Boron complexes of porphyrins and related polypyrrole ligands: unexpected chemistry for both boron and the porphyrin

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The coordination of boron to a range of polypyrrole-containing ligands is explored in this feature article. The boron dipyrromethenes are well-known as laser dyes and fluorescent labels in biology. Subphthalocyanine and subporphyrin macrocycles containing only three pyrrole rings can exist only when templated by a central boron atom. Boron complexes of expanded porphyrins (six or eight pyrroles) can complex boron in dipyrromethene (but not bipyrrole) sites. The primary focus of the article is on boron porphyrin and corrole complexes, where the tight fit of two boron atoms within the very constrained coordination site gives rise to unexpected chemistry at both boron and the porphyrin ligand. These unusual features are described and reasons for their occurrence postulated.

1. Introduction

The porphyrin macrocycle is one of the most comprehensively explored ligands in coordination chemistry, predominantly as a result of the significance of transition metal porphyrins in bioinorganic chemistry. The ready accessibility of the simple tetraarylporphyrins, and more recent developments in synthetic methods and in materials and medicinal applications of porphyrin complexes, have helped to drive this. Porphyrin chemistry is the most developed for the transition metals, especially the 3d elements.[1–3] Porphyrin complexes of group 1 (lithium, sodium and potassium),[4,5] the metallic main group elements,[2,6] the lanthanides[7] and limited examples of actinides[8] are also established. In more recent times the chemistry of some of the non- and semi-metallic main group elements (silicon, germanium, phosphorus, arsenic and antimony)[6,9,10] has been developed. While there are examples containing one element from each of groups 2 (calcium)[11] and 16 (tellurium),[12] porphyrin complexes have not been demonstrated for any of the group 17, or, perhaps not surprisingly, group 18 elements.

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Penny Brothers was born and grew up in Auckland, New Zealand, and completed BSc and MSc(Hons) degrees in chemistry at the University of Auckland. In 1979 she was awarded a Fulbright Graduate Student Fellowship and set off for Stanford University to begin a PhD in chemistry under the supervision of Professor Jim Collman. Her PhD thesis, and much of her subsequent research work, has centered around the chemistry of porphyrin complexes. In 1986 she returned to Auckland and spent two years working as a postdoctoral fellow with Professor Warren Roper, focusing on organometallic chemistry. In 1988 she took up her current academic position in the Department of Chemistry at the University of Auckland. She has been a visiting scientist at Los Alamos National Laboratory as a Fulbright Senior Scholar in 2007 and a visiting professor at the University of California at Davis (1993), the University of Heidelberg (2003) and the University of Burgundy (2004, 2006). Her current research brings together her interests in porphyrin chemistry, the main group elements and organometallic chemistry.

That the porphyrin ligand, with its four nitrogen donors defining a coordination site with a radius close to 2.0 Å, can form complexes with this diverse set of elements is in itself remarkable. The covalent radius (r_{cov}) of nitrogen is approximately 0.75 Å and elements with $r_{\mathrm{cov}} = 1.25 \pm 0.1$ Å might be expected to fit comfortably within the porphyrin hole. Most of the intermediate-sized elements form six-coordinate (octahedral) or five-coordinate (square pyramidal) porphyrin complexes in which the coordinated element either resides in or is only slightly (*ca.* 0.1 Å) displaced from the mean porphyrin N_4 plane.[2,13] Large, heavy elements typically form out-of-plane complexes in which the metal resides up to 1 Å above the porphyrin N_4 plane. Very small elements such as silicon and phosphorus (r_{cov} = 1.18 and 1.10 Å) can form bonds to all four porphyrin nitrogen atoms only if the porphyrin contracts significantly, which can occur through non-planar distortions of the porphyrin macrocycle.

Although the lightest element for which porphyrin complexes have been prepared is lithium, it is the largest of the first period elements (r_{cov} = 1.34 Å) and can form porphyrin complexes in which one or two Li atoms form bonds to all four porphyrin nitrogens. Boron has a sufficiently small radius (r_{cov} = 0.85 Å) that a single boron atom would be unlikely to form bonds to all four nitrogens. Several new structural types of boron porphyrins reported in recent years all contain two boron atoms per porphyrin, with each boron bonded to two porphyrin nitrogen atoms[14–19] and it is these complexes that will be the subject of this review. The result of constraining two boron atoms to the sterically confined location within a porphyrin macrocycle has resulted in chemistry that is unusual for boron. The corollary is also true, and some features unusual in porphyrin chemistry arise as a result of incorporating two coordinated elements, rather than the usual one, within the coordination site.

The boron porphyrin complexes described in this article contain boron coordinated to the porphyrin donor nitrogen atoms, rather than boron appended to the periphery of a porphyrin. Interest in boron porphyrin chemistry derives in part from intrinsic factors, for example the novelty of a porphyrin containing two central coordinated elements rather than the more usual single atom, the incommensurate size of the small boron atom with the porphyrin coordination site, and the incompatibility of the usual square-planar, square-pyramidal or octahedral geometry of typical porphyrin complexes with the tetrahedral or trigonal planar geometry adopted by boron compounds. Potential applications of porphyrinic boron species have been noted in sugar sensing through appending a porphyrin to a boronic acid function,[20] in boron neutron capture therapy, in which the localising function of porphyrins on the surface of solid tumours is used to deliver peripherally attached carboranes,[21] and in aryl coupling reactions using peripherally boronated porphyrins.[22] To date, however, none of these applications have featured boron coordinated within the porphyrin macrocycle. Boron pyrrolyl complexes are not new, and comprise species which have both significant applications (for example, the boron dipyrromethene fluorescent dyes) and novelty (the boron subphthalocyanine and subporphyrin complexes). To help give a context for the boron porphyrin complexes, the scope of this review will be expanded to consider a brief overview of these other boron pyrrolyl species, including expanded porphyrins and corroles.

