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Octaethylporphyrin and expanded porphyrin complexes containing coordinated BF_2 groups†

Thomas Köhler,[a] Michael C. Hodgson,[b] Daniel Seidel,[a] Jacqueline M. Veauthier,[a] Sylvie Meyer,[a] Vincent Lynch,[a] Peter D. W. Boyd,*[b] Penelope J. Brothers*[b] and Jonathan L. Sessler*[a]

[a] *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, TX 78712-0165, USA. E-mail: sessler@mail.utexas.edu*

[b] *Department of Chemistry, The University of Auckland, Private Bag 92109, Auckland, New Zealand. E-mail: p.brothers@auckland.ac.nz*

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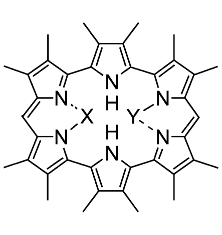
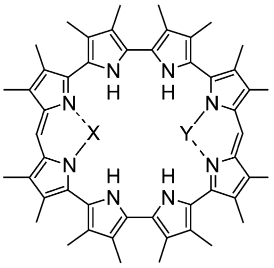
In contrast to octaethylporphyrin, which forms a very labile bis-BF_2 complex, treatment of the hexa- and octapyrrolic expanded porphyrins amethyrin and [32]octaphyrin with $BF_3{\cdot}OEt_2$ under standard reaction and work-up conditions gives rise to stable, non-labile mono- and bis-BF_2 complexes; these were readily characterised by, *inter alia*, X-ray diffraction analyses.

Extensive studies of dipyrromethanes have led to the isolation of BF_2-coordinated dipyrromethene complexes upon treatment with BF_3.[1] These highly fluorescent species are characterised by high stability and planar pyrrole(N)–B–(N)pyrrole fragments. By contrast, treatment of tetraarylporphyrins with $BF_3{\cdot}OEt_2$ leads, after chromatographic work-up on silica gel, to complexes that contain an F–B–O–B–F fragment in which each boron is coordinated to two of the porphyrin nitrogens in an asymmetric manner.[2] The reaction of tetraarylporphyrins with BF_3 under strictly anhydrous conditions leads to the isolation of products whose spectroscopic characterisation is consistent with a formulation of $(BF_2)_2$(Por). While these complexes are thought to act as intermediates for the more stable oxygen-containing porphyrin species under hydrolysis conditions, the question of why the chemistry of dipyrromethanes and dipyrromethenes differs so dramatically from that of tetraarylporphyrins remains. One appealing explanation is that the porphyrin core is too small to complex two BF_2 subunits easily. Indeed, analysis of the bond lengths and other structural parameters leads to the conclusion that stabilising two planar dipyrrolylboron subunits within a porphyrin core requires distortion of the relatively rigid porphyrin plane, with the resulting unfavourable steric interactions favouring hydrolysis. To the extent that this is true, larger porphyrin-like systems would be expected to be more robust. To test this hypothesis, we have conducted a study of octaethylporphyrin (OEP, **1**) and two different expanded porphyrins, amethyrin[4] (**2**) and [32]octaphyrin[5] (**3**). We report here that the latter two species permit the isolation of both mono- and bis-BF_2 complexes, whereas the porphyrin gives rise to F–B–O–B–F complexes under analogous conditions.

Previous work involving the reactions of BF_3 with porphyrins has focussed on the use of tetraarylporphyrins. However, the expanded porphyrins **2** and **3** are characterised by alkyl substituents in the β-pyrrolic positions as opposed to aryl groups on the *meso* bridges. To allow for appropriate comparison, free base octaethylporphyrin (H_2OEP) was subject to reaction with $BF_3{\cdot}OEt_2$ under conditions analogous to those used previously.[2] Specifically, the reaction of **1** with $BF_3{\cdot}OEt_2$ in dry dichloromethane and triethylamine, followed by treatment with aqueous base and chromatography over silica gel (eluent CH_2Cl_2–CH_3OH–NEt_3 94.5 : 5 : 0.5) gave rise to B_2OF_2(OEP) (**4**), a species analogous to that observed in the case of tetraarylporphyrin complexes. When the reaction was carried out under rigorously anhydrous conditions, spectroscopic analysis indicated the formation of $(BF_2)_2$(OEP) (**5**). Exposure of this species to water then produces **4** (Scheme 1).[6]



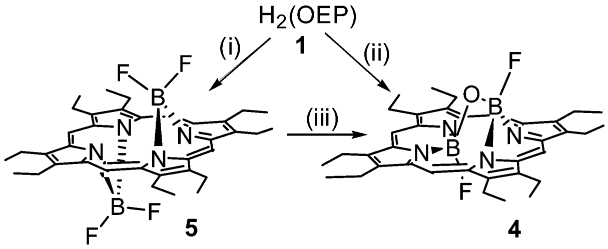
2: X = Y = H
6: X = Y = BF_2
7: X = H; Y = BF_2



