The π and σ Bonding Modes of *meso*-Octaethylporphyrinogen to Transition Metals: the X-Ray Structure of a *meso*-Octaethylporphyrinogen–Zirconium(IV) Complex and of the Parent *meso*-Octaethylporphyrinogen Ligand

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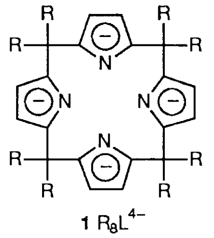
The *meso*-octaethylporphyrinogen tetraanion provides σ and π binding pyrrolyl anions to electron poor transition metals, as shown in the structure of the *meso*-octaethylporphyrinogen–zirconium(IV) complex containing two η^5 and two σ metal-bonded pyrrolyl anions.

The deprotonated form of *meso*-octaalkylporphyrinogen **1**[1,2] is a tetrapyrrolyl tetraanion which, owing to its conformational flexibility,[3] may bind to a metal in a σ and/or π form depending on the demands of the metal. It is isoelectronic with a cyclic form of a tetracyclopentadienyl tetraanion. The number of valence electrons it can provide to a metal is $4(2 + n)$, where n (ranging from 0 to 4) is the number of η^5-bonded pyrrolyl anions.

Complexation of transition metals by **1** was reported recently.[4] In addition to the electronic flexibility, the use of **1**



1 R_8L^{4-}

has the advantage that it stabilizes high oxidation states of metals and favours the intramolecular interaction between unsaturated metals and *meso*-alkyl substituents.[4]

The X-ray analysis of the *meso*-octaethylporphyrinogen **2**†‡ is shown in Fig. 1. Its synthesis was analogous to that of the octamethyl analogue.[1] This is the first X-ray analysis§ on a *meso*-octaalkylporphyrinogen; it crystallizes with acetone in a 2:1 molar ratio.

The asymmetric unit contains two crystallographically independent molecules A and B, and the values discussed refer to the A molecule only. Molecules are associated in dimers by an acetone molecule *via* a weak NH · · · O(acetone) · · · HN bridging hydrogen bond. The four N atoms are almost coplanar, the average deviation being 0.104(2) Å, and are alternately tilted up and down with respect to the N_4 plane. The dihedral angles between opposite pyrrole rings are 23.6(1) and 58.6(1)°. Significant parameters for defining the overall conformation of **2** seem to us to be the dihedral angles the pyrrole rings form with the N_4 plane, and these are listed in the caption to Fig. 1.

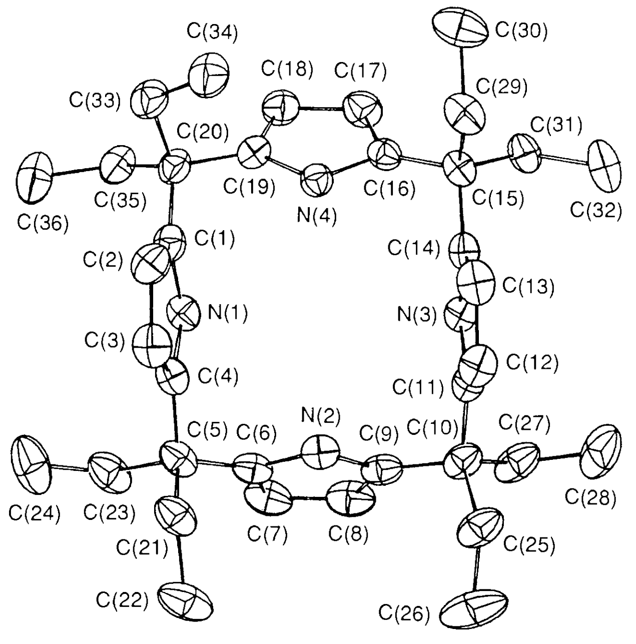


Fig. 1 An ORTEP drawing (30% probability ellipsoids) for molecule A for compound **2** (values in square brackets refer to molecule B). Bond distances (Å): N(1)–C(1) 1.382(3) [1.377(3)], N(1)–C(4) 1.378(3) [1.370(3)], N(2)–C(6) 1.373(3) [1.369(4)], N(2)–C(9) 1.380(4) [1.376(3)], N(3)–C(11) 1.373(4) [1.378(3)], N(3)–C(14) 1.370(3) [1.384(3)], N(4)–C(16) 1.377(3) [1.381(4)], N(4)–C(19) 1.379(3)]. Relevant dihedral angles (°): PL(1)–N_4 107.1(1) [108.1(1)], PL(2)–N_4 112.7(1) [118.2(1)], PL(3)–N_4 96.5(1) [99.0(1)], PL(4)–N_4 125.9(1) [117.8(1)]. PL(1), PL(2), PL(3) and PL(4) refer to the planes of the aromatic rings containing N(1), N(2), N(3) and N(4) respectively. N_4 indicates the mean least-squares plane containing N(1), N(2), N(3) and N(4).

