COMMUNICATION

Dalton
www.rsc.org/dalton

Structural control of metalloporphyrinogens by macrocycle modification: steric blocking of the macrocyclic cavity through *trans*-*N*,*N*′-dimethylation

Jun Wang,[a] Michael G. Gardiner,*[a] Evan J. Peacock,[b] Brian W. Skelton[c] and Allan H. White[c]

[a] *School of Chemistry, University of Tasmania, Private Bag 75, Hobart, TAS, 7001, Australia. E-mail: Michael.Gardiner@utas.edu.au;*

[b] *Central Science Laboratory, University of Tasmania, Private Bag 74, Hobart, TAS, 7001, Australia*

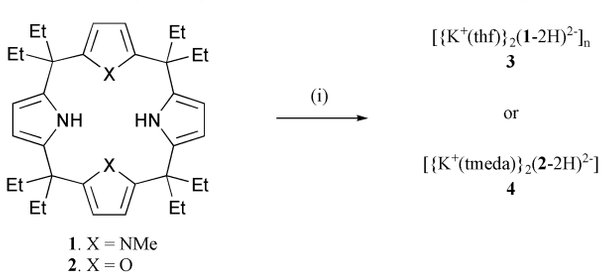
[c] *Chemistry Department, University of Western Australia, Crawley, WA, 6009, Australia*

Received 28th October 2002, Accepted 2nd December 2002
First published as an Advance Article on the web 11th December 2002

Reactions of potassium metal with *trans*-*N*,*N*′-dimethyl-*meso*-octaethylporphyrinogen or *meso*-octaethyldioxaporphyrinogen afford dipotassium complexes with one potassium cation excluded from the cavity on steric grounds in the former case, or both potassium cations bound inside the macrocyclic cavity in the latter case.

A decade of metalloporphyrinogen chemistry[1] has established the macrocyclic system as being capable of providing a flexible coordination framework for an extensive range of s-, d- and f-block metals.† Applications being pursued include nitrogen fixation, molecular batteries and their use as non-participative ligands for the stabilisation of novel chemistry. Control over the stoichiometry and/or structure of metalloporphyrinogen complexes has been an unsolved problem in some areas, where alkali metal inclusion and dinuclear complex formation are frequently observed. These features stem from the high anionic charge of the tetrametallated macrocycle and the ability of the macrocycles to bind more than one metal in the macrocyclic cavity. Whilst numerous modifications of porphyrinogens have been reported for supramolecular applications such as anion recognition,[2] the range of macrocycles studied in organometallic applications has been limited solely to variations *via* the *meso*-substituents which have had minimal structural influence on the derived complexes. Herein, we report the synthesis and structure of the first complex of a *N*-modified porphyrinogen (and a related analogue), whose structural features highlight the greatly improved reactivity control in metalloporphyrinogen chemistry that is possible through modification of the macrocycles, whilst achieving a desirable reduction in the anionic charge of the metallated macrocycles.

The reactions of potassium metal with macrocycles **1** and **2**, respectively,[3,4] in thf (thf = tetrahydrofuran) reach completion after several hours reflux. Complex **3** precipitated as a crystalline polymeric thf adduct after adding toluene to a saturated thf solution. Complex **4** was obtained as a crystalline monomeric tmeda (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) adduct from a thf/petroleum ether (bp 40–60 °C) solution in the presence of 6 equivalents of tmeda, Scheme 1.‡ The products have been analysed by ^{1}H and ^{13}C NMR spectroscopy,§ microanalysis and the solid state structures established by single crystal X-ray crystallography.¶



1. X = NMe
2. X = O

Scheme 1 Reagents and conditions: i, K, thf, then toluene (for **3**) or petroleum ether (bp 40–60 °C)/6 equivalents tmeda (for **4**).