2. Boron porphyrin complexes

Two reports of boron porphyrin complexes appeared during the 1960's and 1970's. The first of these described the reaction of H_2(oep) with diborane, and the second, the reaction of $BCl_3{\cdot}MeCN$ with H_2(tpp) in chlorobenzene.[23] Difficulties with assigning stoichiometry and interpreting spectroscopic data meant that apart from establishing the B : porphyrin ratio of 2 : 1 in the complexes they remained incompletely characterised.[24] However, in each case the products were determined to contain oxygen, introduced during workup procedures. These results underscore the hydrolytic sensitivity of the boron halides. Although the first well-characterised examples of boron porphyrins also contained B–O–B links, the simple boryl porphyrins which are precursors to the partially hydrolysed complexes will be discussed first.

All of the boron porphyrin complexes prepared to date contain two boron atoms per porphyrin, with each boron coordinated to two porphyrin nitrogen atoms. Both three- and four-coordinate boron have been observed. The structures have been established by X-ray crystallography or by DFT optimisations, each in concert with spectroscopic characterisation. The structural types so far established for diboron porphyrin and corrole complexes are summarised in Chart 1. The two boron atoms can lie both in the porphyrin N_4 plane, one in-plane and one out-of-plane, both out-of-plane but displaced to opposite faces of the porphyrin, and both out-of-plane on the same face of the porphyrin. Depending on the arrangement of boron atoms, the porphyrin undergoes a complementary out-of-plane distortion. A feature of all the boron porphyrin complexes is that the porphyrin has undergone a marked in-plane tetragonal distortion. This can be measured by taking the difference between the non-bonded N···N distances parallel and perpendicular to the B···B axis. This value, Δ(N···N), ranges from 0.84 to 1.27 Å for the boron complexes. Porphyrins which are sterically overcrowded on the periphery of the macrocycle have been observed to exhibit this kind of tetragonal, in-plane distortion, but for these, Δ(N···N) values are typically of the order of 0.5 Å.[25]

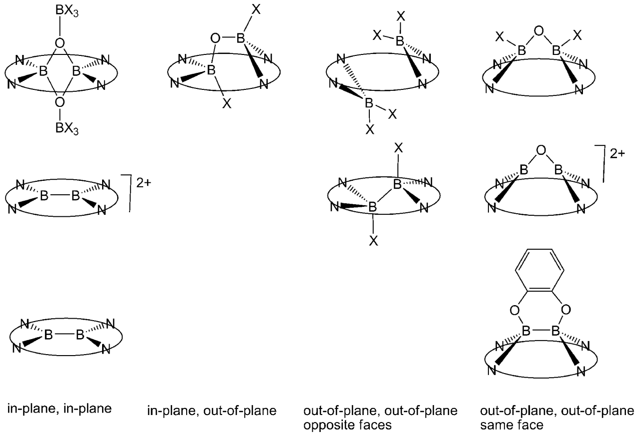


Chart 1 Structural types established for boron porphyrin and corrole complexes.

2.1 Porphyrin complexes containing BX_2 groups (X = halide)

The direct products of boron halides with porphyrins require that the reactions are conducted under rigorously anhydrous conditions. The key to this was beginning with the lithium porphyrins Li_2(por) as precursors rather than the free-base porphyrins H_2(por). Salt elimination reactions using the lithium porphyrins have been shown to be cleaner, and the products generally do not require chromatography for purification.[4] The reaction of $BCl_3{\cdot}MeCN$ with Li_2(ttp) in hexane produced the diboryl porphyrin complex $(BCl_2)_2$(ttp). This extremely hydrolytically sensitive product showed a ^1H nmr spectrum consistent with the transoid arrangement in which the boryl groups are each bonded to two porphyrin nitrogens and are displaced to opposite faces of the macrocycle (Fig. 1), and DFT calculations indicated that this structure was an energy minimum.[16] The analogous compound $(BF_2)_2$(ttp) could be prepared from $BF_3{\cdot}OEt_2$.[18] DFT calculations on the two diboryl complexes show that the porphyrin ligands show strong distortions, both out-of-plane and tetragonal in-plane, with Δ(N···N) calculated to be 1.15 Å (F) and 1.28 Å (Cl). The diboryl complex $(BCl_2)_2$(ttp) can also be prepared from the reaction of $BCl_3{\cdot}MeCN$ with the free base porphyrin H_2(ttp), although this reaction produces a lower yield as

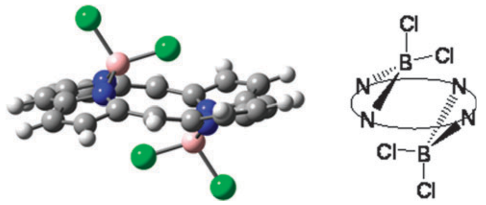


Fig. 1 Calculated structure of $(BCl_2)_2$(porphine) (B3LYP/6-311G(d,p)).[18] Reproduced with permission from ref. 18, copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA.

H_2(ttp) also acts as a base, forming one equivalent of the salt $[H_4(ttp)]^{2+}$ as a by-product.

