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Synthesis, Characterization, and Properties of a Lithium 21-Thiaporphyrin Complex

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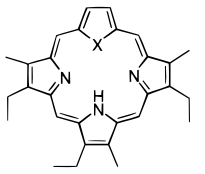
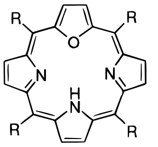
Introduction

The fundamental importance of porphyrins in biochemical processes has led to many diverse studies of their properties and activity.[1−3] These include, for example, attempts to understand and mimic their activity in biochemical catalysis,[4] oxygen transport and activation,[4] and electron transfer.[5] These efforts are facilitated by the tunability of porphyrins and metalloporphyrins, which can be done on several levels, such as modification of the centrally bound metal, outer rim modification (i.e., *meso* and β-substituent modification), and also core alteration.[2] This latter approach has been suggested as an independent means to control the reactivity and catalytic properties of porphyrins.[6]



1a. X = O
1b. X = S



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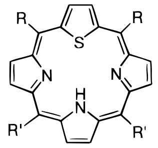

3a. R = phenyl, R' = tolyl
3b. R = R' = phenyl
3c. R = R' = tolyl

Core-modified porphyrins are obtained when one or more of the internal nitrogen atoms are substituted with another heteroatom or carbon. The total number of heteroatoms and the basic framework of the porphyrin macrocycle are maintained. If one of the nitrogen atoms is replaced with, for example, an oxygen or sulfur, a monoanionic porphyrin is obtained (structures **1**−**3**). Depending on the heteroatom introduced into the core, the size of the macrocyclic cavity changes substantially.[6] This, in turn, affects the metal binding ability and influences the stability of resulting complexes of the heteroporphyrin macrocycle.

The first heterosubstituted porphyrins, 21-oxa- and 21-thiaporphyrin **1a** and **1b**, were synthesized by Broadhurst et al. in 1971.[7] These workers also reported the syntheses of Zn(II) and Ni(II) complexes of 21-oxaporphyrin and obtained spectroscopic evidence for the formation of a 21-thiaporphyrin Zn(II) complex. In the early 1990s, Latos-Grazynski and coworkers prepared and studied complexes of 21-oxa- (e.g., **2**) [Ni(I) and Ni(II)] and 21-thiaporphyrins (**3a**−**c**) [Fe(II), Ni(I), Ni(II), Co(II), Pd(I), and Rh(III)].[6,8−13]

These studies served to establish the reactivity and properties of late transition metal complexes of monoanionic heteroporphyrins. Thus far, there have been no reports of the alkali metal and early transition metal chemistry of these materials. We were interested in studying the early metal chemistry of the heteroporphyrin ligand and the effect of the smaller core size on the stability of the resulting complexes in an attempt to prepare unusual metal complexes with novel catalytic properties. We were particularly interested in the lithium salt as a potential Li-conducting electrolyte in polymer battery applications. Toward this end, we prepared the lithium complex of 21-thiaporphyrin as a possible synthon to these compounds, as described here.

Experimental Section

General Considerations. Standard Schlenk and glovebox techniques were used unless stated otherwise. Hexanes, dichloromethane, acetonitrile, and tetrahydrofuran (THF) were purified by passage through a column of activated silica and degassed with nitrogen. All other reagents were used as received.

All electrochemical experiments were performed on a BAS 100B electrochemical analyzer inside a drybox, using a platinum disk working electrode, a Ag reference electrode, and a platinum wire auxiliary electrode. UV−vis spectra were recorded using a Cary 50 spectrometer. Proton, ^{13}C, and ^{7}Li NMR spectra were recorded on a Bruker DRX-500 spectrometer. Elemental analysis and mass spectra were determined at the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