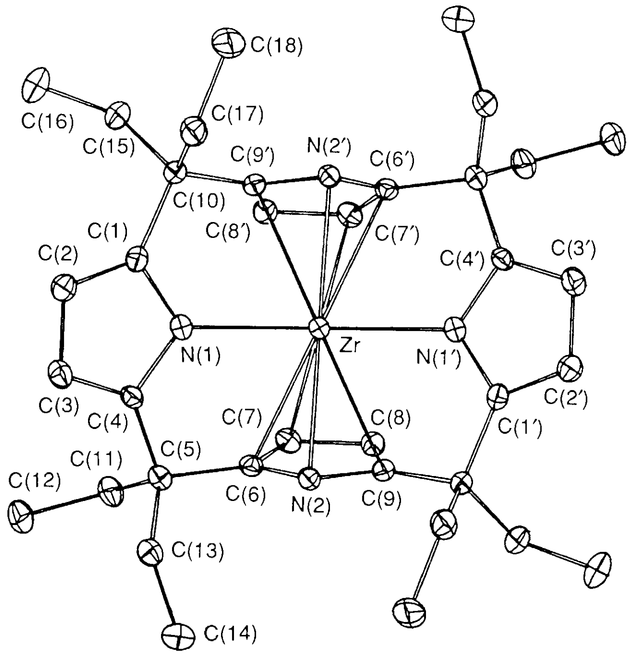


Fig. 2 An ORTEP drawing for complex **4** (30% probability ellipsoids). The coordinated thf molecule has been omitted for clarity. Bond distances (Å): Zr–N(1) 2.261(3), Zr–N(2) 2.446(2), Zr–C(6) 2.531(2), Zr–C(7) 2.552(2), Zr–C(8) 2.535(2), Zr–C(9) 2.494(2), Zr–O(1) (thf) 2.235(3), Zr–cp 1.843(3). Bond angles (°): N(1)–Zr–N(1′) 164.5(1), N(1)–Zr–cp 95.9(1), N(1)–Zr–cp′ 90.1(1), cp–Zr–cp′ 134.7(1), N(1)–Zr–O(1) 82.3(1), O(1)–Zr–cp 112.7(1). Relevant dihedral angles (°): A–N_4 151.4(1), B–N_4 73.6(1). A and B refer to the planes of the aromatic rings containing N(1) and N(2) respectively. N_4 indicates the mean least-squares plane containing N(1), N(2), N(1′) and N(2′). cp refers to the centroid of the aromatic ring containing N(2). Prime indicates the transformation $-x, y, 0.5 - z$.

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† Satisfactory analytical data have been obtained.

‡ ^1H NMR data: compound **2** (δ, CD_2Cl_2) at 325 K: 6.93 (br.s, 4 H, NH), 5.92 (s, 4 H, C_4H_2N), 5.90 (s, 4 H, C_4H_2N), 1.82 (q, 16 H, CH_2) and 0.62 (t, 24 H, Me); at 293 K: 6.95 (br.s, 4 H, NH), 5.90 (s, 4 H, C_4H_2N), 5.88 (s, 4 H, C_4H_2N), 1.80 (br.m, 16 H, CH_2) and 0.58 (t, 24 H, Me). Complex **4** (δ, C_7H_8) at 320 K: 6.25 (s, 8 H, C_4H_2N), 3.22 (m, 4 H, thf), 2.66 (m, 4 H, CH_2), 2.14 (m, 12 H, CH_2), 1.31 (m, 4 H, thf), 1.23 (t, 12 H, Me) and 1.07 (t, 12 H, Me); at 290 K: 6.31 (s, 4 H, C_4H_2N), 6.24 (s, 4 H, C_4H_2N), 3.25 (m, 4 H, thf), 2.70 (m, 4 H, CH_2), 2.15 (m, 12 H, CH_2), 1.30 (m, 4 H, thf), 1.25 (t, 12 H, Me) and 1.09 (t, 2 H, Me).

