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Solvent-dependent Forms of Lithiated 5,5,10,10,15,15,20,20-Octaethylporphyrinogen in Solution and in the Solid State and Reaction with Tetrahydrofuran

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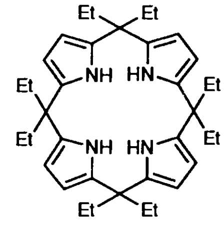
The fully lithiated form of 5,5,10,10,15,15,20,20-octaethylporphyrinogen (H_4L) synthesized in tetrahydrofuran (thf) has been structurally characterized in its solvated form $Li_4L{\cdot}3thf$, while its unsolvated form from *n*-hexane behaves as a 'superbase' capable of decomposing thf to the lithium enolate identified in the aggregate $Li_6L(OCH{=}CH_2)_2{\cdot}4thf$.

The chemistry of lithium is well documented in co-ordination,[1,2] organometallic, and organic[3] chemistry, owing to the variety of its interaction modes with hetero and carbon atoms. Furthermore, a very large number of syntheses rely on lithium-based reagents. In this context we became interested in the lithiated forms of potential polydentate ligands having both heteroatoms and unsaturated carbon peripheries. Lithium derivatives of porphyrin-based ligands are widely employed[4] and we report here the synthesis and characterization of the lithium derivative of 5,5,10,10,15,15,20,20-octaethylporphyrinogen (H_4L) and its solvent-dependent forms, including the reaction with tetrahydrofuran (thf).



H_4L

The synthesis of H_4L dates back to the nineteenth century,[5] but its use in co-ordination and organometallic chemistry is far more recent.[6–8] The binding of the tetraanion L^{4-} to transition metals has been achieved *via* the tetralithium intermediate **1**[6a] [equation (1)], usually generated in thf. The lithiated derivative

$$H_4L + 4LiBu^n \xrightarrow[-BuH]{thf} \underset{\mathbf{1}}{Li_4L{\cdot}4thf} \qquad (1)$$

1 contains three firmly bonded thf molecules, while the fourth one can be lost either by prolonged drying *in vacuo* or when **1** is suspended or recrystallized from hydrocarbons, *e.g.* toluene, giving $Li_4L{\cdot}3thf$ **2**.† Both **1** and **2** display the same ^1H NMR resonances in C_6D_6, and we conclude that complex **2** is the thf-solvated form of H_4L present in non-co-ordinating solvents. The crystal structure of **2** has been determined‡ and a simplified view of it is shown in Fig. 1, with a selection of structural parameters. One of the lithium cations, Li(1), is bonded to the four nitrogen atoms, displaced by 0.248(5) Å from their mean plane and bonded by a significantly shorter distance to N(1) and N(4) than to N(2) and N(3). The cations Li(2), Li(3) and Li(4) are η^2 bonded to a pyrrole ring and σ bonded to the nitrogen of the adjacent one. Co-ordination around Li(2)–Li(4) is completed by a thf molecule. The η^2-bonding mode of the pyrrolyl anions is mainly suggested by the narrow range of the lithium–pyrrole-ring distances, which vary from 2.249(7) to 2.396(7) Å for Li(2) and Li(3) respectively, though the rather short contacts of 2.547(6) [Li(2)–C(8)] and

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† Compound **1** was prepared following the procedure given in ref. 6(*a*), compound **2** from the recrystallisation of **1** from toluene–hexane (Found: C, 73.90; H, 9.45; N, 7.10. $C_{48}H_{72}Li_4N_4O_3$ requires C, 73.85; H, 9.30; N, 7.15%). ^1H NMR (C_6D_6, room temperature): δ 6.31 (s, 8 H, pyrrole), 3.23 (m, 12 H, thf), 2.12 (q, 16 H, CH_3CH_2), 1.19 (m, 12 H, thf), 1.08 (t, 24 H, CH_3CH_2).

