$, $a = 13.618(6)$ Å, $b = 17.109(8)$ Å, $c = 14.865(7)$ Å, $\beta = 114.863(9)°$, $V = 3142(3)$ Å^3, $D = 1.312$ Mg/m^3, $T = 100$ K, final R indices [$I > 2\sigma(I)$] R1 = 0.0777, wR2 = 0.1434 (GOF = 1.079) for 6972 independent reflections. **1LiTHF**: triclinic, $P\bar{1}$, $a = 10.925(3)$ Å, $b = 14.848(4)$ Å, $c = 15.029(4)$ Å, $\alpha = 71.677(4)°$, $\beta = 114.863(9)°$, $\gamma = 72.110(4)°$, $V = 2194.4(10)$ Å^3, $D = 1.048$ Mg/m^3, $T = 100$ K, final R indices [$I > 2\sigma(I)$] R1 = 0.0633, wR2 = 0.1538 (GOF = 0.903) for 9496 independent reflections. **2LiTHF**: triclinic, $P\bar{1}$, $a = 10.205(2)$ Å, $b = 13.255(3)$ Å, $c = 14.877(3)$ Å, $\alpha = 87.189(4)°$, $\beta = 71.921(3)°$, $\gamma = 73.611(3)°$, $V = 1833.6(6)$ Å^3, $D = 1.280$ Mg/m^3, $T = 100$ K, final R indices [$I > 2\sigma(I)$] R1 = 0.0919, wR2 = 0.2201 (GOF = 1.058) for 7091 independent reflections.

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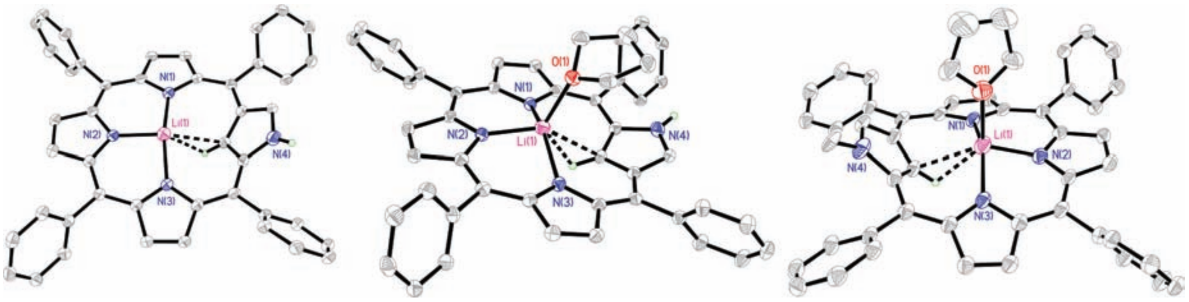

Figure 3. Structures of **1Li**, **1LiTHF**, and **2LiTHF** with 35% thermal ellipsoids. Hydrogen atoms, except those on the internal carbon and external nitrogen positions, have been omitted for clarity.

is shown in Figure 3. The overall structure of the N-methylated adduct is similar to that seen in **1LiTHF**, but the angle of the inverted pyrrole is increased relative to that in **1Li** or **1LiTHF** (~40°). The Li$-$N bonds [1.969(6), 2.155(7), and 2.172(7) Å] and the Li$-$C distance [2.416(6) Å] are nearly identical with those observed in **1LiTHF**, and the out-of-plane displacement of the lithium atom is ~0.51 Å.

The ^{7}Li isotope has a natural abundance of ~93% and is a $I = {}^{3}/_{2}$ nucleus, and thus ^{7}Li NMR is an ideal technique for characterizing porphyrinic complexes.[10] In particular, the chemical shift of the lithium ion is affected by the ring current of the macrocycle. In the absence of an axial solvent, such as a benzene solution, the resonance appears at -7.8 ppm. In a dimethyl sulfoxide (DMSO) solution, the ^{7}Li isotopes of **1Li** and **1LiTHF** appear at the even more shielded resonance of -10.1 ppm. In both cases, the identical nature of the spectra arises from the binding of DMSO to the axial position. In the same solvent, compound **2LiTHF** exhibits a ^{7}Li NMR resonance of -9.1 ppm. Although the overall ring shielding effect is the same in all three complexes, the differences between the observed resonances most likely result from the changes in the position of the lithium ion relative to the ring current as well as the presence or absence of an axial solvent.

In conclusion, we present the first lithium complexes of N-confused porphyrin. Unlike normal porphyrin, N-confused porphyrin can adopt a monoanionic charge via its external tautomeric form and thus can form a 1:1 stoichiometry with lithium. The lithium cation either can form a pseudo-four-coordinate geometry with no axial ligand in the absence of a coordinating solvent or can be readily ligated by solvents such as THF. We are continuing our work of investigating the metalation chemistry of N-confused porphyrin as well as other novel porphyrin and phthalocyanine analogues.

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Supporting Information Available: X-ray crystallographic data in CIF format and synthesis and characterization for **1Li**, **1LiTHF**, and **2LiTHF**. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files for the three structures have also been deposited with the Cambridge Crystallographic Data Centre as CCDC numbers 778666$-$778668. Copies can be obtained upon request, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44 1223-336-033 or e-mail deposit@ccdc.cam.ac.uk).