Complex **3** is polymeric in the solid state, Fig. 1 . One potassium cation is bound within the macrocyclic cavity and the other potassium cation necessarily binds outside of the cavity in consequence of the inhibition of access to the opposite opening of the cavity by the *N*-methyl substituents. The macrocycle adopts the 1,3-alternate conformation. The *endo*-cavity-bound potassium exhibits η^5:η^1:η^5:η^1 binding, with η^5-interactions to both *N*-methyl pyrrole rings and σ-bonding to both nitrogen centres of the pyrrolide rings. A thf molecule also coordinates to the *endo*-cavity-bound potassium. The *exo*-cavity-bound potassium bridges two porphyrinogen units by way of binding to two pyrrolide rings of adjacent macrocycles by η^5- and η^2-bonding modes (the latter to the β-carbons). In addition, the *exo*-cavity-bound potassium is coordinated by a thf molecule and has close contacts with two methyl groups of the adjacent *meso*-ethyl substituents of the macrocycle to which it is η^5-bound.

Complex **4** adopts a monomeric structure in the solid state, Fig. 2 . The macrocycle here also adopts a 1,3-alternate conformation. In contrast to complex **3**, both potassium cations reside inside the macrocyclic cavity on either side of the average N_2O_2 plane, each displaying an η^5:η^1:η^5:η^1 bonding mode. Thus one potassium features η^5-binding to the nitrogen centres of both pyrrolide units and σ-binding to the oxygen centres of both furan units, and *vice versa* for the other potassium. Chelating tmeda molecules complete the coordination spheres of both potassium cations. The structure of **4** differs from the disodium complex of the *meso*-octamethyl analogue of **2**.[5] The conformational change underlying the observed binding modes of the potassium cations in **4** is in response to providing a larger macrocyclic cavity to bind the larger cations. In the sodium complex, both nitrogen centres are involved in μ-bridges to the sodium cations through the macrocyclic cavity with the pyrrolide units flat with respect to the macrocyclic cavity. Each sodium is bound in η^5-fashion to a single furan ring and further coordinated by a 1,2-dimethoxyethane molecule, defining a partially flattened double cone conformation for the macrocycle. The same conformation exists for a cobalt(II) complex,[5] the only other structurally characterised metallodioxaporphyrinogen.

The qualitative structural features of complexes **3** and **4** are in consequence of the differences in the macrocycles **1** and **2**. The two modifications that achieve reduction of the anionic charge of the metallated macrocycles, furan replacement or *N*-methyl substitution, drastically alter the accessibility of the macrocyclic cavities for metal binding. An extensive series of Group 1 metal complexes[1d] has established that unmodified porphyrinogens exclusively contain two metal cations bound in the macrocyclic cavity with various η^5- and η^1-interactions, which can thus be assumed to be the most favourable binding

DOI: 10.1039/b210600k

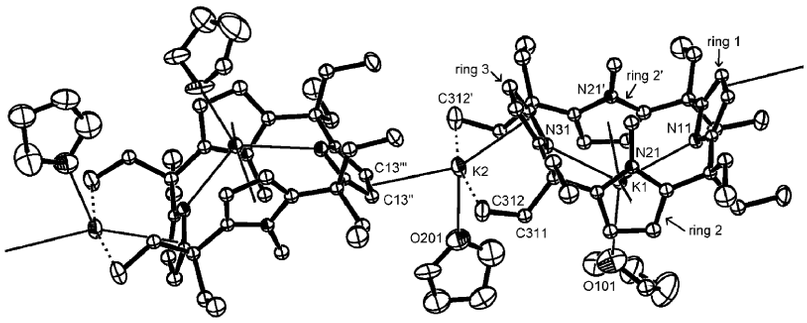


Fig. 1 Molecular structure of **3**. Selected distances (Å): K1–N11, N31 2.820(2), 2.815(2), K1–C2o 2.82$_2$, K1–O101 2.757(3), K2–C13 3.065(2), K2–C3o 2.77$_8$, K2–O201 2.678(2), K2–C312 3.143(2), K2–C311 3.371(2), K2–H312c, H312b 2.70(2), 3.15(2). ′, ″ and ‴ indicate transformations x, ½ − y, z; x − ½, ½ − y, ¾ − z and x − ½, y, ¾ − z, respectively. "Cno" is the centroid of ring n.