‡ Crystal data. Compound **2**. $C_{48}H_{72}Li_4N_4O_3$, $M = 780.9$, triclinic, space group $P\bar{1}$, $a = 12.163(3)$, $b = 19.259(4)$, $c = 10.837(2)$ Å, $\alpha = 95.95(2)$, $\beta = 111.61(2)$, $\gamma = 84.28(2)°$, $U = 2342.2(9)$ Å^3, $Z = 2$, $F(000) = 848$, $D_c = 1.107$ g cm^{-3}, Cu-Kα radiation ($\lambda = 1.541\ 78$ Å), μ(Cu-Kα) = 4.83 cm^{-1}, crystal dimensions 0.42 × 0.47 × 0.74 mm. Structure solved by SHELXS 86[9] and anisotropically refined for non-H atoms, except for 3 thf molecules, which were found to be disordered. Hydrogen atoms located from Fourier-difference maps and given fixed $U_{iso} = 0.10$ Å^2. 6693 Unique observed reflections [$I < 4\sigma(I)$] collected at 295 K ($6 < 2\theta < 140°$) on a Siemens AED diffractometer, $R = 0.076$ (unit weights {$R = \Sigma|\Delta F|/\Sigma|F_o|$, $R' = \Sigma[(w\Delta F^2)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}}$; $w = k/[\sigma^2(F_o) + g|F_o|^2]$}. Compound **4**, $C_{56}H_{86}Li_6N_4O_6$, $M = 953.0$, monoclinic, space group $P2_1/n$, $a = 12.843(1)$, $b = 20.373(2)$, $c = 21.796(1)$ Å, $\beta = 93.64(1)°$, $U = 5691.4(8)$ Å^3, $Z = 4$, $F(000) = 2064$, $D_c = 1.112$ g cm^{-3}, Cu-Kα radiation ($\lambda = 1.541\ 78$ Å), μ(Cu-Kα) = 5.08 cm^{-1}, crystal dimensions 0.18 × 0.22 × 0.36 mm. Structure solved as for **2** above, with the 4 thf molecules and the methylene carbons of the enolato groups found to be disordered (U_{iso} for the H atoms 1.2 times the U_{eq} of the corresponding carbon atoms). Refinement based on all the 9279 unique reflections collected at 295 K ($6 < 2\theta < 140°$) on a Rigaku AFC 65 diffractometer and corrected for absorption. $R = 0.062$ for 1971 unique observed reflections [$I > 2\sigma(I)$].

Atomic coordinates, bond lengths and angles and thermal parameters for **2** and **4** have been deposited at the Cambridge Crystallographic Data Centre. See Instruction for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

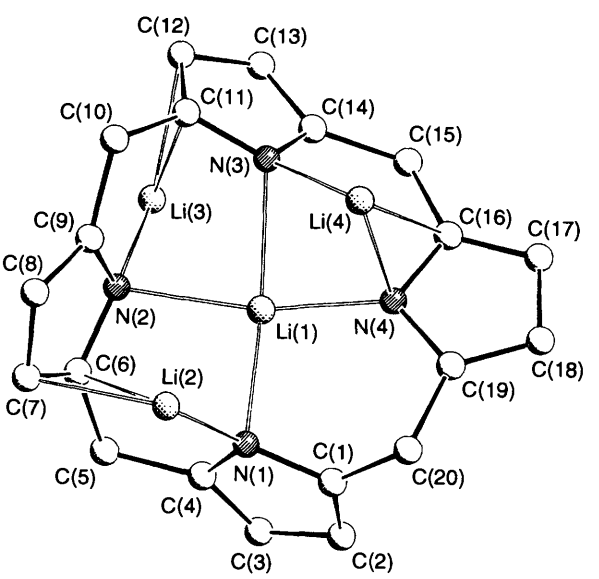

Fig. 1 A simplified SCHAKAL[10] view of complex **2**. Selected bond distances (Å): Li(1)–N(1) 2.057(5), Li(1)–N(2) 2.186(5), Li(1)–N(3) 2.228(5), Li(1)–N(4) 1.970(4), Li(2)–N(1) 1.962(6), Li(2)–C(6) 2.396(7), Li(2)–C(7) 2.249(7), Li(3)–N(2) 2.051(7), Li(3)–C(11) 2.312(7), Li(3)–C(12) 2.304(6), Li(4)–N(3) 1.991(7), Li(4)–N(4) 2.048(6), Li(4)–C(16) 2.362(7). Ethyl groups and a thf molecule bonded to Li(2), Li(3) and Li(4) have been omitted for clarity

