An improved protocol for the synthesis of antipodal β-tetrabromo-tetraphenylporphyrin and the crystal structure of its Zn(II) complex

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Abstract—This work reports an improved protocol for the regioselective synthesis of 2,3,12,13-tetrabromo-5,10,15,20-tetra-phenylporphyrin (H_2TPPBr_4) and the crystal structure of its Zn(II) complex which shows saddle shaped geometry. © 2003 Elsevier Science Ltd. All rights reserved.

Over the past decade there has been a significant number of reports on the synthesis and properties of a wide variety of haloporphyrins. These porphyrins are of interest owing to their unique physico-chemical properties.[1] Such properties arise partly from the nonplanarity of the macrocycle induced by repulsive interactions among the peripheral substituents. Besides their interesting properties, their high-valent metal complexes exhibit remarkable stability towards strong oxygen donors[2] which have been ascribed to the electron withdrawing effect of the peripheral halogen substituents.

Of particular interest, an increase in the number of bromo groups at the β-pyrrole positions induces dramatic changes in physico-chemical properties.[1,3] Callot[4,5] reported the first β-bromo-substituted *meso*-tetraphenylporphyrins, $H_2TPP(Br_n)$ ($n=1$–4). Partially substituted bromoporphyrins are of growing importance, not only for their interesting properties, but also as precursors for the synthesis of other porphyrins which are otherwise synthetically inaccessible.[6,7] Extensive literature is available on the synthesis of brominated porphyrins.[8] Among the bromoporphyrins, a synthesis of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenyl-porphyrin, H_2TPPBr_4 was reported by Crossley et al.[9] However, detailed synthetic methods are largely unknown for the preparation of H_2TPPBr_4. It was observed that the synthesis of H_2TPPBr_4 from a Ni TPP complex lead to non-antipodal brominated product.[10] Herein, we report a simple method for the regioselective synthesis of the antipodal tetra-

bromoporphyrin, H_2TPPBr_4, and describe the crystal structure of its Zn(II) complex (Fig. 1).

In a typical procedure,[11] H_2TPP[12] was treated with freshly recrystallised *N*-bromosuccinimide, NBS, in a 1:6 ratio in refluxing $CHCl_3$. H_2TPPBr_4 was isolated exclusively in 65% yield. Under these conditions, no lower brominated products were observed. An increase in the amount of NBS up to 12 equiv. resulted in no higher brominated TPP [$H_2TPP(Br_n)$ ($n>4$)] products, however, lower yields of the product were observed. The purity of the product was examined by UV–vis, ^{1}H NMR and mass spectroscopic methods. The antipodal disposition of the bromo substituents at the β-pyrrole positions was evident from the singlet for the pyrrole proton resonances and the characteristic red-shift in the UV–vis spectrum. The observed UV–vis and mass spectroscopic data were in conformity with the reported literature values.[4,9] The $ZnTPPBr_4$ complex was pre-
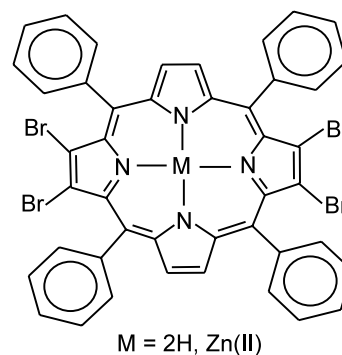

Figure 1. Chemical structure of $MTPPBr_4$ derivatives.

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pared via a metallation reaction of H_2TPPBr_4 using the reported procedure.[13]

In an effort to determine the distribution of the bromo-substituents at the pyrrole positions, we examined the crystal structure of the Zn(II) complex.[14] The crystals of $ZnTPPBr_4$ were grown by diffusing methanol into a solution of the porphyrin in tetrahydrofuran, THF. The ORTEP[15] diagram of the $ZnTPPBr_4(THF)\cdot THF$ complex is shown in Figure 2. The Zn(II) centre shows a penta-coordination mode with four bromo substituents at the antipodal β-pyrrole positions. The average Zn–N distance of 2.088 (4) Å is quite similar to that found in Zn(II)–porphyrins. Further, the axial Zn–O distance is 2.1643 (2) Å and is similar to penta-coordinated Zn(II)–porphyrins.[16,17] Further, the Zn(II)–ion is about 0.2688 (3) Å above the plane formed by the four nitrogen atoms. Notably, the porphyrin core shows distortion resulting in a saddle shaped conformation. This is caused by the steric constraints arising from the antipodal bromo substituents that push the adjacent phenyl rings towards the unsubstituted pyrroles to prevent unfavourable contact. Upon examination of the porphyrin core, the β-pyrrole carbons show an average displacement of 0.428 (5) Å from the mean plane formed by the 24-atom core. Furthermore, the phenyl rings form an average dihedral angle 64.7 (0.3)° from the mean plane formed by the 24-atom core.