2.2 Porphyrin complexes containing B–O–B linkages

The reaction of H_2(ttp) with $BF_3 \cdot OEt_2$ in chlorobenzene at room temperature, followed by chromatography on silica gel led to a compound whose elemental composition was B_2OF_2(ttp). Multinuclear nmr studies (^{1}H, ^{13}C, ^{19}F, ^{11}B) indicated that the compound had much lower symmetry than the D_{4h} or C_{4v} symmetry typically observed for free-base porphyrins and 5- or 6-coordinated metalloporphyrin complexes. The two fluorine and two boron atoms were each chemically inequivalent, and the pattern of resonances in the ^{1}H nmr spectrum was consistent with overall C_s symmetry with the molecule possessing a single plane of symmetry. The structure of the compound was determined from the spectroscopic results complemented by a computational study (force field calculations, AM1 semi-empirical MO theory and density functional theory), and subsequently confirmed by an X-ray structure determination on B_2OF_2(t*p*Clpp).[14] This structure was disordered, and a more recent structural determination on the oep analog, B_2OF_2(oep), gave good metrical data which agrees closely with the optimised structure.[17] B_2OF_2(por) contains an F–B–O–B–F group threaded through the centre of the porphyrin, with each boron atom coordinated to two porphyrin nitrogen atoms. One boron lies approximately in the N_4 plane of the porphyrin, while the other is displaced out of the plane (Fig. 2).

The corresponding reaction of $BCl_3 \cdot MeCN$ with H_2(t*p*Clpp) gave a blue-green precipitate which precipitated directly from the reaction mixture. Careful recrystallisation in the presence of BCl_3 gave crystals suitable for X-ray crystallography, which revealed a second type of B–O–B porphyrin, $B_2O_2(BCl_3)_2$(t*p*Clpp), in this instance containing a B_2O_2 four-membered ring coordinated in the cavity of the porphyrin with the plane of the B_2O_2 ring perpendicular to the plane of the macrocycle (Fig. 3). The two oxygen atoms act as donors towards BCl_3 acceptors.[15]

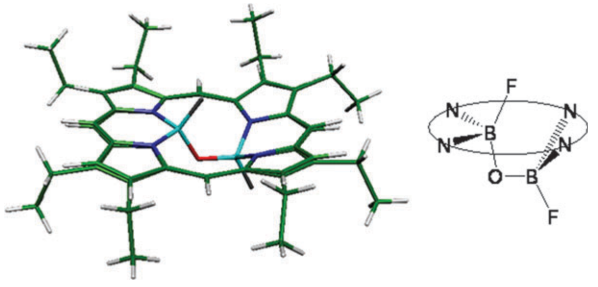


Fig. 2 Superposition of the molecular structure of B_2OF_2(oep)[17] and optimised structure of B_2OF_2(porphine) (B3LYP/6-311(d,p)).

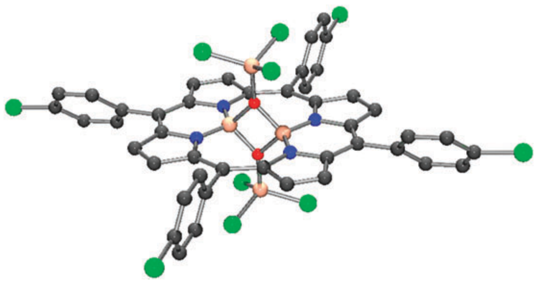


Fig. 3 Molecular structure of $B_2O_2(BCl_3)_2$(t*p*Clpp).[15]

Chromatography of $B_2O_2(BCl_3)_2$(ttp) on basic alumina gives $B_2O(OH)_2$(ttp), the hydroxy-boron analog of B_2OF_2(ttp), as evidenced by the same C_s symmetry deduced from the ^{1}H nmr spectrum. The two OH protons can be observed at −3.70 and −9.05 ppm, indicative of the marked effect of the porphyrin diamagnetic ring current effect.[15,19] A detailed computational study on the complexes B_2OX_2(por) for X = F or OH, and por = ttp or t*p*Clpp, confirmed our own experimental and computational results, that the *transoid* arrangement is lower in energy than the alternative cisoid geometry (Chart 2) by a substantial margin for B_2OF_2(por), but by only 1–2 kcal mol^{-1} for $B_2O(OH)_2$(por).[26]

The link between the diboryl complexes $(BX_2)_2$(ttp) and the boron–oxygen porphyrins was established by careful addition of two equivalents of water to $(BCl_2)_2$(ttp) to give the already established complex $B_2O_2(BCl_3)_2$(ttp) and one equivalent of the protonated porphyrin salt, $[H_4(ttp)]^{2+}$.[16] The relationship between $(BX_2)_2$(por) (X = F, Cl), B_2OF_2(por), $B_2O(OH)_2$(por) and $B_2O_2(BX_3)_2$(por) is illustrated in Scheme 1. $B_2O_2(BX_3)_2$(por) is only observed from the reaction of $BCl_3 \cdot MeCN$ with H_2(por), never from the reaction of $BF_3 \cdot OEt_2$, indicative of the stronger B–F bonds which are more resistant to complete hydrolysis. The reaction of $B_2O(OH)_2$(por) with excess $BCl_3 \cdot MeCN$ reforms $B_2O_2(BCl_3)_2$(por). However, $B_2O_2(BX_3)_2$(por) is unstable in solution in the absence of excess BCl_3 and quickly demetallates.

Very few structurally characterised examples of complexes containing B_2O_2 four-membered rings have been reported.[27,28] The most closely related example, $[B_2O_2F_4(BF_3)_2]^{2-}$,[27] contains the same central motif as the porphyrin complex, a B_2O_2 ring with BF_3 acceptors bonded to the oxygen atoms, but with four F^- ligands in place of the porphyrin ligand (Chart 3). A computational study on this molecule indicated that the small size of the B_2O_2 ring allows strongly anti-bonding cross-ring

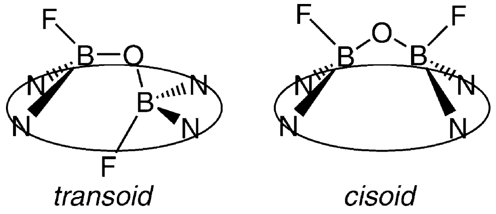
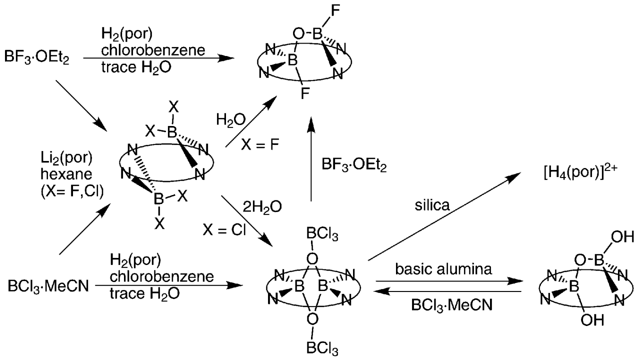


Chart 2 Cisoid and transoid stereochemistry of B_2OF_2(por).