2.567(7) Å [Li(3)–C(13)] do not rule out a η^3-bonding mode. The fourth lithium atom experiences a different environment, being η^2 bonded to a CN edge. As a consequence of the bonding modes adopted to the lithium cations, the conformation of the porphyrinogen is remarkably different from the usual saddle one.[7,8]

In order to obtain metal complexes of H_4L with no co-ordinated solvent, the lithiation reaction was carried out in *n*-hexane, resulting in compound **3** [equation (2)].* The ^1H

$$4\mathrm{LiBu^n} \xrightarrow[-\mathrm{BuH}]{\text{hexane}} \underset{\mathbf{3}}{\mathrm{Li_4L}} \tag{2}$$

NMR spectrum of **3** in C_6D_6 shows the presence of a small amount of *n*-hexane of crystallization and, contrary to **1** and **2**, two sets of methylene and two sets of methyl groups for the peripheral ethyl substituents.[6–8] This has often been observed when particularly rigid conformations imposed by the presence of certain metal cations differentiate the ethyl groups, owing to the rather short C–H ••• M contacts of the *meso*-ethyl groups. With excess of LiBu^n, the solid product can contain some adventitious coprecipitated LiBu^n. The dissolution of **3** free from LiBu^n in thf at room temperature led to the simple solvation of **3** to **2**. However, when a freshly prepared solution of **3** was immediately refluxed in thf overnight, a procedure which is often employed in the synthesis of metal complexes, a ^1H NMR spectrum and crystal structure determination (Fig. 2) revealed the presence of the lithium enolate in the structure of **4** [equation (3)]. Although not quantitative, reaction (3)

$$\underset{\mathbf{3}}{\mathrm{Li_4L}} \xrightarrow[\text{reflux}]{\text{thf}} \underset{\mathbf{4}}{\mathrm{Li_6L(OCH{=}CH_2)_2{\cdot}4thf}} \tag{3}$$

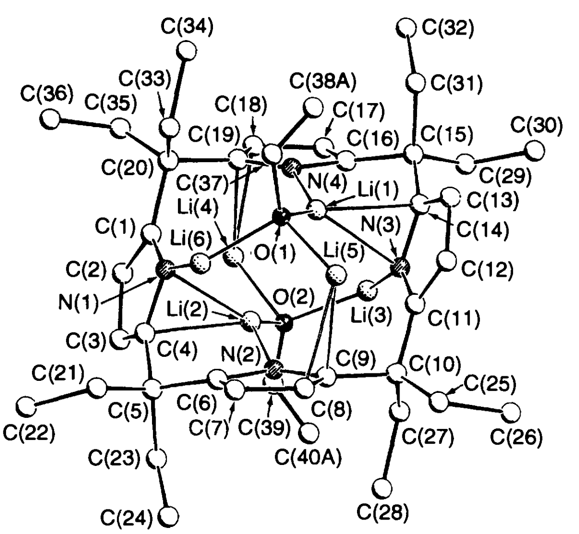

Fig. 2 A simplifed SCHAKAL[10] view of complex **4**. Selected bond distances (Å): Li(1)–O(1) 1.905(11), Li(1)–N(3) 2.218(11), Li(1)–N(4) 1.970(11), Li(1)–C(14) 2.241(13), Li(2)–O(2) 1.898(11), Li(2)–N(1) 2.231(12), Li(2)–N(2) 1.960(12), Li(2)–C(4) 2.291(13), Li(3)–O(2) 1.903(12), Li(4)–O(2) 1.871(13), Li(3)–N(3) 2.019(11), Li(4)–C(18) 2.291(13), Li(4)–C(19) 2.564(12), Li(5)–O(1) 1.857(11), Li(5)–C(8) 2.440(12), Li(5)–C(9) 2.551(12), Li(6)–O(1) 1.915(12), Li(6)–N(1) 2.017(11), O(1)–C(37) 1.451(9), O(2)–C(39) 1.396(9). The thf molecules bonded to Li(3), Li(4), Li(5) and Li(6) have been omitted for clarity

produces a considerable amount of **4** as a crystalline solid.† The formation of CH_2CHOLi from the reaction of thf with a very strong base is well known, being its most common decomposition pathway.[11] Consequently, the monoprotonated form of H_4L, $Li_3HL{\cdot}2.5thf$, derived from the deprotonation of thf has been identified.‡ This suggests that using the lithiated form of H_4L under drastic conditions in thf (or other non-innocent solvents) may generate undesirable reactive species during the synthesis of metal complexes.

