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Functionalizable 5,5,10,10,15,15,20,20-Octaethylporphyrinogen Complexes of Early Transition Metals: Synthesis and Crystal Structure of Titanium-, Vanadium- and Chromium-(III) Derivatives and a Two-electron Oxidation of the Porphyrinogen Skeleton

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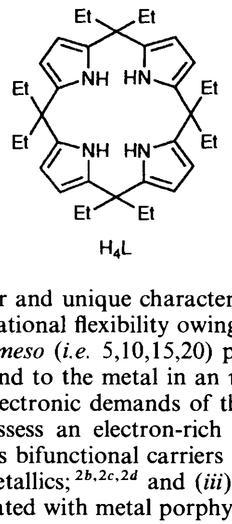
Titanium-, vanadium- and chromium-(III) complexes of 5,5,10,10,15,15,20,20-octaethylporphyrinogen (L) have been synthesized and characterized by X-ray crystallography. They show bifunctional binding of LiCl. A hemiporphyrin–hemiporphyrinogen chromium(III) derivative, which forms *via* a two-electron oxidation of L under slightly different reaction conditions, has also been isolated and the crystal structure determined.

5,5,10,10,15,15,20,20-Octaethylporphyrinogen H_4L[1] has recently been shown to display a highly interesting co-ordination chemistry.[2] The corresponding tetralithiated form $Li_4L{\cdot}4thf$ (thf = tetrahydrofuran),[2c] greatly aids the synthesis of transition-metal complexes of L under non-protic conditions.



H_4L

Some of the peculiar and unique characteristics of this ligand are: (*i*) the conformational flexibility owing to the presence of sp^3 carbons in the *meso* (*i.e.* 5,10,15,20) positions allows the pyrrolyl anion to bind to the metal in an η^5, η^3 or σ fashion depending on the electronic demands of the metal;[2b,2c,2e] (*ii*) complexes of L possess an electron-rich periphery and can therefore function as bifunctional carriers for ion-pair species and polar organometallics;[2b,2c,2d] and (*iii*) a variety of redox processes are associated with metal porphyrinogen complexes. Most notable are the reversible formation of one or two cyclopropane units,[2f,3] and a four-electron oxidative dealkylation at two *meso* positions.[4]

We now report the first series of early transition-metal M^{III} complexes of L [M = Ti, V or Cr] which have been synthesized by treating the corresponding $MCl_3{\cdot}3thf$ species with $Li_4L{\cdot}4thf$[2c] in toluene under very mild conditions [equation (1); M = Ti **1**, V **2** or Cr **3**].†

Complexes **1**–**3** have all been obtained as crystalline solids in good yield (*ca.* 70%) and on a scale of up to 10 g. Their magnetic moments (μ_{eff} = 1.75, **1**; 2.80, **2**; 3.70 μ_B, **3** at 300 K) are as expected for magnetically dilute monomeric species. The complexes are isostructural, and details are given only for the chromium(III) derivative. The structure of **3** (Fig. 1)‡ reveals a