§ *Crystal data* for **2**: $C_{36}H_{52}N_4 \cdot 0.5C_3H_6O \cdot 0.10H_2O$, $M = 572.2$, monoclinic, space group $P2_1/n$, $a = 20.484(2)$, $b = 24.375(2)$, $c = 15.146(2)$ Å, $\beta = 108.89(2)°$, $U = 7158.6(16)$ Å^3, $Z = 8$, $D_c = 1.062$ g cm^{-3}, Cu-Kα radiation ($\lambda = 1.54178$ Å), μ(Cu-Kα) = 4.51 cm^{-1}; crystal dimensions $0.32 \times 0.56 \times 0.82$ mm^3. The structure was solved by direct methods and the non-hydrogen atoms were anisotropically refined [with the exception of the methyl carbon C(22B), the acetone solvent molecule and the O(2) water atom] by blocked full-matrix least-squares. For 7424 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 140°$, the R value is 0.053 ($R_w = 0.061$). Carbon atom C(22B) was found to be disordered over two positions with site occupation factors of 0.6 and 0.4 respectively. The hydrogen atoms put in calculated positions were introduced as fixed contributors prior to the final stage of refinement.

Crystal data for **4**: $C_{36}H_{48}N_4Zr \cdot C_4H_8O$, $M = 700.1$, orthorhombic, space group *Pbcn*, $a = 12.935(3)$, $b = 12.704(3)$, $c = 21.949(3)$ Å, $U = 3557.5(13)$ Å^3, $Z = 4$, $D_c = 1.307$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 3.38 cm^{-1}; crystal dimensions $0.43 \times 0.45 \times 0.48$ mm^3. The structure was solved by the heavy atom Patterson method and the non-hydrogen atoms anisotropically refined by full-matrix least-squares. For 3105 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on an Enraf-Nonius CAD 4 diffractometer in the range $6 < 2\theta < 60°$, the R value is 0.037 ($R_w = 0.041$). The carbon atom C(22) was found to be disordered over three positions each with site occupation factor of 0.3333. The hydrogen atoms located from difference Fourier maps were introduced as fixed contributors prior to the final stage of refinement. All calculations were carried out using SHELX86 and SHELX76.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$$\underset{\mathbf{2}}{\mathrm{Et_8LH_4}} \xrightarrow[\mathrm{thf}]{\mathrm{LiBu}} \underset{\mathbf{3}}{\mathrm{Et_8LLi_4(thf)}_n} \xrightarrow[-\mathrm{LiCl}]{\mathrm{ZrCl_4\cdot 2thf}} \underset{\mathbf{4}}{[\mathrm{Et_8LZr\cdot(thf)}]} \quad (1)$$

thf = tetrahydrofuran

The use of zirconium(IV) to study complex formation with **1** was mainly dictated by its d^0 configuration, its rich cyclopentadienyl chemistry[5] and the existence of a single report on zirconium-pyrrolyl anion[6] ligation showing that the σ interaction is the preferred one. Complex **4** was isolated from the reaction sequence (1) in a good yield (94%) as pale yellow crystals.†‡

A simplified view of the structure of **4** is shown in Fig. 2 with some structural parameters.§ Two of the pyrrolyl anions are η^5-bonded and two are σ-bonded *via* the nitrogen atoms. The angle between zirconium and the centroids of the two η^5-pyrrolyl units [134.7(1)°] and the Zr–η^5-pyrrolyl distance [1.843(3) Å] are very close to the values found in $[(\eta^5\text{-}C_5H_5)_2Zr(\sigma\text{-}NC_4H_4)_2]$ **5**[6] for the η^5-cyclopentadienyl ligands. A relevant difference is the N(1)–Zr–N(1′) angle for the two σ-bonded pyrrolyl anions, which is 164.5(1)° in **4** *vs.* 95.68(8)° in complex **5**. This leads to a description of the coordination geometry, when thf is considered, as a pseudo-trigonal bipyramid, with N(1) and N(1′) occupying the axial positions. The widening of the N(1)–Zr–N(1′) angle leads to coordinative unsaturation of the metal, which is filled by the fifth ligand, thf, a phenomenon not observed in $(C_5H_5)_2ZrX_2$ complexes, where the metal shows coordinative saturation.

The ^1H NMR spectrum of **4**‡ shows two distinct singlets for the σ- and η^5-pyrrolic protons at room temperature, collapsing to a singlet at 320 K. This suggests a fast exchange role, between the σ- and η^5-forms of the pyrrolyl anion, at high temperature. The ligand **1** adapts its bonding modes to the electronic demands of the metal; the two metal complexes we recently reported contain the σ-binding form exclusively.[4]

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