Scheme 1 Chemistry of complexes containing BOB linkages.

O···O interactions which destabilise the ring. The BF_3 acceptors mediate this interaction and help to stabilise the ring.[27] This rationalises the observation that the porphyrin complex is unstable in the absence of excess boron halide.

A variety of other boron reagents apart from $BCl_3·MeCN$ and $BF_3·OEt_2$ were investigated for coordination of boron to the porphyrin. Similar conditions were used, the reaction of the free-base porphyrin with the boron halide in chlorobenzene, with subsequent chromatography on silica gel used to purify the product. The only other reagent that was successful was $PhBCl_2$, which under these conditions with $H_2(ttp)$ gave $B_2O(Ph)(OH)(ttp)$.[19] This was characterised by nmr spectroscopy, and deduced to have a similar Ph–B–O–B–OH arrangement to that observed for $B_2OF_2(ttp)$ and $B_2O(OH)_2(ttp)$, with the phenyl group bonded to the out-of-plane boron and the OH group to the in-plane boron (Fig. 4). The three multiplets observed for the phenyl ring are shifted markedly upfield to 3.7 (*ortho*), 6.0 (*meta*) and 6.2 (*para*) ppm, evidence for their coordination above the plane of the porphyrin and subject to the effect of the porphyrin diamagnetic ring current effect. The OH proton appears at −8.08 ppm.

The OH groups in $B_2O(OH)_2(ttp)$ and $B_2O(Ph)(OH)(ttp)$ are labile and derivatives $B_2O(OR)_2(ttp)$ (R = Et, *p*-C_6H_4-CH_3) and $B_2O(Ph)(OR)(ttp)$ (R = Et) can be prepared, either by treatment of the complexes with alcohols or by addition of alcohol during workup of the reactions of $BCl_3·MeCN$ or $PhBCl_2$ with $H_2(ttp)$. The asymmetry in $B_2O(OR)_2(ttp)$ is evident from the presence of two sets of R-group proton resonances.[19]

In the structurally characterised boron porphyrins B_2OF_2(t*p*Clpp), B_2OF_2(oep) and $B_2O_2(BCl_3)_2$(t*p*Clpp), the in-plane tetragonal distortion, Δ(N···N), was measured to be 1.06, 1.15, and 1.14 Å for these three complexes. The two B_2OF_2(por) complexes (with one in-plane and one out-of-plane boron atom) also show a step-like, out-of-plane distortion of the macrocycle, whereas $B_2O_2(BCl_3)_2$(t*p*Clpp), with both boron atoms in-plane, does not.

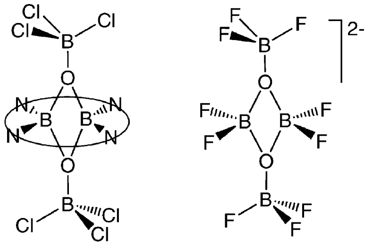


Chart 3 $B_2O_2(BCl_3)_2$(por) and $[B_2OF_4(BF_3)_2]^{2-}$.

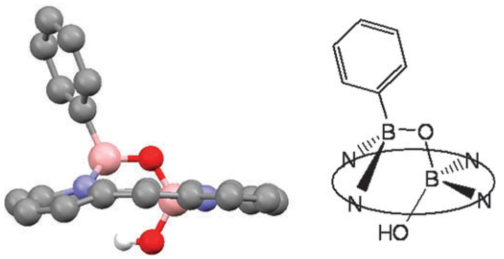


Fig. 4 Calculated structure of $B_2O(Ph)(OH)$(porphine) (B3LYP/6-31G*, all hydrogen atoms except the OH proton removed for clarity).[19]

An attempt to prepare the bromine analog of $(BCl_2)_2$(t*p*Clpp) by the reaction of Li_2(t*p*Clpp) with BBr_3 gave instead another oxygen-containing product, formed by diffusion of a trace amount of water into an nmr tube containing the reaction product in toluene solution. This complex was identified by X-ray crystallography as $[B_2O$(t*p*Clpp)$][BBr_4]_2$, which comprised an example of another structural type of boron porphyrin.[19] This was the first to contain three-coordinate, trigonal planar boron, and to have both boron atoms displaced to one face of the porphyrin. The structure of the tpp complex optimised by DFT agrees closely with the X-ray crystal structure (Fig. 5). The macrocycle shows a folded out-of-plane distortion. The Δ(N···N) value observed for this complex, 1.01 Å, is less than the 1.14 Å measured for the related complex $B_2O_2(BCl_3)_2$(t*p*Clpp), which is understandable given that there is less steric strain in the $[B_2O$(t*p*Clpp)$]^{2+}$ cation in which both boron atoms are "popped out" on one face of the macrocycle.[19]

2.3 Porphyrin complexes containing diboranyl groups

The observation of two in-plane, non-bonded boron atoms in $B_2O_2(BCl_3)_2$(t*p*Clpp) indicated that there should be more than enough room within the cavity of the porphyrin to accommodate a B–B single-bonded moiety. The appropriate boron reagent would be B_2Cl_4, and although difficult to prepare and