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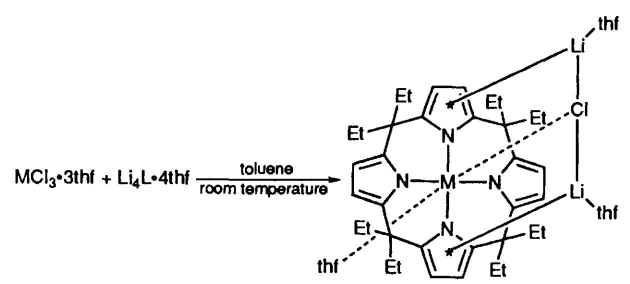
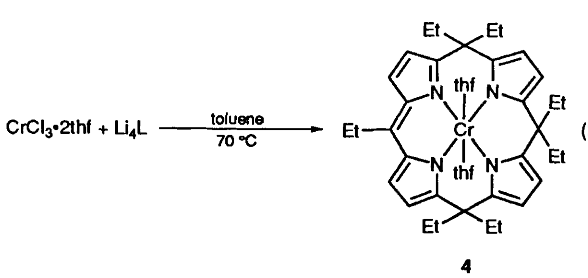
† The three complexes have been synthesized similarly. Details for **3**: $CrCl_3{\cdot}3thf$ (5.20 g, 13.88 mmol) was added to a toluene (400 cm^3) solution of $Li_4L{\cdot}4thf$ (11.91 g, 13.96 mmol) at 20 °C. A sudden reaction occurred with the formation of a red-brown suspension, which was stirred at 20 °C for 12 h. Lithium chloride was filtered off, and the solution evaporated to dryness. The residue was washed with *n*-hexane (100 cm^3) (70%) (Found: C, 67.60; H, 8.45; N, 6.72. $C_{48}H_{72}ClCrLi_2N_4O_3$ requires C, 67.80; H, 8.05; N, 6.60%) (**1**, Found: C, 67.95; H, 8.90; N, 6.70. $C_{48}H_{72}ClLi_2N_4O_3Ti$ requires C, 67.70; H, 8.45; N, 6.60. **2**, Found: C, 67.30; H, 8.45; N, 6.70. $C_{48}H_{72}ClLi_2N_4O_3V$ requires C, 67.50; H, 8.45; N, 6.55%). Crystals suitable for X-ray analysis were obtained from a dilute solution of *n*-hexane.

‡ Crystal data. **1**, $C_{48}H_{72}ClLi_2N_4O_3Ti$, $M = 850.4$, monoclinic, space group $C2/c$, $a = 25.205(3)$, $b = 12.662(2)$, $c = 16.525(5)$ Å, $\beta = 116.94(1)°$, $U = 4702(2)$ Å^3, $Z = 4$, $F(000) = 1828$, $D_c = 1.201$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 2.77 cm^{-1}, 0.26 × 0.31 × 0.38 mm. **2**, $C_{48}H_{72}ClLi_2N_4O_3V$, $M = 853.4$, monoclinic, space group $C2/c$, $a = 25.257(3)$, $b = 12.659(2)$, $c = 16.432(3)$ Å, $\beta = 117.05(1)°$, $U = 4679(2)$ Å^3, $Z = 4$, $F(000) = 1832$, $D_c = 1.211$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 3.03 cm^{-1}. **3**, $C_{48}H_{72}ClCrLi_2N_4O_3$, $M = 854.5$, monoclinic, space group $C2/c$, $a = 25.130(1)$, $b = 12.424(6)$, $c = 16.420(5)$ Å, $\beta = 117.28(4)°$, $U = 4556(4)$ Å^3, $Z = 4$, $F(000) = 1836$, $D_c = 1.246$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 3.46 cm^{-1}. The structure of complex **3** was solved by the heavy atom method starting from a three-dimensional Patterson map and anisotropically refined for the non-hydrogen atoms except for C(33) and C(34) of a thf molecule which were found to be statistically distributed over two positions (A and B). The hydrogen atoms, apart from those related to the disordered carbons, were located from a Fourier-difference map and introduced as fixed atom contributions in the last stage of the refinement ($U_{iso} = 0.05$ Å^2). For 2047 unique observed reflections [$I > 2\sigma(I)$] collected at 143 K ($6 < 2\theta < 50°$) and corrected for absorption, $R = 0.073$, $R' = 0.085$) $\{R = \Sigma|\Delta F|/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$, $w = k/[\sigma^2(F_o) + g|F_o|^2]$, where $k = 2.4272$ and $g = 0.030\}$. All calculations were carried out using SHELX 76[6] on an Encore 91 computer. **4**, $C_{42}H_{59}CrN_4O_2$, $M = 704.0$, orthorhombic, space group $Pbca$, $a = 20.191(5)$, $b = 23.119(6)$, $c = 15.608(4)$ Å, $U = 7286(3)$ Å^3, $Z = 8$, $F(000) = 3032$, $D_c = 1.284$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 3.45 cm^{-1}, 0.09 × 0.21 × 0.24 mm. The structure was solved as for **3** (no disorder) using SHELX 92[7] and was based on all the 7497 unique reflections collected at 143 K ($6 < 2\theta < 60°$) and corrected for absorption, $R = 0.070$ for 1922 unique observed reflections [$I > 2\sigma(I)$], $wR_2 = 0.213$ $\{R = \Sigma|\Delta F|/\Sigma|F_o|$, $wR_2 = [\Sigma(w\Delta F^2)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (0.0874p)^2]$, where $p = (F_o^2 + 2F_c)/3\}$. All calculations were carried out on an Encore 91 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters for **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



