The First Structurally Characterized Alkali Metal Porphyrin: ^{7}Li NMR Behaviour and X-Ray Crystal Structure of the Dilithium Salt of Octaethylporphyrin(2−)

John Arnold

*Department of Chemistry, University of California, Berkeley, CA 94720, USA*

Reaction of H_2oep (oep = dianion of octaethylporphyrin) with two equivalents of $LiN(SiMe_3)_2$ in tetrahydrofuran (thf) yields the dilithium salt [Li(thf)$_4$][Li(oep)], characterized in the solid state by X-ray crystallography; in solution, ^{7}Li NMR and conductivity measurements show a more complex, solvent-dependent structure consistent with either solvent-separated or contact ion pairs depending on the nature of the solvent.

Since reports of their spectroscopic properties appeared many years ago,[1] little chemistry has emerged of porphyrin complexes of the alkali metals, and almost nothing is known of their stoicheiometry and structure.[2,3] Our interest in these compounds derives, in part, from their possible use as reagents in the synthesis of porphyrin derivatives of the early transition metals.

Reaction of H_2oep (oep = dianion of octaethylporphyrin) with 2 equiv. of $LiN(SiMe_3)_2$ at 50—60 °C in tetrahydrofuran (thf) leads to a colour change from brown to claret, and is complete (judged by UV/VIS spectroscopy) within 30 min. The Soret band shifts from λ 397 nm in H_2oep to 416 nm in the product; the Q-bands in the free base (λ 622, 568, 528, and 496 nm) are replaced by two peaks of comparable intensity at λ 588 and 552 nm.[1a—c,4] Concentration and cooling of the reaction solution gave dark red needles in 90% yield. NMR tube reactions in [$^2H_8$]tetrahydrofuran confirmed the stoicheiometry shown in equation (1).

$$2\ LiN(SiMe_3)_2 + H_2oep \rightarrow (thf)_nLi_2(oep) + 2\ HN(SiMe_3)_2 \quad (1)$$
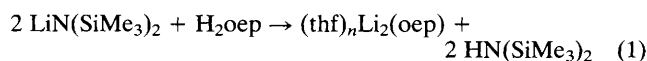
On filtration and drying, crystalline samples rapidly lose co-ordinated thf, crumbling to a purple powder within hours at room temperature; consequently, elemental analyses were of little use in assessing the nature or purity of the product. Solvent loss is also evident by ^{1}H NMR spectroscopy† in $(CD_3)_2$SO or CD_3CN: the vacuum-dried product shows a