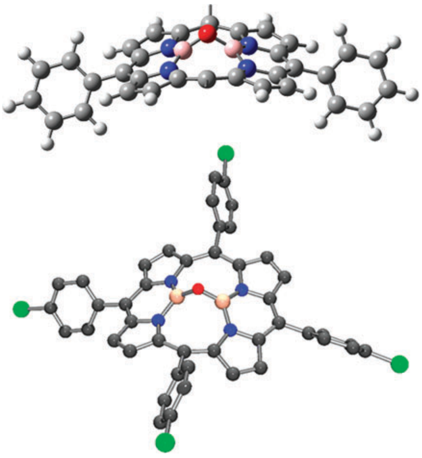


Fig. 5 Optimised structure of $[B_2O(tpp)]^{2+}$ (B3LYP/6-311G(d,p), front and rear *meso*-phenyl rings have been removed for clarity) and molecular structure of the dication of $[B_2O$(t*p*Clpp)$][BBr_4]_2$.[19]

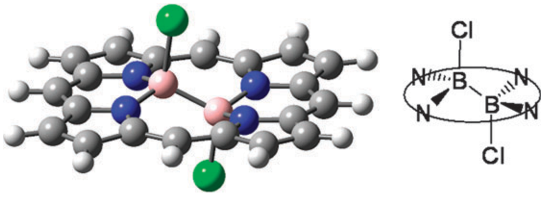


Fig. 6 Calculated structure of $(BCl)_2$(porphine) (B3LYP/6-311G(d,p)).[18] Reproduced with permission from ref. 18, copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA.

handle,[29] it proved to be successful for the preparation of a porphyrin containing a coordinated B–B unit. The reaction of B_2Cl_4 with either Li_2(ttp) or H_2(ttp) in hexane produced the diboranyl complex $(BCl)_2$(ttp), characterised by mass spectrometry, multinuclear nmr spectroscopy, and by comparison with the model complex optimised by DFT.[16] The compound contains a Cl–B–B–Cl group in a transoid arrangement with one boron above and one below the plane of the porphyrin (Fig. 6). The B–B distance is calculated to be 1.737 Å, typical of a B–B single bond.[30] The $\Delta(N \cdots N)$ value of 0.84 Å is much less than that in the diboryl complex $(BCl_2)_2$(por), as might be expected for the less strained B–B single bonded complex. Without access to the tetrafluorodiborane B_2F_4, it was not possible to prepare $(BF)_2$(ttp) using B_2F_4 as the precursor. However, halogen exchange on $(BCl)_2$(ttp) using SbF_3 as the source of fluoride was successful in producing $(BF)_2$(ttp).[18]

A butyl derivative of $(BCl)_2$(ttp) was prepared by treatment with ^{n}BuLi. The product, (B^{n}Bu)$_2$(ttp), provided crystals suitable for X-ray crystallography, determining unequivocally the presence of a B–B single bond and the transoid geometry. The structural features determined by X-ray crystallography and by DFT were in close agreement, giving B–B bond distances of 1.769(7) and 1.790 Å, and $\Delta(N \cdots N)$ values of 0.79 and 0.83 Å (Fig. 7).[16] The porphyrin diamagnetic ring current effect resulted in marked upfield shifts for the butyl protons in the ^{1}H nmr spectrum, with the α-CH_2 protons closest to the porphyrin shifted the furthest upfield to -5.70 ppm.[18]

Another derivative of $(BCl)_2$(ttp) was prepared from its reaction with catechol, to give the catecholate complex $B_2(1,2\text{-}O_2C_6H_4)$(ttp) (Scheme 2). Although this complex was not structurally characterised, its spectroscopic features are consistent with a cisoid geometry with the two boron atoms and the catecholate ligand on one face of the porphyrin. The catecholate protons are shifted to high field (4.1 and 5.4 ppm) in the ^{1}H nmr.[16,18]

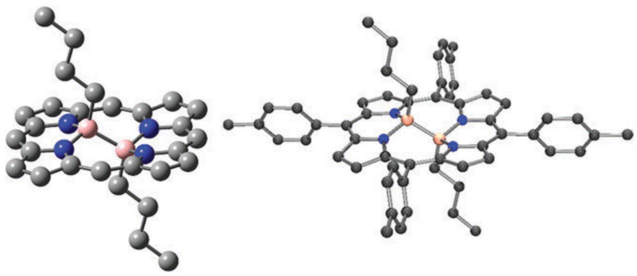
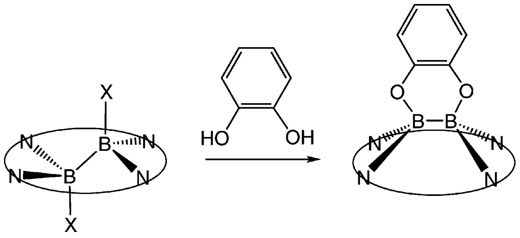


Fig. 7 Calculated (B3LYP/6-311G(d,p)) structure of (B^{n}Bu)$_2$-(porphine) (*meso*-phenyl rings removed for clarity) and molecular structure of (B^{n}Bu)$_2$(ttp).[16,18]



Scheme 2 Preparation of $B_2(1,2\text{-}O_2C_6H_4)$(ttp).

Abstraction of the chloride ions from $(BCl)_2$(ttp) was achieved using $Na[B(Ar_F)_4]$ ($Ar_F = 3,5\text{-}C_6H_3(CF_3)_2$) at low temperature with elimination of NaCl. The extremely reactive cationic product $[B_2(ttp)]^{2+}$ was observed by mass spectrometry and ^{1}H nmr spectroscopy, and its properties were compared with those optimised by DFT. The calculations showed the compound to have two trigonal planar boron atoms connected by a B–B bond residing in the plane of the porphyrin ligand (Fig. 8). The symmetry of the complex (D_{2h}) means that all four pyrrole rings are equivalent.[18]

2.4 Reductive coupling reactions

The diboryl and diboranyl complexes $(BCl_2)_2$(ttp) and $(BCl)_2$(ttp) contain boron in the +3 and +2 oxidation states, respectively, suggesting that chemical reduction of the former might give the latter. This proved to be true, and reduction of $(BCl_2)_2$(ttp) using two equivalents of potassium produced $(BCl)_2$(ttp).[18] This is a useful result, as it means that the diboranyl complex can be produced from H_2(ttp) with $BCl_3 \cdot MeCN$ followed by reduction, avoiding the use of B_2Cl_4.