(1)



(2)

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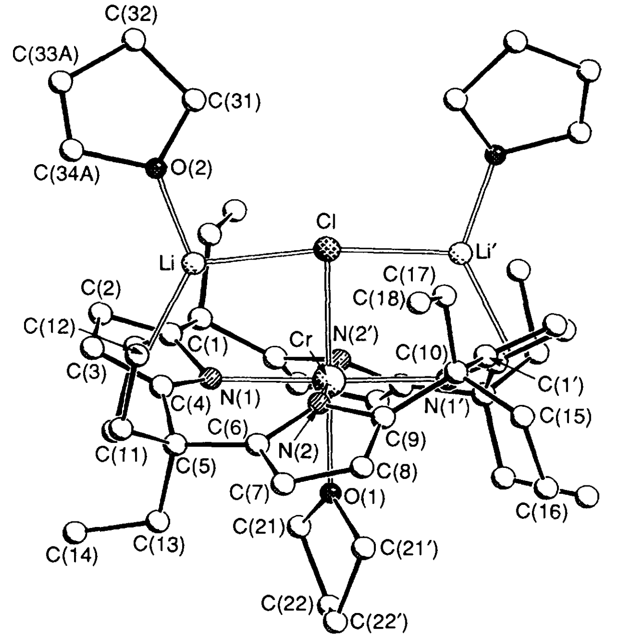

Fig. 1 A SCHAKAL[5] view of complex **3**. Selected bond distances (Å) and angles (°): Cr–Cl 2.435(3), Cr–O(1) 2.076(8), Cr–N(1) 2.053(4), Cr–N(2) 2.039(8), Li–Cl 2.336(16), Li–Cp 1.968(15), Li–N(1) 2.279(16), Li–C(1) 2.279(18), Li–C(2) 2.286(15), Li–C(3) 2.330(17), Li–C(4) 2.305(17); N(2′)–Cr–N(2) 179.3(3), N(2′)–Cr–N(1) 90.2(3), N(1′)–Cr–N(1) 177.4(3), N(1)–Cr–N(2) 89.8(3), Cl–Cr–O(1) 180.0(–), Cr–Cl–Li 85.6(4), Li–Cl–Li′ 171.1(5). Primed atoms derived by the transformation of $-x$, y, $0.5 - z$. Cp refers to the centroid of the pyrrole ring containing N(1)