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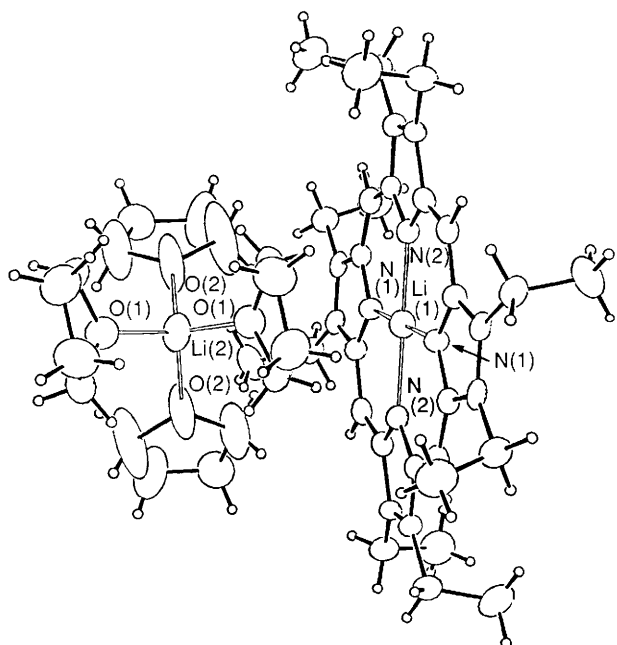
Figure 1. Crystal and molecular structure of [Li(thf)₄][Li(oep)]. Thermal ellipsoids depicted at 50% probability level. Selected distances (Å): Li(1)–N(1) 2.032(3), Li(1)–N(2) 2.042(3), Li(2)–O(1) 1.892(6), Li(2)–O(2) 1.875(6). Selected bond angles (°): N(1)–Li(1)–N(1) 180.0, N(1)–Li(1)–N(2) 89.9(1), 90.1(1), O(1)–Li(2)–O(1) 110.8(5), O(1)–Li(2)–O(2) 107.8(2), 106.1(1), O(2)–Li(2)–O(2) 118.3(6).
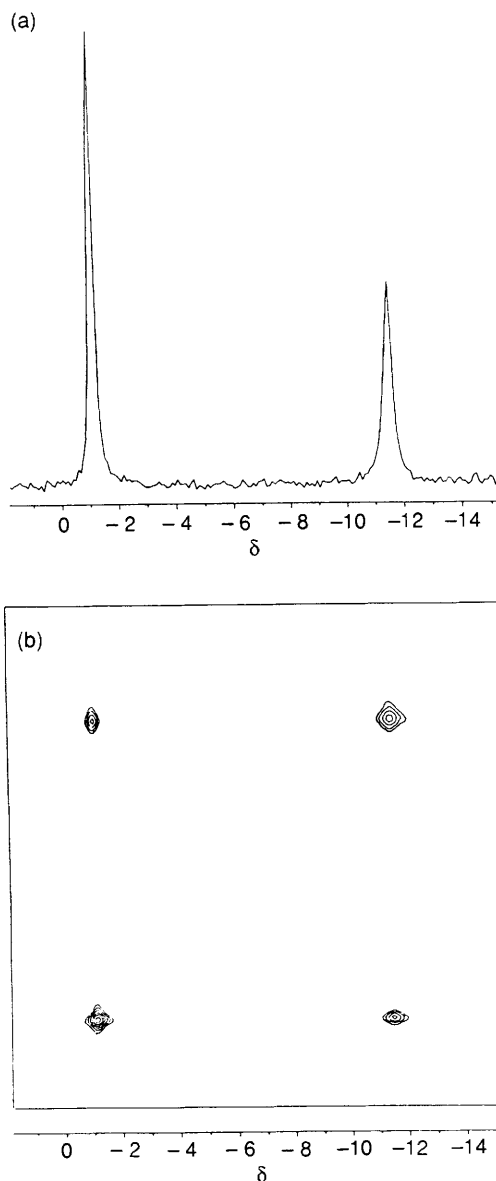
thf : oep ratio of *ca.* 2 : 1, whereas for freshly isolated samples this value approaches the value of 4 : 1 determined by *X*-ray crystallography (see below). Loss of solvent is reversible, however, as the original product can be regenerated quantitatively by dissolution and crystallization from thf.

The complex is quite moisture-sensitive, especially in solution. Hydrolysis is rapid and quantitative in thf as determined by UV/VIS spectroscopy and preparative scale reactions followed by titration of the liberated base [equation (2)].

$$(\text{thf})_4\text{Li}_2(\text{oep}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{oep} + 2\text{LiOH} + 4\text{thf} \quad (2)$$
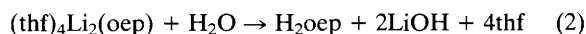
The remarkable solid-state structure of the product, determined unequivocally by *X*-ray crystallography (Figure 1),‡ consists of well separated tetrahedral Li(thf)₄⁺ cations and Li(oep)⁻ anions containing a square-planar lithium bound at a crystallographically imposed inversion centre in the middle of the porphyrin ring. The Li–N bonds are equal within experimental error [av. = 2.037(3) Å] [*cf. d*(Li–N) 1.942(5) Å