As described above, the reaction of the diboranyl complex $(BCl)_2$(ttp) with ^{n}BuLi gave the butyl complex (B^{n}Bu)$_2$(ttp). In a surprising result, the reaction of the diboryl complex $(BCl_2)_2$(ttp) with ^{n}BuLi gave the same product, even though this represents a net chemical reduction of boron(III) to boron(II). The butyl radical is presumably the reductant in this spontaneous reductive coupling reaction, although its fate could not be determined.[16] This is not an isolated example of spontaneous reductive coupling in the boron porphyrin complexes. The reactions of $BF_3 \cdot OEt_2$ and $BCl_3 \cdot MeCN$ with Li_2(ttp) give the diboryl complexes $(BX_2)_2$(ttp) (X = F and Cl). The same reaction was repeated with BBr_3 and BI_3, intending to prepare the bromo and iodo analogs. However, the reaction with BBr_3 gave a mixture of $(BBr_2)_2$(ttp) and the reduced complex $(BBr)_2$(ttp), while BI_3 gave only the diboranyl complex $(BI)_2$(ttp).[18] The methods for preparing the diboryl complexes $(BX_2)_2$(ttp) (X = F, Cl, Br or Bu) and

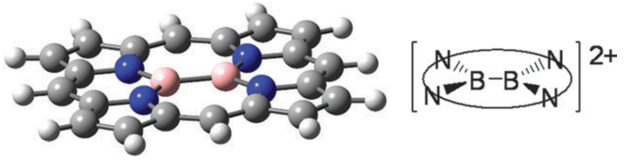
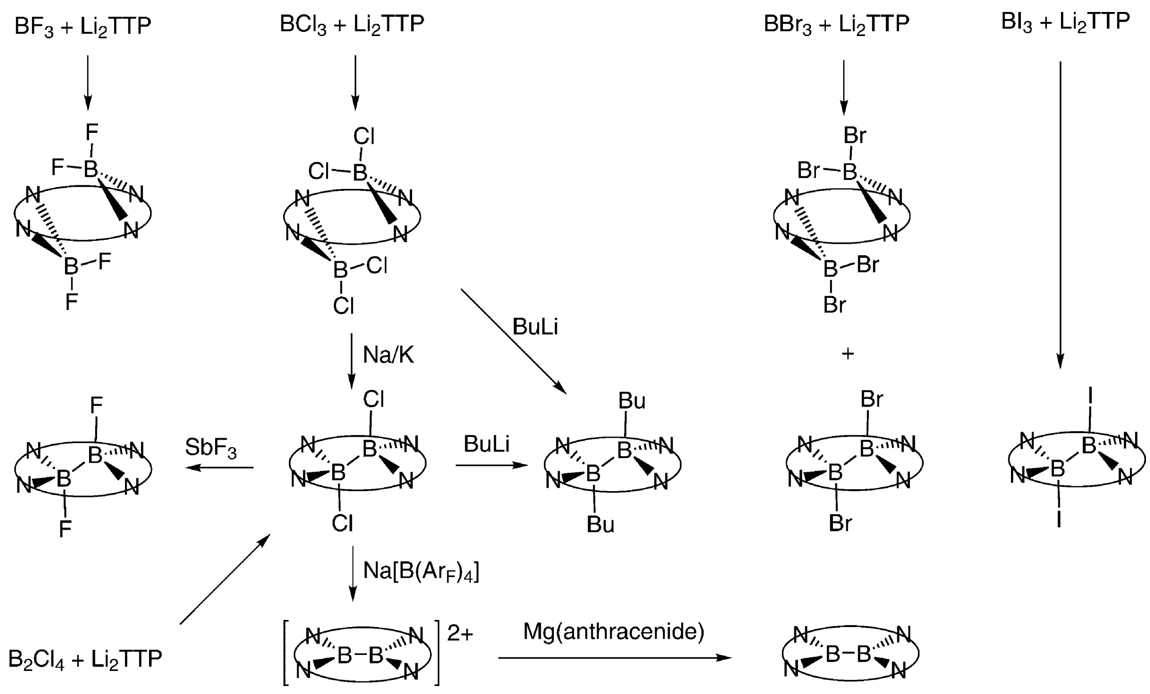


Fig. 8 Calculated structure of $[B_2(porphine)]^{2+}$ (B3LYP/6-311G(d,p)).[18] Reproduced with permission from ref. 18, copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA.



Scheme 3 Chemistry of diboryl and diboranyl porphyrin complexes.

the diboranyl complexes $(BX)_2(ttp)$ (X = F, Cl, Br, I, Bu or no ligand) are summarised in Scheme 3.

Spontaneous reductive coupling of BBr_3 or BI_3 to give B–B bonded halides in the absence of a reducing agent was an unexpected result. DFT calculations were undertaken in order to test the hypothesis that the crowded environment of the porphyrin ligand, together with the reducing ability of bromide and iodide, were drivers for this reaction. The structures of all four diboranyl complexes $(BX_2)_2$(porphyrin) were calculated for X = F, Cl, Br and I. Increasing steric strain in the complexes as the halide becomes heavier is evident in the BX_2 portions of the molecule, which show a decrease in the X–B–X angle from 110.3° for X = F to 99.0° for X = I. In addition, on descending the group, one B–X bond (directed away from the porphyrin) becomes progressively longer relative to the other (Fig. 9, Table 1). Gas phase thermochemical data were calculated for the reductive coupling reaction and the results, given in Fig. 10, show that for X = F and Cl both ΔH and ΔG are positive, indicating that the reaction is both endothermic and non-spontaneous. On the other hand, for X = Br and I, both ΔH and ΔG are negative, in accordance with the experimental results, showing that the reductive elimination is exothermic and spontaneous.