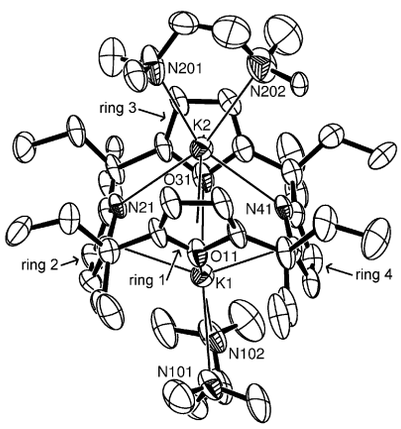


Fig. 2 Molecular structure of **4**. Selected distances (Å): K1–O11, O31 2.976(4), 2.972(4), K1–C2o, C4o 2.88$_1$, 2.93$_1$, K1–N101, N102 3.046(7), 3.080(7), K2–N21, N41 2.952(4), 2.898(4), K2–C1o, C3o 2.91$_0$, 2.92$_3$, K2–N201, N202 2.916(7), 3.076(8). "Cno" is the centroid of ring n.

mode for unmodified alkali metal porphyrinogen complexes. In these tetrametallated complexes the remaining two metal cations bind to outside faces of the pyrrolide rings leading to polymeric structures in the solid state. Thus, furan replacement in the porphyrinogen skeleton has maintained the *endo*-cavity metal binding characteristics of the macrocycle and, in contrast, *N*-methyl substitution has altered the *endo*-cavity metal binding characteristics of the porphyrinogen. In both **3** and **4**, the ubiquitous η^5:η^1:η^5:η^1 *endo*-cavity metal binding mode is observed, which is characteristic for large radii metals.

The structures of complexes **3** and **4** highlight the high level of control that can be attained by modification of the porphyrinogen skeleton. Reaction products from metathetical exchanges with **3** and **4** and metal halides are less likely to incorporate alkali metals owing to the reduced anionic charge of the macrocycles and, in the case of **3**, the sterically hindered cavity. This offers excellent promise that the structures of metalloporphyrinogen complexes can be greatly influenced by this approach. We are currently investigating the structure and reactivity of other modified metalloporphyrinogen complexes.

We thank the Australian Research Council for support.

Notes and references

† Porphyrinogens share many similarities to the well studied calixarene class of macrocycle and are also commonly referred to as calixpyrroles.

‡ Synthesis of **3**. Potassium metal (0.24 g, 6.0 mmol) was added to a solution of **1** (1.70 g, 3.0 mmol) in thf (100 mL) and refluxed for 6 hours. The thf was removed *in vacuo* and the solid washed twice with toluene. Drying *in vacuo* gave the product (2.25 g, 95%). Crystals of **3** suitable for X-ray analysis were obtained by the addition of an equal volume of toluene to a saturated thf solution. Anal. calc. for $C_{46}H_{70}K_2N_4O_2$: C, 70.00; H, 8.94; N, 7.10. Found: C, 67.64; H, 8.99; N, 6.85%. ^{1}H NMR (ppm): 0.69 (t, ^3J = 7.20 Hz, 24H, CH_3), 1.91–2.15 (m, 24H, CH_2 and thf), 3.05 (s, 6H, NCH_3), 3.76–3.82 (m, 8H, thf), 5.75 (s, 4H, =CH, pyr), 5.89 (s, 4H, =CH, pyrMe). ^{13}C NMR (ppm): 9.6, 9.8 (CH_3), 26.0 (thf), 27.0, 31.8 (CH_2), 33.5 (NCH_3), 46.4 (CEt_2), 68.9 (thf), 101.1 (=CH, pyr), 104.6 (=CH, pyrMe), 142.5 (=CR, pyrMe), 144.5 (=CR, pyr).

Synthesis of **4**. Potassium metal (0.29 g, 7.2 mmol) was added to a solution of **2** (1.63 g, 3.0 mmol) in thf (60 mL) and refluxed for 3 h. The solution was filtered from the excess potassium and other undissolved species and concentrated to *ca.* 20 mL *in vacuo*. Addition of tmeda (2.10 g, 18 mmol), followed by petroleum ether (40 mL, bp 40–60 °C) and storage for one week at −4 °C yielded **4** as colourless crystals (2.25 g, 88%). Anal. calc. for $C_{48}H_{80}K_2N_6O_2$: C, 67.72; H, 9.47; N, 9.87. Found: C, 67.69; H, 9.51; N, 9.79%. ^{1}H NMR (ppm): 0.64 (t, ^3J = 7.20 Hz, 12H, CH_3), 0.78 (t, ^3J = 7.20 Hz, 12H, CH_3), 1.90–2.10 (m, 16H, CH_2), 2.48 (s, 8H, NCH_2), 2.32 (s, 24H, NCH_3), 5.89 (s, 4H, = CH, pyr), 6.18 (s, 4H, =CH, fur). ^{13}C NMR (ppm): 9.6, 8.7 (CH_3), 28.2, 30.7 (CH_2), 46.8 (NCH_3), 47.4 (CEt_2), 59.5 (NCH_2), 102.9 (=CH, pyr), 105.5 (=CH, fur), 145.0 (=CR, pyr), 164.5 (=CR, fur).