Diphenylditolyl-21-thiaporphyrin (MTPH, 5). In a 2-L round-bottom flask, 2,5-bis(tolylhydroxymethyl)thiophene (**4**, 1.95 g, 6.01 mmol) was dissolved in dry dichloromethane (1 L) under nitrogen. Pyrrole (2.8 mL, 40 mmol) and benzaldehyde (3.5 mL, 34 mmol) were added, followed by the addition of $BF_3{\cdot}Et_2O$ (2 mL). The resulting dark mixture was stirred at room temperature for 1 h, and then chloranil (8 g, 40 mmol) was added. The mixture was heated to reflux for 1 h and cooled, and the solvent was removed using a rotary evaporator. The black residue was filtered through neutral alumina using dichloromethane as the solvent. After removal of the solvent, the purple metallic-looking residue was separated on a silica gel column (200−300 mesh, 3 × 20 cm) using hexanes/dichloromethane, 3:2, as eluent. Three fractions were eluted. The first, red-violet fraction contained tetraphenylporphyrin (TPP), the second, red-brown fraction contained the desired MTPH (**5**, 381 mg, 8.5%), and the third, red-brown fraction contained tetratolyldithiaporphyrin. mp > 220 °C (dec). Found: C, 83.48; H, 5.06; N, 6.24%. $C_{46}H_{33}N_3S$ requires: C, 83.73; H, 5.04; N, 6.37%; M^+ 660. ^{1}H NMR (500 MHz, $CDCl_3$) δ: −2.65 (s), 2.70 (s), 7.62 (d), 7.75 (m), 8.15 (d), 8.21 (d), 8.61 (d), 8.72 (d), 8.93 (d), 9.79

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10.1021/ic000202w CCC: $19.00

Table 1. Crystallographic Data for MTPH and MTPLi

	MTPH	MTPLi
empirical formula	$C_{46}H_{33}N_3S$	$C_{52}H_{43}N_4OS$
fw	659.85	778.94
space group	$P2_1/c$, monoclinic	$P\bar{1}$, triclinic
a, Å	20.5516(4)	11.390(2)
b, Å	8.8077(3)	11.905(2)
c, Å	19.7461(3)	17.090(2)
α, deg	90.000(0)	108.041(2)
β, deg	101.174(2)	97.446(2)
γ, deg	90.000(0)	103.226(3)
V, Å^3	3506.5(1)	2093.9(5)
Z	4	2
D_{calc}, g/cm^3	1.250	1.240
λ, Å	0.71069	0.71069
temp, °C	−95.0	−108.0
R^a	0.073	0.056
$R_w{}^b$	0.077	0.042
GOF	2.08	1.04
μ, cm^{-1}	0.130	0.121

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

(s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.5, 123.6, 126.6, 127.8, 128.3, 128.8, 131.6, 133.2, 134.2, 134.4, 135.3, 137.6, 138.1, 138.9, 142.5, 147.3, 154.4, 157.5. HRMS (FAB+): calcd for $C_{46}H_{33}N_3S$, 659.2395; found, 659.2403. UV−vis (THF, [nm]): 429, 517, 548.

Lithium Ditolyldiphenylmonothiaporphyrin (6). Ditolyldiphenyl-21-thiaporphyrin (**5**, 0.27 g, 0.41 mmol) and lithium bis(trimethylsilyl)-amide (75 mg, 0.45 mmol) were placed in a 100-mL Schlenk tube. Tetrahydrofuran (20 mL) was added via cannula, resulting in a dark green solution. This solution was stirred at room temperature for 4 h, and then it was filtered and the volume was reduced to ca. 5 mL. Hexanes (25 mL) was added and the mixture was placed in the freezer at −40 °C overnight. The resulting precipitate was filtered off and dried in vacuo, resulting in a dark green powder (250 mg, 90%). The complex decomposes within minutes at room temperature, presumably by loss of THF. We therefore made no attempt to further characterize the compound by elemental analysis. ^{1}H NMR (500 MHz, C_6D_6) δ (ppm): 2.41 (s), 7.38 (d), 7.47 (m), 8.17 (d), 8.26 (m), 8,84 (d), 9.06 (m), 9.45 (s). ^{13}C NMR (125 MHz, C_6D_6) δ: 21.7, 24.3, 66.0, 132.8, 134.0, 134.1, 135.4, 135.9, 136.5, 137.8, 140.2, 145.3, 145.4, 154.2, 154.4. ^{7}Li NMR (298 K, 194.5 MHz, C_6D_6) δ: −10.15. UV−vis (THF, [nm]): 346, 458, 570, 619.