3: X = Y = H
8: X = Y = BF_2
9: X = H; Y = BF_2

An ordered X-ray crystal structure of **4** (Fig. 1),‡ which co-crystallised with $[HNEt_3][BF_4]$, shows the porphyrin to have an unusual distortion in which the two pyrrole rings and the in-plane boron are coplanar, whereas the pyrrole rings attached to the out-of-plane boron are tilted away from the plane, indicative of the strain in the porphyrin.[7]

The treatment of H_2-amethyrin·2MeOH (**2**) with $BF_3{\cdot}OEt_2$ under conditions very similar to those used for the H_2OEP reaction (CH_2Cl_2–NEt_3) resulted in the isolation of the bis-BF_2-containing product $(BF_2)_2$(amethyrin) (**6**). This product persisted, even after treatment with aqueous base and chromatography over silica gel (eluent CH_2Cl_2–NEt_3 99.5 : 0.5). The mono-BF_2 product (BF_2)(H-amethyrin) (**7**) is also formed in the same reaction and was separated by increasing the polarity of the eluent used during chromatography. In marked contrast to what proved true in the case of OEP, the amethyrin products **6** and **7** could not be readily



Scheme 1 *Reagents and conditions*: (i) $BF_3{\cdot}OEt_2$, CH_2Cl_2–NEt_3; (ii) $BF_3{\cdot}OEt_2$, CH_2Cl_2–NEt_3, aq. NaOH; (iii) CH_2Cl_2–H_2O.

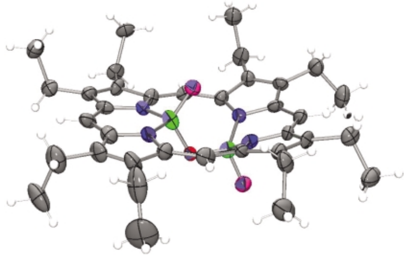


Fig. 1 Side view of an ORTEP-POVray-rendered image of **4**. The thermal ellipsoids are scaled to the 50% probability level.

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† Electronic supplementary information (ESI) available: experimental details for **4–9** and complete X-ray data for **4**, **6** and **8**. See http://www.rsc.org/suppdata/cc/b4/b400596a/

converted to oxygen-containing hydrolysis products, even under forcing conditions. For instance, heating complex **6** at reflux temperature for 2 h in chlorobenzene containing a small amount of water returned this complex unchanged.[8]

The bis-BF_2 amethyrin complex **6** was characterised by X-ray crystallography (Fig. 2).‡ The amethyrin macrocycle adopts a bowl-shaped conformation, within which the two boron dipyrromethene fragments each maintain a planar arrangement. The coordination geometry around each boron atom is close to tetrahedral, with one fluorine atom on each boron projecting towards the centre of the bowl and the other two below the base of the bowl. The two fluorine atoms within the bowl participate in hydrogen bonds to the two uncoordinated amethyrin pyrrole-NH moieties, resulting in two B–F···H···F–B bridges. This overall configuration is quite different from that observed for free base H_2-amethyrin·2MeOH,[4] illustrating the significant effect of the F···H hydrogen-bonding interactions. The average B–N distance (1.54 Å) is the same as that observed for the BF_2(dipyrromethene) complex BODIPY,[9] while the B–F bonds average 1.36 Å for the non-hydrogen-bonded fluorines and 1.41 Å for the hydrogen-bonded fluorine atoms. The B–F bonds in BODIPY average 1.38 Å.[9]

The reaction of the H_2[32]octaphyrin (**3**) with $BF_3·OEt_2$ was carried out under identical reaction conditions and work-up to those used for **2**, and gave a similar result, with first the bis-BF_2 complex $(BF_2)_2$([32]octaphyrin) (**8**) and then the mono-BF_2 complex (BF_2)(H[32]octaphyrin) (**9**)[10] eluting from the silica gel column as the solvent polarity was increased. The [32]octaphyrin complexes **8** and **9** are formed in lower yields and are more difficult to handle than the amethyrin analogues **6** and **7**. In particular, the mono-BF_2 [32]octaphyrin complex **9** shows a tendency to demetallate in $CHCl_3$ or CH_2Cl_2 solution.