Figure 2. (a) 194.37 MHz ⁷Li NMR spectrum of [Li(thf)₄][Li(oep)] in (CD₃)₂SO at 41 °C. (b) ⁷Li NOESY spectrum in (CD₃)₂SO at 41 °C; *t*₁ was incremented in 256 steps and the data zero-filled to 512 words prior to Fourier transformation. Eight scans were recorded for each increment with *t*_mix 5 ms and a relaxation time of 200 ms.
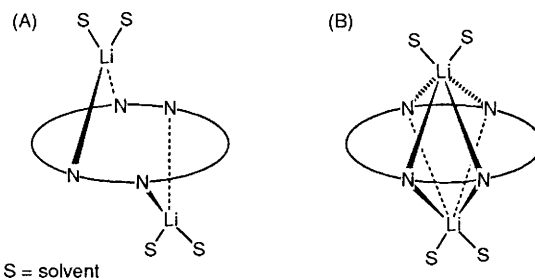
in the phthalocyanine radical Li(pc)⁵], and the planar porphyrin ring shows no evidence for puckering.⁶ Metrical parameters associated with the Li(thf)₄⁺ cation appear to be normal.⁷

In solution, ^{7}Li NMR[8] and conductivity measurements[9] suggest two different patterns of behaviour. In $(CD_3)_2SO$ at 25 °C two signals of equal intensity are observed: a sharp peak at δ 1.12 ($\nu_{1/2}$ 4 Hz) assigned to the tetrahedral Li(solvent)$_4^+$ species, and a much broader, high-field[8a] resonance at δ −11.55 ($\nu_{1/2}$ 52 Hz) due, presumably, to the heavily shielded square-planar lithium in the porphyrin ring.[10] These signals broaden considerably and coalesce on warming to a single broad peak (δ −6) at 100 °C (probe limit) consistent with lithium exchange; this was confirmed by a ^{7}Li NOESY experiment at 41 °C (Figure 2) which exhibits the expected cross-peaks for a two-site exchange process.[11] Similar results were observed in $(CD_3)_2CO$ but with a much lower coalescence temperature (−13 °C). By contrast, in more weakly donating solvent such as [$^2H_8$]thf, C_6D_6 and $N,N,N,'N'$-tetramethylethylenediamine (tmeda), the complex shows only a single, relatively sharp, temperature-independent signal at δ −12.8 in [$^2H_8$]thf, and δ −16.5 in C_6D_6 and tmeda.[12] In addition, conductivity measurements in acetonitrile and acetone accord with a 1 : 1 electrolyte, but in thf the complex is essentially non-conducting.[9] These data are interpreted as evidence for a solvent-separated, ion-pair complex (analogous to that seen in the solid state) in strong donor solvents such as Me_2SO or acetone, and a symmetrical, contact-ion-pair structure (possibly such as **A** or **B**) in poor donor solvents such as thf and tmeda.[10a,12,13] Reasons for the differing solid-state and solution structures when Li_2(oep) is crystallized from thf are, as yet, unclear, but we note that strong crystal-packing forces are known to play an important role in porphyrin chemistry.[14]

The corresponding tetra-aryl porphyrin derivatives are readily prepared by the above method, and we have now structurally characterized an analogous dilithium salt of *meso*-tetrakis-(3,4,5-trimethoxyphenyl)porphyrin, which also contains a square-planar lithium at the centre of an unruffled, planar porphyrin core.[15] The study of related derivatives with sodium and potassium and the use of these materials as synthetic reagents is underway.

I thank Dr Mark A. Gallop for assistance with the ^{7}Li NMR and NOESY experiments and a referee for helpful comments.

Received, 30th March 1990; Com. 0/01400A

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9 See: W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81. Conductivity data for Li_2(thf)$_4$(oep), in acetone (2.7 mM; 20 °C), Λ_M 100 Ω^{-1} cm^2 mol^{-1}; in MeCN (5.7 mM; 20 °C), Λ_M 93 Ω^{-1} cm^2 mol^{-1}; in thf (3.7 mM; 20 °C), Λ_M 0.11 Ω^{-1} cm^2 mol^{-1}. For comparison, Bu_4NPF_6 in thf (4.9 mM; 20 °C), Λ_M 4.9 Ω^{-1} cm^2 mol^{-1}; Bu_4NPF_6 in MeCN (4.5 mM; 20 °C), Λ_M 129 Ω^{-1} cm^2 mol^{-1}.

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13 Although aggregated structures may also be considered, it was found that the NMR data were independent of concentration in the range 0.3—0.9 M. See: W. White, in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, vol. V, p. 303.

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