

Multimetallc porphyrin monomers

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Complexation of triosmium clusters to pyridyl functionalised metalloporphyrins gives heterometallic derivatives that possess the overall recognition and spectroscopic properties of the porphyrin fragment, while incorporating the electronic and structural characteristics of the cluster.

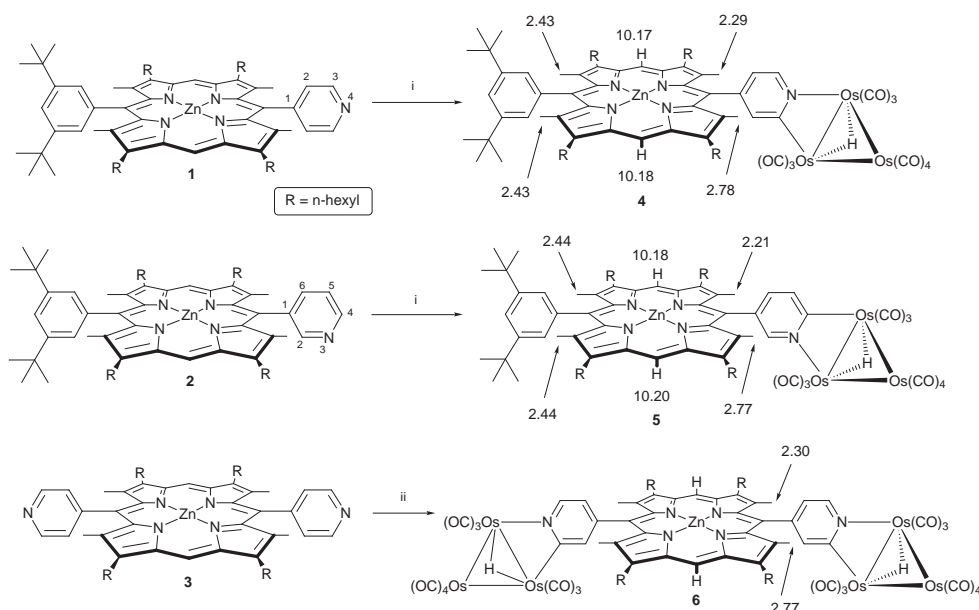
In recent years a range of porphyrin complexes incorporating numerous metal centres have been prepared as components for molecular-scale devices,¹ conjugated porphyrin polymers,² supramolecular systems³ and light harvesting models.⁴ These designs exploit the ability of the metal centre to control the manner in which a supramolecular assembly is constructed, and therefore dictate the properties of the final arrangement. Here we report on the preparation and characterisation of a series of triosmium cluster zinc porphyrin derivatives.

The porphyrin monomers **1–3** were synthesised by routes analogous to those previously reported.⁵ Their key feature is the incorporation of one or more peripheral pyridyl groups available for metallation by an osmium cluster.⁶ The pyridyl ring nitrogen is situated in either the 3-position, from which we might expect two cluster substitution products, or the 4-position from which only one product is possible. Treatment of **1** or **2** with Os₃(CO)₁₀(NCMe)₂ (1.1 equiv.) in dichloromethane at room temperature affords, after purification by preparative TLC (SiO₂, hexane : chloroform : ethyl acetate, 20 : 1 : 1), the metallated products **4** and **5** in 42% (*R_f* = 0.28) and 31% (*R_f* = 0.32) yields respectively (Scheme 1). Under similar reaction conditions, the bis-coordinated cluster compound **6** was isolated in 35% yield from the reaction of Os₃(CO)₁₀(NCMe)₂ (2.2 equiv.) with **3** after preparative TLC (SiO₂, hexane : chloroform : ethyl acetate, 10 : 1 : 1, *R_f* = 0.29).[†]

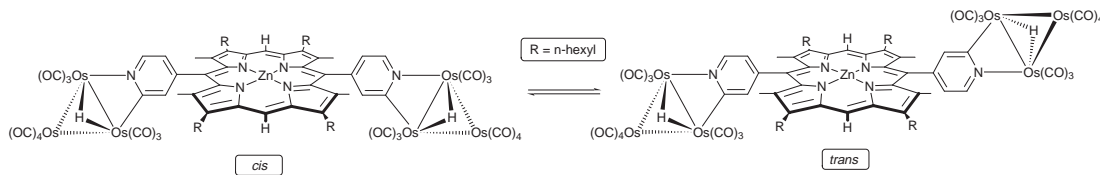
Single crystals of **4** and **5** suitable for X-ray crystallographic analysis were obtained by slow solvent diffusion of methanol into a toluene solution at room temperature.[‡] The molecular structure of **4** is as expected: the pyridyl ring of the porphyrin is orthometallated and bridges one edge of the Os₃ triangle to afford a four membered ring containing Os, Os, C and N with the hydride ligand bridging one Os–Os edge. This is consistent with the structure of [(μ-H)Os₃(CO)₁₀(μ-NC₅H₄)].⁶ The molecular structure of **5** is isostructural with **4**, the Os₃ unit residing on the 3- and 4-positions on the pyridyl ring (Scheme 1). The unoccupied site nearest to the porphyrin ring (2-position) is presumably inhibited to metallation on steric grounds.