In the structure of complex **4** (Fig. 2)§ the nitrogen atoms of the pyrrole rings are coplanar [maximum displacement 0.002(4) Å]. The six lithium cations are arranged in two sets, three above and three below the N_4 plane. Each set is triply bridged by the oxygen of the enolate. Each group of lithiums defines a plane roughly parallel to the N(2) and N(4) pyrrole rings with the angles between these planes being as follows: Li(1)Li(5)Li(6) and N(2) pyrrole 18.7(3), Li(1)Li(5)Li(6) and N(4) pyrrole 16.2(3), Li(2)Li(3)Li(4) and N(2) pyrrole 19.4(3) and Li(2)Li(3)-Li(4) and N(4) pyrrole 15.4(3)°. The two sets of lithium cations display the same overall bonding mode to porphyrinogen; Li(1) and Li(2) bridge two adjacent pyrrole rings, as previously seen in complex **1**, the η^2 interaction of Li(4) and Li(5) is analogous, but occurs *via* C(18), C(19) and C(8), C(9) respectively, while Li(6) and Li(3) are σ bonded to the nitrogen from opposite pyrroles. The porphyrinogen anion displays an unusual 'chaise-longue' conformation, in which pairs of adjacent pyrroles [N(1), N(4) and N(2), N(3)] face the same direction with respect

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* Compound **3** was obtained by refluxing a suspension of H_4L in *n*-hexane treated with LiBu^n in a 1:4 molar ratio for 3 h (yield 65%) [Found: C, 76.30; H, 8.90; N, 9.70. $C_{38}H_{52.5}Li_4N_4$ ($Li_4L{\cdot}\frac{1}{3}C_6H_{14}$) requires C, 76.95; H, 8.90; N, 9.45%]. ^1H NMR (C_6D_6, room temperature): δ 6.14 (s, 8 H, pyrrole), 1.93 (q, 8 H, CH_3CH_2), 1.68 (q, 8 H, CH_3CH_2), 1.23 (m, 2.5 H, hexane), 0.92 (t, 12 H, CH_3CH_2), 0.87 (t, 12 H, CH_3CH_2), 0.67 (t, 2 H, hexane).

† Compound **4** was obtained by refluxing a solution of compound **3** (3.10 g) dissolved in thf (80 cm^3) overnight. On addition of *n*-hexane (100 cm^3) and cooling at −20 °C for 4 d, white crystals of **4** formed (yield 35%) (Found: C, 70.95; H, 9.25; N, 6.35. $C_{56}H_{86}Li_6N_4O_6$ requires C, 70.60; H, 9.10; N, 5.90%). ^1H NMR (C_6D_6, room temperature): δ 6.72 (dd, 2 H, $CH_2{=}CHOLi$), 6.34 (s, 8 H, pyrrole), 3.76 (dd, 4 H, $CH_2{=}CHOLi$), 3.51 (m, 16 H, thf), 2.08 (q, 16 H, CH_3CH_2), 1.31 (m, 16 H, thf), 0.92 (t, 24 H, CH_3CH_2).

‡ The use of an appropriate ratio of LiBu^n to H_4L ratio led to the isolation of the mono- and di-protonated forms of H_4L, $Li_3HL{\cdot}2.5thf$ **5** and $Li_2H_2L{\cdot}2thf$ **6**, which have been fully characterized, in the case of **6** by a crystal-structure determination.

§ See footnote ‡ on previous page.

to the N_4 core and opposite pyrroles [N(1), N(3) and N(2), N(4)] are parallel, angles between the N_4 plane and the pyrrole rings being 68.5(2), 124.6(2), 116.0(2) and 54.6(2)°, respectively, with angles between the N(1) and N(3), and N(2) and N(4) pyrrole rings 4.7(2) and 3.8°. An element of disorder unfortunately prevents a thorough discussion of the structural parameters of the enolate anions, although the structural characterisation of the lithium enolate unit is rather unique.[3b]

Acknowledgements

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