§ Spectra recorded in d_8-thf at 298 K on a Varian Inc. Unity Inova 400 MHz WB system (5 mm PFG inverse probe). Resonances assigned by interpretation of gCOSY, gHMQC, gHMBC and gNOESY spectra. The upfield ^{13}C NMR thf resonance was obscured by the resonance of d_8-thf.

¶ Crystals of both **3** and **4** were mounted in thin-walled glass capillaries. Intensity data were collected on a Bruker SMART system using Mo-Kα radiation (λ = 0.71073 Å). Anisotropic displacement parameters were refined for the non-hydrogen atoms and hydrogens were included at geometrically estimated positions. Both thf molecules in **3** were disordered across the mirror plane on y = ¼ and one tmeda molecule was disordered in **4** (both modelled with 50% disordered component occupancies). In Figs. 1 and 2, 50% probability displacement amplitude envelopes are shown for the non-hydrogen atoms and solvent disorder is omitted.

Crystal data for **3**: $C_{46}H_{70}K_2N_4O_2$, M = 789.29, orthorhombic, a = 23.941(3), b = 17.131(2), c = 10.832(1) Å, V = 4442.6(9) Å^3, T = *ca.* 153 K, space group P_{nma} (no. 62) Z = 4, μ = 0.25 mm^{-1}, 43940 reflections measured, 5966 independent (R_{int} = 0.034), 4509 > 4$\sigma(F)$, conventional R = 0.040, R_w = 0.047, crystal dimensions 0.25 × 0.20 × 0.16 mm. CCDC reference number 196193.

For **4**: $C_{48}H_{80}K_2N_6O_2$, M = 851.40, triclinic, a = 12.194(3), b = 12.608(3), c = 17.834(5) Å, α = 80.359(4), β = 80.055(4), γ = 68.724(4)°, V = 2500(1) Å^3, T = *ca.* 153 K, space group $P\bar{1}$ (no. 2), Z = 2, μ = 0.23 mm^{-1}, 24183 reflections measured, 8738 independent (R_{int} = 0.053), 5825 > 4$\sigma(F)$, conventional R = 0.086, R_w = 0.114, crystal dimensions 0.35 × 0.31 × 0.27 mm. CCDC reference number 196192. See http://www.rsc.org/suppdata/dt/b2/b210600k/ for crystallographic data in CIF or other electronic format.

1 For papers dealing with a range of applications, see: (*a*) J. Jubb and S. Gambarotta, *J. Am. Chem. Soc.*, 1994, **116**, 4477–4478; (*b*) M. Rosi, A. Sgamellotti, F. Franceschi and C. Floriani, *Chem. Eur. J.*, 1999, **5**, 2914–2920; (*c*) T. Dubé, S. Gambarotta and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 1999, **38**, 1432–1435; (*d*) L. Bonomo, E. Solari, R. Scopelliti and C. Floriani, *Chem. Eur. J.*, 2001, **7**, 1322–1332.

2 For reviews, see: (*a*) P. A. Gale, J. L. Sessler and V. Král, *Chem. Commun.*, 1998, 1–8; (*b*) P. A. Gale, P. Anzenbacher Jr. and J. L. Sessler, *Coord. Chem. Rev.*, 2001, **222**, 57–102.

3 Y.-S. Jang, H.-J. Kim, P.-H. Lee and C.-H. Lee, *Tetrahedron Lett.*, 2000, **41**, 2919–2923.

4 Y. Furusho, H. Kawasaki, S. Nakanishi, T. Aida and T. Takata, *Tetrahedron Lett.*, 1998, **39**, 3537–3541.

5 R. Crescenzi, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1996, **35**, 2413–2414.