The ¹H NMR spectra of **4** and **5** are consistent with the unsymmetrical nature of the molecule: in the spectrum of **4** we observe the porphyrin ring methyl groups as three singlets in a 1 : 2 : 1 intensity ratio. The peripheral methyl groups nearest to the appended cluster are inequivalent, appearing as two singlets because the cluster is not symmetrically disposed about the pyridine ring. However, the furthest methyl groups are unaffected by the presence of the cluster and are effectively equivalent, giving rise to one singlet. The protons of the first methylene group of the hexyl side chains are diastereotopic; additionally two equal intensity *meso* proton resonances are observed. Both of these observations are consistent with the expected slow rotation on the NMR chemical shift timescale about the cluster substituted aryl–porphyrin bond. Since complex **5** follows the same cluster coordination mode as **4**, the spectrum of **5** exhibits similar resonances to **4**.

For **6** the coordinated clusters can be *cis* or *trans* to one another (relative to the porphyrin plane) as shown in Scheme 2.[§] At ambient temperature the ¹H NMR spectrum of **6** exhibits one



Scheme 1 Reagents and conditions: i, 1.1 equiv. Os₃(CO)₁₀(NCMe)₂, CH₂Cl₂, RT, 3 h; ii, 2.2 equiv. Os₃(CO)₁₀(NCMe)₂, CH₂Cl₂, RT, 4 h. Selected chemical shifts for complexes **4–6**.



Scheme 2 Exchange between the *cis* and *trans* isomeric forms of **6**

meso resonance which splits into a 1 : 2 : 1 multiplet at 280 K indicating the presence of at least two species (*cis* and *trans* isomers). A NOESY experiment at 280 K shows NOE cross-peaks for the outer signals, H_a and H_b , of the 1 : 2 : 1 multiplet only with the central resonance, H_c indicating that the *cis* and *trans* isomers are interconverting on the NOESY timescale. For the methyl groups at room temperature two equal intensity resonances are observed, which remain essentially unchanged at 280 K. The NOESY spectrum at 280 K reveals that these methyl resonances exhibit exchange cross-peaks with each other; in addition the bridging hydride shows a strong NOE cross-peak to the methyl resonance at 2.30 ppm, and a weak NOE cross-peak to the resonance at 2.77 ppm due to magnetisation transfer (Fig. 1). The above observations show that the *meso* protons are sensitive to the overall symmetry of the molecule, while the methyl resonances are only sensitive to the local environment dominated by the orientation of the clusters.⁷

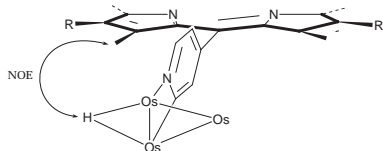


Fig. 1 The orientation of the coordinated cluster relative to the peripheral methyl groups. The CO ligands of the cluster have been omitted.

The absorption spectra of **4–6** were similar to **1–3**, except for a hypochromic shift of 4, 3, and 7 nm of the Soret band respectively and an increase in absorption between 220 and 420 nm where the cluster absorption bands are evident. More pronounced changes were observed in the luminescence spectra of **4–6**. At both room temperature and 77 K the fluorescence spectra intensities and excited state lifetimes of **4–6** were somewhat quenched compared to **1–3**.[¶] Excitation spectra acquired at room temperature at 590 nm, where the fluorescence of the porphyrin is observed, indicate the absence of the cluster bands. In addition, the phosphorescence bands of **4–6** compared to **1–3** at 77 K show an increase in intensity and a decrease in the triplet lifetime. Collectively, these observations suggest that the quenching observed can be ascribed to a heavy atom effect arising from the cluster rather than to energy- or electron-transfer processes between the cluster and the porphyrin.

The mild preparation and spectroscopic eloquence of complexes **4–6** provide potential for the development of functional and structural derivatives. Variation in the nature of the appended cluster, and the porphyrin periphery can be envisaged.

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Notes and References

† Selected spectroscopic data for **4**: ¹H NMR (CDCl₃, 400 MHz) δ 10.18 (s, 1 H), 10.17 (s, 1 H), 8.56 (d, *J* 5.6 Hz, 1 H), 8.26 (d, *J* 1.5 Hz, 1 H), 7.92 (br s, 2 H), 7.82 (t, *J* 1.8 Hz, 1 H), 7.53 (dd, *J* 2.0, 5.8 Hz, 1 H), 3.94 (m, 8 H), 2.78 (s, 3 H), 2.43 (s, 6 H), 2.29 (s, 3 H), 2.16 (m, 8 H), 1.74 (m, 8 H), 1.51 (s, 18 H), 1.48 (m, 8 H), 1.38 (m, 8 H), 0.89 (m, 12 H), –14.83 (s, 1 H); FAB *m/z* 1884.5 (M⁺); IR (CH₂Cl₂) ν_{CO}/cm^{-1} 2103 (m), 2063 (s), 2052 (s), 2018 (br, s), 2010 (br, s), 1989 (br, m), 1969 (br, w); λ_{max} (CH₂Cl₂)/nm 414, 540,