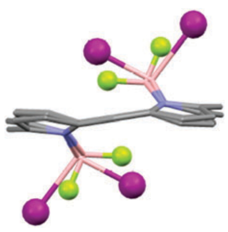


Fig. 9 Superposition of structures calculated for $(BF_2)_2$(porphine) and $(BI_2)_2$(porphine) (B3LYP/6-311G(d,p)), hydrogen atoms omitted for clarity).[18] Reproduced with permission from ref. 18, copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA.

Table 1 Metrical data calculated for $(BX_2)_2$(por) complexes (B3LYP/6-311G(d,p))

$(BX_2)_2$(por)	B···N$_4$ plane/Å	ΔN···N/Å	B–X/Å	Δ(B–X)/Å	X–B–X/°
X = F	0.912	1.15	1.367, 1.396	0.029	110.3
X = Cl	0.950	1.28	1.824, 1.926	0.102	104.8
X = Br	0.946	1.29	1.997, 2.138	0.141	102.2
X = I	0.922	1.30	2.224, 2.505	0.281	99.02

Similar calculations were also performed for the dipyrromethene complexes $(dpm)BX_2$. A dipyrromethene can be considered to be "half" of a porphyrin. Because the strain of constraining the two boryl (BX_2) groups in the porphyrin macrocycle is removed (Fig. 11), this reaction is an unstrained model for the porphyrin coupling reaction. As shown in

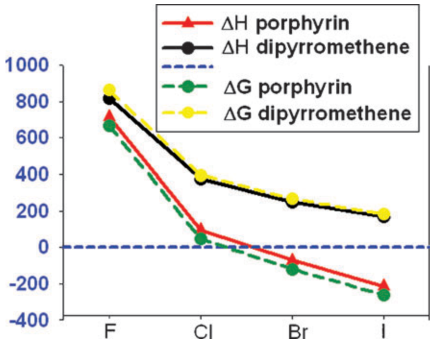


Fig. 10 Thermochemical data calculated for $(BX_2)_2(por) \rightarrow (BX)_2(por) + X_2$ and $2[(BX_2)(dpm)] \rightarrow [(BX)_2(dpm)_2] + X_2$ (optimised structures B3LYP/6-311G(d,p), frequency calculation with unscaled ZPE corrections).[18]

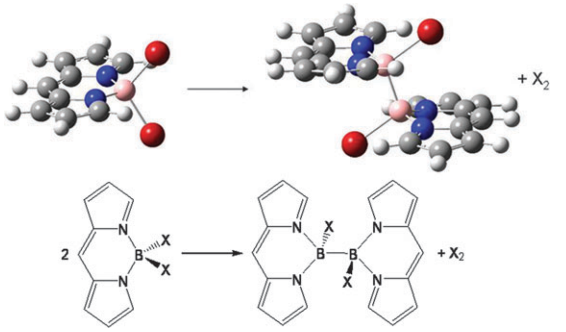


Fig. 11 Structures calculated for boryl and diboranyl dipyrromethene (dpm) (B3LYP/6-311G(d,p)).[18]

Fig. 10, for all four halides both ΔH and ΔG are positive, indicating that the reaction is not favoured for any halide, and supporting the hypothesis that steric strain in the porphyrin system provides the driving force for this unusual reductive coupling reaction.[18]

2.5 Formation of a diboron isophlorin complex

Having demonstrated reduction of the diboryl porphyrin (containing boron(III)) to the diboranyl porphyrin with a B–B single bond, containing boron(II), the next step was to investigate whether a further two-electron reduction might be possible. If this reduction occurred at boron, then the product might be a diborene, formally containing boron(I). However, the porphyrin is potentially a redox-active ligand so the macrocycle is an alternative site for the reduction. The reduction of $(BCl)_2(ttp)$ was achieved using magnesium anthracenide in THF at −30 °C. The product, formulated as the neutral complex $B_2(ttp)$, was characterised by nmr spectroscopy, which showed an interesting result. While the diboranyl complexes $(BCl)_2(ttp)$ and $[B_2(ttp)]^{2+}$ show diamagnetic shifts normal for ttp complexes (*e.g.* β-pyrrolic hydrogens (H_β) at 9.16 and 9.52 ppm, respectively), the neutral B_2ttp complex showed lower symmetry and paratropic shifts (β-pyrrolic hydrogens at 1.05 and 0.51 ppm).[18] The interpretation of this observation was that the porphyrin ring had been reduced by two electrons to form the 20 π-electron isophlorin complex. The structure of the molecule is calculated to be planar with both boron atoms in the porphyrin plane although with lower symmetry (C_2) than the D_{2h} symmetry calculated for $[B_2(ttp)]^{2+}$. The HOMO calculated by DFT (B3LYP/6-31G(d), NBO analysis) is consistent with the isophlorin tetraanion. The HOMO also shows partially localised π electrons in the antiaromatic isophlorin, giving rise to alternating bonds around the periphery of the macrocycle, in contrast to the fully delocalised 18 π-electron porphyrin ring (Fig. 12).