X-ray Experimental. X-ray quality crystals of MTPH, **5**, were grown from a THF solution layered with pentane. A red plate of **5** having approximate dimensions of 0.31 × 0.15 × 0.10 mm was mounted on a glass capillary using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART diffractometer with graphite monochromated MoKα ($\lambda = 0.71069$) radiation. Heteroatoms (N and S) were refined anisotropically, whereas carbon atoms were refined isotropically, and hydrogen atoms were included, but not refined. No disorder seemed apparent in this structure.

X-ray quality crystals of MTPLi, **6**, were grown from a THF solution layered with acetonitrile. A green plate of **6** having approximate dimensions of 0.30 × 0.18 × 0.12 mm was mounted on a glass capillary using Paratone N hydrocarbon oil. Collection of X-ray diffraction data and solution of the resulting structure proceeded in the usual manner. All atoms were refined isotropically, with the exception of the acetonitrile carbon and nitrogen atoms, which were refined anisotropically, and hydrogen atoms were included, but not refined. Table 1 shows crystallographic data for MTPH and MTPLi.

Results and Discussion

The 21-thiaporphyrin employed in these studies was synthesized using Lindsey conditions.[14] Specifically, thiophene was lithiated in the 2- and 5- positions and immediately reacted with tolylaldehyde to form the 2,5-bis(tolylhydroxymethyl) thiophene (Scheme 1).[15] Condensation of the latter with pyrrole and benzaldehyde in dichloromethane with $BF_3 \cdot Et_2O$ as catalyst then led to the diphenylditolyl-21-thiaporphyrin (MTPH), together with the formation of tetraphenylporphyrin (TPP) and tetratolyl-21,23-dithiaporphyrin (DTP). We chose to work with the 21-thiaporphyrin because its precursors are accessible in larger quantities and are prepared more easily than those of the corresponding 21-oxaporphyrin. This is a prerequisite to undertaking synthetic-scale metalation studies with this material. The *meso*-di(phenyl)-di(tolyl) substitution pattern was chosen in order to obtain a material that was less likely to exhibit disorder in later solid-state crystallographic studies.

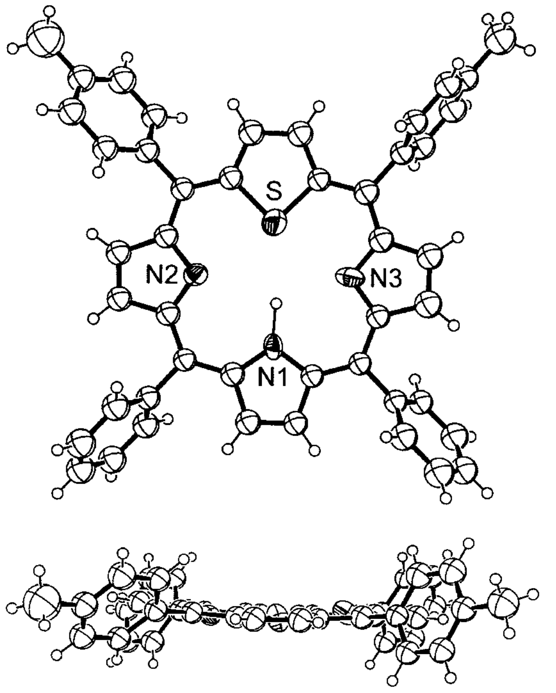
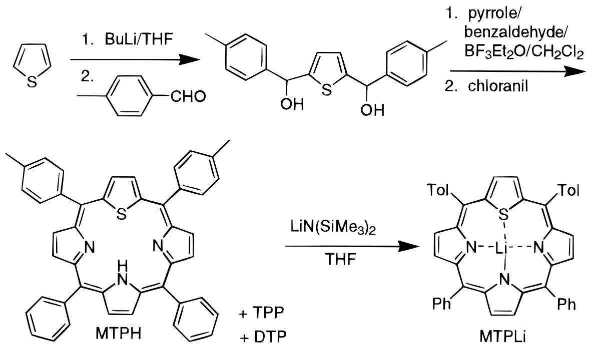


Figure 1. Front (top) and side (bottom) views of the solid-state structure of MTPH.