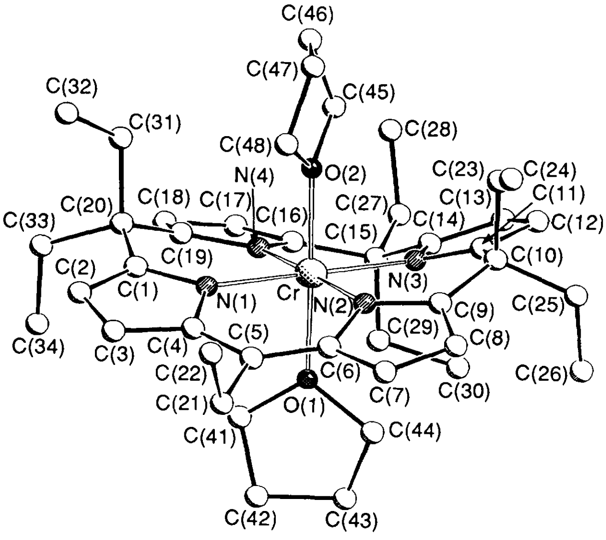

Fig. 2 A SCHAKAL[5] view of complex **4**. Selected bond distances (Å) and angles (°): Cr–N(1) 2.059(4), Cr–N(2) 2.067(5), Cr–N(3) 2.016(4), Cr–N(4) 2.015(5), Cr–O(1) 2.034(5), Cr–O(2) 2.032(5), C(4)–C(5) 1.366(10), C(5)–C(6) 1.398(9), C(5)–C(21) 1.543(9), C(1)–N(1) 1.367(8), C(4)–N(1) 1.428(8), C(6)–N(2) 1.404(8), C(9)–N(2) 1.355(8), C(11)–N(3) 1.410(9), C(14)–N(3) 1.406(8), C(16)–N(4) 1.405(9), C(19)–N(4) 1.397(9); N(3)–Cr–N(4) 91.9(2), N(2)–Cr–N(4) 177.6(2), N(2)–Cr–N(3) 88.9(2), N(1)–Cr–N(4) 90.0(2), N(1)–Cr–N(3) 178.1(2), N(1)–Cr–N(2) 89.2(2), O(1)–Cr–O(2) 175.5(2), C(4)–C(5)–C(21) 116.0(6), C(4)–C(5)–C(6) 127.8(6), C(6)–C(5)–C(21) 116.2(6)

bifunctional nature in binding LiCl, using the periphery for Li^+ and the metal centre for Cl^-, and thus their potential use in carrying polar organometallics.[2c,2e]

The molecule has a crystallographically imposed C_2 symmetry, through Cr, Cl and O(1). The chromium atom lies almost in the plane of the N_4 core [displaced by 0.017(2) Å]. The Cr–N bond distances are close to those generally observed in tetrapyrrole derivatives,[8] although the Cr–Cl bond distance is rather long, this is in accord with the triply bridging bonding mode of the chlorine atom. The narrow range of the Li–N and Li–C bond distances [2.279(16)–2.330(17) Å] suggests an η^5-pyrrole–Li bonding mode. The overall conformation is similar to that observed previously,[2d] the dihedral angles between the N(1), C(1)–C(4) and N(2), C(6)–C(9) pyrrole rings and the N_4 core being 151.5(3) and 149.6(3)° respectively.

Reaction (1) is highly affected by the thf content of the reagents. In fact, when the reaction was carried out with Li_4L synthesized in hexane and a partially solvated form of $CrCl_3$, *i.e.* $CrCl_3$•2thf, complex **4** formed [equation (2)]. The reaction was carried out in toluene at 70 °C for 6 h. The porphyrinogen tetraanion undergoes, *via* an as yet unclear pathway, a two-electron oxidation with the loss of one of the *meso*-ethyl groups to afford a *meso*-heptaethyl hemiporphyrin–hemiporphyrinogen Cr^{III} complex **4*** [$\mu_{eff} = 3.82\ \mu_B$ at 293 K] in the form of green crystals. Complexes **1**–**3** can be plausible intermediates in the dealkylation of L.

The structure of complex **4** is shown in Fig. 2. Co-ordination around chromium is pseudo-octahedral. The metal lies just 0.015(1) Å out of the equatorial plane. However, the Cr–N bond distances are significantly shorter [Cr–N(3) and Cr–N(4)] in the hemiporphyrinogen than in the hemiporphyrin [Cr–N(1) and Cr–N(2)] moiety.[8] The bond distances within the half-hemiporphyrin fragment of **4** strongly support complete electron delocalization. The partial aromatization results in a slightly different conformation to that usually observed,[2] the dihedral angles between the N_4 core and the pyrrole rings [162.6(2), 159.8(2), 161.0(2), 168.4(2)°] indicating a flattened saddle-shape conformation. Furthermore, the chromium atom is displaced from the pyrrole rings containing N(1), N(2), N(3) and N(4) by 0.192(1), 0.410(1), 0.489(1) and 0.073(2) Å respectively.

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* Satisfactory analytical data have been obtained (Found: C, 71.30; H, 8.10; N, 7.60. $C_{42}H_{59}CrN_4O_2$ requires C, 71.60; H, 8.40; N, 8.00%).

We emphasize this preliminary step in the aromatization of L involving a metal-mediated dealkylation. Aromatization involving double dealkylation of two *meso* positions has recently been reported in the reaction between $[RuCl_2(PhCN)_4]$ and $Li_4L{\cdot}4thf$ carried out under rather drastic conditions.[4] The latter reaction is formally a four-electron oxidation of L, the preliminary two-electron step being exemplified by reaction (2).

Acknowledgements

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