In summary, an efficient procedure for the synthesis of H_2TPPBr_4 has been presented which involves the direct bromination of H_2TPP with an excess of *N*-bromosuccinimide. The crystal structure of $ZnTPPBr_4$ showed a saddle shaped conformation with pyramidal geometry about the Zn(II) ion.

Acknowledgements

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11. General procedure for the synthesis of H_2TPPBr_4: H_2TPP[14] (300 mg, 0.49 mmol) was dissolved in $CHCl_3$ (60 ml). To this solution, freshly recrystallised NBS (0.52 g, 2.93 mmol) was added (recrystallised from hot water and dried at 80°C under vacuum at 10^{-2} torr for 6 h). The reaction mixture was refluxed for a period of 4 h, cooled to room temperature and then the $CHCl_3$ was evaporated to dryness. The residue thus obtained was washed with methanol (2×20 ml) to remove any soluble succinimide impurities. The purple coloured solid was redissolved in $CHCl_3$ and chromatographed on a silica gel column using chloroform as the eluant. The first moving fraction was collected and the $CHCl_3$ removed in vacuo. The product, H_2TPPBr_4 was recrystallised from $CHCl_3/CH_3OH$ (1:3, v/v) and dried under vacuum (10^{-2} torr) at 85°C for 6 h to yield 0.295 g (65%). UV–vis (CH_2Cl_2): λ_{max} (nm) (log ε): 436 (5.52), 533 (4.30), 612 (3.58), 685 (4.02). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.69 (s, 4H, β-pyrrole-H), 8.17 (m, 8H, *o*-phenyl-H), 7.78 (m, 12H, *m*- and *p*-phenyl-H), −2.82 (s, 2H, imino-H). MS (FAB, *m*-nitrobenzyl alcohol matrix): M$^+$ (m/z) 931 (calcd 930.33).
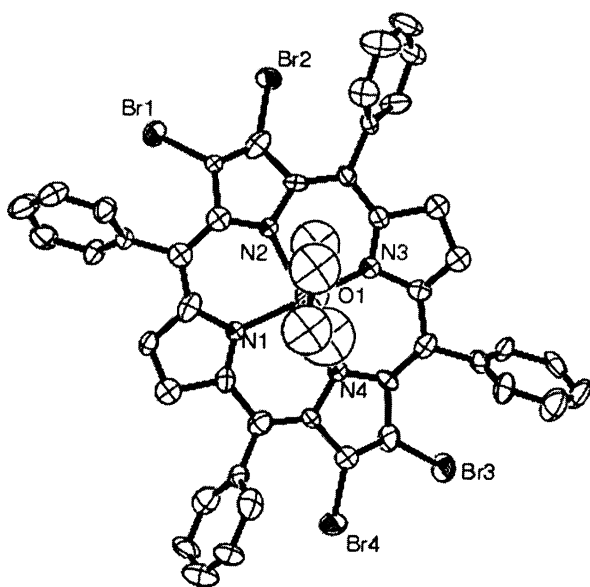

Figure 2. ORTEP diagram of the $ZnTPPBr_4(THF)\cdot THF$ complex (thermal ellipsoids at 50% probability). Only bromo, nitrogen and axially ligated oxygen (from THF) are labelled for clarity. The lattice THF and H-atoms are not shown for simplicity.

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13. The Zn(II) complex was prepared using a reported procedure, see: Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443. The yield of the product was found to be 80%. UV–vis (THF): λ_{max} (nm) (log ε): 434 (5.47), 568 (4.11), 611 (3.86). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 8.59 (s, 4H, β-pyrrole-H), 8.02 (d, 8H, *o*-phenyl- H), 7.77 (m, 12H, *m*- and *p*-phenyl-H). MS (FAB, *m*-nitrobenzyl alcohol matrix): M$^+$ (m/z) = 994 (calcd 993.7).

14. Crystal structure data was collected on a CAD-4, Enraf–Nonius diffractometer at 293 K. Monoclinic, space group, $P2_1/n$, $a = 13.731$ (5), $b = 18.278$ (13), $c = 18.491$ (5) Å, $\alpha = \gamma = 90.00$, $\beta = 94.61(3)°$, $V = 4626$ (4) Å^3, $Z = 4$. d$_{calcd} = 1.473$ g/m^3, (Cu K$_\alpha$) = 0.71073 Å, $2\theta_{max} = 30°$, $R = 0.0588$, $W_R = 0.1525$ for 8124 unique reflections, refinements on F^2. Structure refinement was performed using SHELX-97 software.

15. The crystallographic data for Figure 2, (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 205380. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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