Scheme 1



A solid-state structural analysis of MTPH demonstrated that the chosen substitution pattern worked in the desired manner, because no apparent disorder was present (Figure 1). The macrocyclic core is slightly ruffled (planes: thiophene (T), N1-pyrrole (N1), N2-pyrrole (N2), N3-pyrrole (N3); dihedral angles: T−N1 = 1.4°, T−N2 = 9.6°, T−N3 = 2.1°, N1−N2 = 9.9°, N1−N3 = 2.7°, N2−N3 = 7.5°). These data are in agreement with previous X-ray structures of analogous 21-

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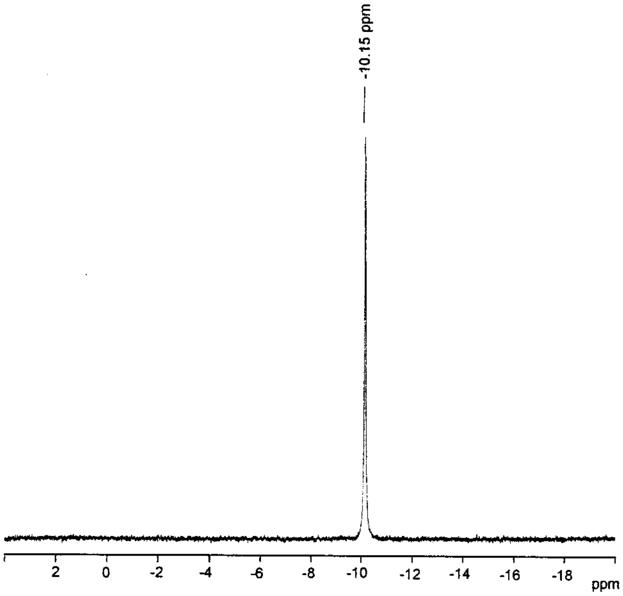

Figure 2. Room temperature ^{7}Li NMR spectrum of MTPLi (194.5 MHz, C_6D_6).

thiaporphyrins.[6] The internal NH-proton is localized at the nitrogen opposite of the thiophene sulfur, another fact previously established for this type of monoanionic porphyrin using ^{1}H NMR spectroscopy.[6]

Reaction of MTPH with lithium bis(trimethylsilyl)amide in THF leads to the formation of the lithium 21-thiaporphyrin (MTPLi) as evidenced by a color change from brown-red to green in the course of the reaction. The resulting complex is soluble in solvents such as dichloromethane, benzene, and acetone, but not in acetonitrile. The Li-salt was also found to be very water sensitive, with even traces of humidity leading to immediate demetalation and formation of the free base MTPH. The UV−vis spectrum shows a weaker, broad absorption at 346 nm, one strong Soret-like absorption band at 458 nm, and two Q-type absorption bands at 570 and 619 nm (Figure 1). The free base MTPH, on the other hand, shows the Soret-like absorption band at 429 nm and three weak Q-type absorption bands at 517, 548, and 678 nm.

The first proof for the insertion of the lithium cation into the center of the macrocycle was obtained using ^{7}Li NMR spectroscopy. The compound shows only a single peak at −10.15 ppm at room temperature (Figure 2). Previous studies with dianionic porphyrins revealed that most dilithiated tetraarylporphyrins show one equilibrium signal at around −5 ppm at room temperature.[16−18] Upon cooling the compound to −60 C, two signals are observed at around 1 ppm and −10 ppm which are ascribable to the solvated lithium cation and the lithium cation bound in the macrocyclic core, respectively. Because of the strong diamagnetic ring current and shielding effect, the ^{7}Li signal of the centrally bound Li atom is shifted to a higher field. By analogy, it can be concluded that the lithium cation in the case of MTPLi is localized in the center of the macrocycle.