575 (log [$\epsilon/M^{-1} cm^{-1}$] 5.3, 4.1, 3.8). For **5**: ¹H NMR (CDCl₃, 400 MHz) 10.20 (s, 1 H), 10.18 (s, 1 H), 8.92 (d, *J* 1.4 Hz, 1 H), 7.97 (dd, *J* 2.0, 7.9 Hz, 1 H), 7.92 (br s, 2 H), 7.83 (t, *J* 1.7 Hz, 1 H), 7.80 (d, *J* 7.6 Hz, 1 H), 3.96 (m, 8 H), 2.77 (s, 3 H), 2.44 (s, 6 H), 2.21 (s, 3 H), 2.19 (m, 8 H), 1.74 (m, 8 H), 1.51 (s, 18 H), 1.46 (m, 8 H), 1.41 (m, 8 H), 0.92 (m, 12 H), –14.74 (s, 1 H); FAB *m/z* 2621.1 (M⁺); IR (CH₂Cl₂) ν_{CO}/cm^{-1} 2103 (m), 2063 (vs), 2052 (s), 2017 (vs), 2008 (sh), 1998 (sh), 1970 (sh). λ_{max} (CH₂Cl₂)/nm 414, 540, 575 (log [$\epsilon/M^{-1} cm^{-1}$] 5.2, 4.0, 3.7). For **6**: ¹H NMR (CDCl₃, 400 MHz) 10.17 (s, 2 H), 8.57 (d, *J* 5.6 Hz, 2 H), 8.23 (d, *J* 1.0 Hz, 2 H), 7.48 (dd, *J* 1.7, 4.7 Hz, 2 H), 3.95 (m, 8 H), 2.77 (s, 6 H), 2.30 (s, 6 H), 2.17 (m, 8 H), 1.72 (m, 8 H), 1.49 (m, 8 H), 1.35 (m, 8 H), 0.91 (m, 12 H), –14.83 (s, 2 H); FAB *m/z* 2621.1 (M⁺); IR (CH₂Cl₂) ν_{CO}/cm^{-1} 2103 (m), 2063 (vs), 2052 (s), 2017 (br, s), 2008 (br, s), 1998 (br, m), 1970 (br, w); λ_{max} (CH₂Cl₂)/nm 417, 541, 578 (log [$\epsilon/M^{-1} cm^{-1}$] 5.3, 4.1, 3.8).

‡ Crystal data for **4**: C₇₇H₉₁N₅O₁₀Os₂Zn, 0.35 × 0.25 × 0.20 mm, *T* = 180(2) K, *M* = 1882.5, triclinic, space group *P*1̄, *a* = 18.139(5), *b* = 19.184(7), *c* = 12.811(5) Å, α = 103.81(3), β = 108.47(3), γ = 102.88(3)°, *U* = 3884(2) Å³, *Z* = 2, *D_c* = 1.60 Mg m^{–3}, λ = 0.71069 Å, *F*(000) = 1852, μ = 5.253 mm^{–1}, *R*₁ = 0.0672 [18337 reflections with *I* > 2 σ (*I*)], *wR*₂ = 0.1580 for 17790 independent reflections and 810 parameters. The crystal data for **4** were collected on a Rigaku AFC7r diffractometer. For **5**: C₇₇H₉₁N₅O₁₀Os₂Zn, 0.12 × 0.10 × 0.10 mm, *T* = 180(2) K, *M* = 1882.5, triclinic, space group *P*1̄, *a* = 18.135(5), *b* = 19.048(6), *c* = 12.739(5) Å, α = 103.55(3), β = 108.74(3), γ = 102.88(3)°, *U* = 3833(2) Å³, *Z* = 2, *D_c* = 1.63 Mg m^{–3}, λ = 0.71069 Å, *F*(000) = 1852, μ = 5.324 mm^{–1}, *R*₁ = 0.0615 [36807 reflections with *I* > 2 σ (*I*)], *wR*₂ = 0.1624 for 13666 independent reflections and 832 parameters. The crystal data for **5** were collected on a R-Axis IIC diffractometer. All non-hydrogen atoms except the disordered carbons of the hexyl chains are anisotropic in both crystals. CCDC 182/989.

§ Each cluster has the possibility of the hydride bridges being *cis* (i.e. both at the back or front) or *trans*, with one at the front and one at the back (Scheme 2). Presumably both the *cis* and *trans* isomers of **6** consist of a mixture of front/front and front/back forms, but the distance between the clusters is so great that the two isomers are spectroscopically indistinguishable.

¶ The fluorescence lifetimes at 298 K were 0.76, 0.70, 0.76, 0.30, 0.37 and 0.21 ns for **1–6** respectively.

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