The crystal structure of **8** (Fig. 3) bears superficial resemblance to that of **6**, with planar boron dipyrromethene moieties.‡ However, the bridging dipyrrole units are strongly twisted and the complex approaches a figure-of-eight conformation. Such highly non-planar conformations have been seen in a range of other octapyrrolic systems, including free base **3**.[5]

All three ligands form bis-BF_2 complexes in which each BF_2 moiety interacts with two adjacent dipyrromethene-like pyrrole rings. The resulting complexes are all susceptible to demetallation in acidic conditions. However, the startling difference between the octaethylporphyrin and expanded porphyrin (amethyrin and [32]octaphyrin) chemistry is the extreme lability towards hydrolysis observed for **5**; it forms **4** unless prepared and handled under rigorously anhydrous conditions. The proximity of the two BF_2 groups in the very crowded coordination environment of the OEP ligand, together with the thermodynamic stability of the B–O–B motif in boron chemistry, provides a driving force for this ready hydrolysis. The wider separations of the two BF_2 groups in the larger amethyrin and [32]octaphyrin macrocycles do not permit the close approach of the boron atoms necessary for the formation of B–O–B linkages. The result is that hydrolytically stable BF_2 complexes are formed. In the tetraarylporphyrin series, other boron–oxygen species, such as $B_2O(OH)_2$(TTP)[2] (TTP is the dianion of 5,10,15,20-tetra-*p*-tolylporphyrin) and $B_2O_2(BCl_3)_2$(TTP),[11] have been isolated from the reactions of the porphyrins with the heavier boron trihalides. Currently, the preparation and study of the corresponding BX_2-expanded porphyrin complexes is in progress. These could give rise to species containing novel B–O–B or $B(OH)_2$ fragments, which would expand the scope of boron macrocycle coordination chemistry and provide a potential entry into chemical sensor applications.

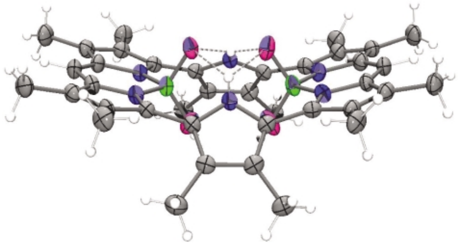

Fig. 2 Side view of an ORTEP-POVray-rendered image of **6**. The thermal ellipsoids are scaled to the 50% probability level.

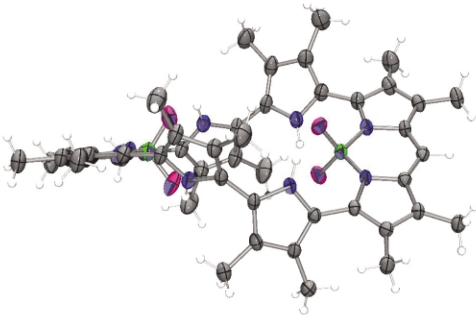

Fig. 3 Side view of an ORTEP-POVray-rendered image of **8**. The thermal ellipsoids are scaled to the 50% probability level.

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Notes and references

‡ *Crystal data* for **4**: $C_{42}H_{60}B_3F_6N_5O$, M_w = 797.38 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 10.2302(3), b = 13.7883(5), c = 15.1221(6) Å, α = 88.661(2), β = 84.853(2), γ = 79.504(2)°, V = 2088.88(13) Å^3, T = 153(2) K, Z = 2, μ(Mo-K$_\alpha$) = 0.094 mm^{-1}; 9847 reflections measured, 9847 independent; final R indices [$I = 2\sigma(I)$] R_1 = 0.0708, wR_2 = 0.1162. For **6**: $C_{44}H_{54}B_2Cl_2F_4N_6$, M_w = 835.45 g mol^{-1}, orthorhombic, space group $P2_12_12_1$, a = 13.4372(1), b = 15.8642(1), c = 20.6260(2) Å, V = 4396.85(6) Å^3, T = 153(2) K, Z = 4, μ(Mo-K$_\alpha$) = 0.203 mm^{-1}; 10 067 reflections measured, 10 067 independent; final R indices [$I = 2\sigma(I)$] R_1 = 0.0649, wR_2 = 0.1675. For **8**: $C_{53}H_{58}B_2Cl_6F_4N_8$, M_w = 1117.39 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 12.1909(2), b = 13.2259(2), c = 19.4190(3) Å, α = 93.425(1), β = 103.208(1), γ = 99.454(1)°, V = 2991.34(8) Å^3, T = 153(2) K, Z = 2, μ(Mo-K$_\alpha$) = 0.340 mm^{-1}; 25 852 reflections measured, 13 719 independent (R_{int} = 0.0457); final R indices [$I = 2\sigma(I)$] R_1 = 0.0819, wR_2 = 0.1668. CCDC 228378–228380. See http://www.rsc.org/suppdata/cc/b4/b400596a/ for crystallographic data in CIF or other electronic format.

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6 Unlike the tetraarylporphyrins (see ref. 2 and 3), the reaction of $BF_3·OEt_2$ with Li_2(OEP) gave only $[H_4(OEP)]^{2+}$.
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