Further proof for the structural identity of the lithium complex was obtained using solid-state single-crystal X-ray crystallography (Figure 3). The structure shows that the porphyrin macrocycle is quite distorted from planarity. The three pyrrolic subunits are almost planar, whereas the thiophene moiety is rotated out of the plane, forming a dihedral angle of 12.5° to the plane defined by the tripyrrane subunit. This dihedral angle is smaller than that found for the previously studied nickel(I)-21-thiaporphyrin complex (14.6°),[19] but larger than that found for the corresponding iron(II) complex (11.8°).[10]

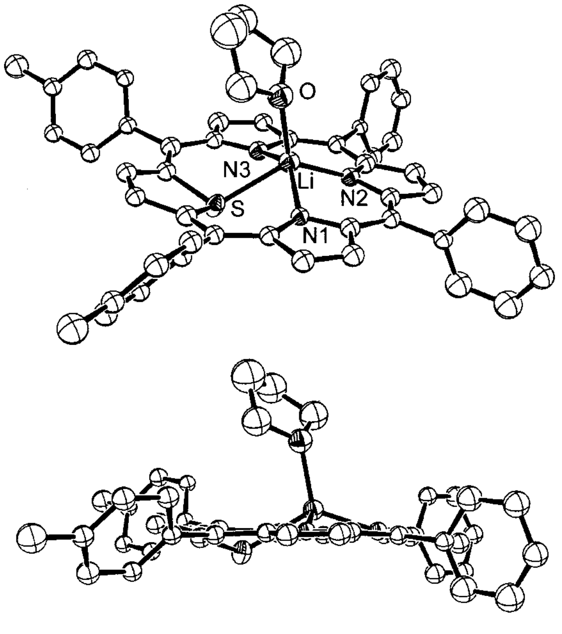

Figure 3. Two perspective views of the solid-state structure of MTPLi. Hydrogen atoms were omitted for clarity.

The lithium cation is located 0.64 Å above the tripyrranic plane. This macrocycle to metal distance is greater than those found for transition metals such as Ni(I) (0.042 Å)[19] or Fe(II) (0.538 Å).[10] The five-coordinate lithium ion is in a roughly square pyramidal arrangement, with the shortest bonding interaction of 1.92(2) Å formed to the N2 atom. This is the nitrogen atom which, in the case of MTPH, binds the hydrogen atom. Bond lengths to the remaining nitrogen atoms N1 and N3 are 2.20(2) and 2.23(2) Å, respectively. The sulfur to lithium distance is 2.33(2) Å, comparable to those found in the corresponding Ni(I) (2.143(6) Å)[19] and Fe(II) complexes (2.388(3) Å),[10] and is therefore short enough for us to assume that there are bonding interactions between these atoms. The fifth bonding interaction of 1.97(2) Å is formed to the oxygen atom of a coordinated THF molecule, which is localized on the side of the thiophene subunit and tilted inward filling the gap formed by the rotation of the thiophene out of the macrocyclic plane. Finally, the unit cell contents are completed by incorporation of two molecules of acetonitrile. They are omitted from Figure 3 because they do not appear to influence the structure of the macrocyclic complex.

To compare the electrochemical properties of MTPH to those of MTPLi, it was first necessary to establish that the latter did not react with the electrolyte (tetrabutylammonium hexaflurophosphate, TBAPF$_6$) used in the electrochemical experiment. Mixing MTPLi with an excess of TBAPF$_6$ in C_6D_6 or THF (spiked with C_6D_6 as lock solvent) did not lead to any apparent reaction. The ^{7}Li NMR spectrum recorded for these solutions was identical to that recorded for MTPLi in pure C_6D_6 (see Figure 2).

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The electrochemical experiments were performed in THF containing 0.1 M $TBAPF_6$ and internally referenced to the Fc/Fc^+ couple. MTPH shows one reversible oxidation and one reduction wave at 0.68 and −1.73 V, respectively. This ΔE (2.40 V) is higher than that previously recorded for 21-thiaporphyrin in dichloromethane ($\Delta E = 2.12$ V).[20] MTPLi, however, shows one reversible oxidation and one reversible reduction wave at 0.70 and −1.74 V, respectively ($\Delta E = 2.43$ V), and one additional irreversible oxidation process at 0.37 V (40 mV/s). The source of this oxidation process is currently unknown and makes the assignment of the observed reversible oxidation process impossible.

Preliminary studies to explore the reactivity of both MTPH and MTPLi were also undertaken. Reaction of MTPH with metal alkyls such as $AlMe_3$, $MgMe_2$, or $ZrBn_4$ led to decomposition of the starting materials as the only observable reaction. Salt metathesis reactions of MTPLi with a variety of metal halides under various conditions were unsuccessful, leading only to the isolation of the free base porphyrin.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research for support of this work.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles for MTPH and MTPLi (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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