This result compares to that observed for the Zn(ttp) which has been reduced by two electrons to form $[Zn(ttp)]^{2-}$.[31] The ^1H nmr chemical shifts for Zn(ttp) (H_β at 8.95 ppm) and $[Zn(ttp)]^{2-}$ (H_β at −0.9 ppm) show the same effect with normal diamagnetic shifts for Zn(ttp) and paratropic shifts for $[Zn(ttp)]^{2-}$ which are very similar to those observed for $B_2(ttp)$. Further recent examples of related antiaromatic complexes are the silicon and germanium porphyrin and phthalocyanine (pc) complexes $M(pyridine)_2(tpp)$ and $M(pyridine)_2(pc)$ (M = Si, Ge)[32,33] which are formulated as M(IV) complexes with reduced porphyrin or phthalocyanine ligands. Porphyrin antiaromaticity and isolable isophlorin complexes are rare phenomena and the redox chemistry for the boron porphyrin complexes represents an elegant route into a new example.

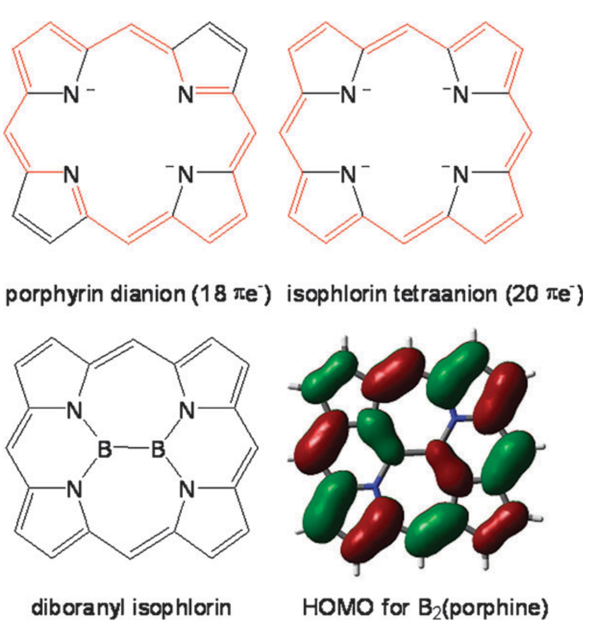
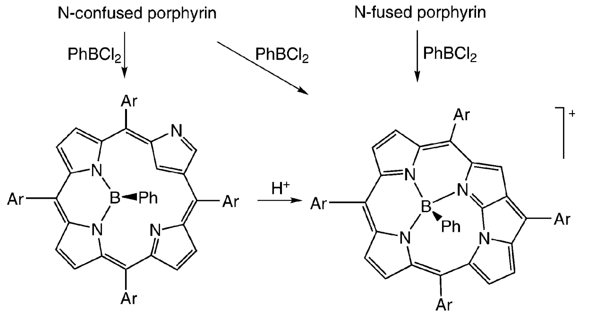


Fig. 12 Sketches of porphyrin dianion (18 π electrons), isophlorin tetraanion (20 π electrons), the diboranyl isophlorin, and the calculated HOMO for the diboranyl isophlorin B_2(porphine) (B3LYP/6-31G(d,p)).[18] Reproduced with permission from ref. 18, copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA.

2.6 Boron N-confused and N-fused porphyrin complexes

N-confused porphyrins, first isolated in 1994,[34] are porphyrin isomers in which one of the pyrrole rings is inverted such that the nitrogen is on the periphery of the ring and a pyrrole CH group is directed towards the centre of the ring. A related, reduced porphyrin isomer is N-fused porphyrin,[35] in which the ring is contracted through fusing of two adjacent pyrroles across a *meso*-carbon. Both of these ligands react with $PhBCl_2$ to give mono-boron complexes in which the phenylboron group is retained (Scheme 4).[36] In the N-confused porphyrin complex the single boron atom coordinates to two adjacent



Scheme 4 Formation of boron N-confused porphyrin and N-fused porphyrin complexes.

Fig. 13 Molecular structure of the phenylboron N-fused porphyrin cation.[36]

pyrrole nitrogens (essentially a dipyrromethene site) as established for the boron porphyrin complexes, although the lack of a second binding site means that only one boron can coordinate. The cationic N-fused porphyrin complex also contains a single boron atom, this time in a distorted trigonal pyramidal arrangement with three pyrrole nitrogens in the equatorial positions and the phenyl group at the apex, as demonstrated by X-ray crystallography (Fig. 13). Remarkably, the phenylboron N-confused porphyrin complex can be converted to the phenylboron N-fused porphyrin species by the addition of acid.[36]

3. Boron corrole complexes

Corroles are porphyrinoid macrocycles which are missing one methine carbon, resulting in a direct pyrrole–pyrrole linkage. They retain the 18 π electron aromatic configuration, but key differences from porphyrins are the three internal NH protons (resulting in a trianionic ligand), the lower symmetry and slightly smaller hole size in the N_4 coordination site. Recent studies on transition metal corroles show that the ligand is effective at stabilising higher oxidation states relative to the comparable metalloporphyrin complexes.[37]

The chemistry of boron corroles was investigated using the same methodology originally used for the preparation of boron porphyrins. The reaction of $BF_3\cdot OEt_2$ with free-base triaryl corroles $H_3(cor)$ gave, after chromatography, the corrole complexes $[B_2OF_2(cor)]^-$.[38] These at first compare with the analogous porphyrin complexes $B_2OF_2(por)$, noting that the corrole complexes are anionic because they contain cor^{3-} in place of the por^{2-} ligand, but the key difference is the stereochemistry of the corrole complexes in which the FBOBF group adopts the cisoid arrangement in contrast to the transoid porphyrin complexes (Chart 4). The corrole ligand contains two different bidentate binding sites, dipyrromethene (two pyrrole groups linked by a methine carbon) and dipyrrole (two pyrroles with a direct C_α–C_α link). The nmr and X-ray crystal structures confirm that the two boron atoms prefer the dipyrromethene sites (Fig. 14). DFT calculations confirm that the cisoid dipyrromethene isomer is the most stable. The $\Delta N\cdots N$ value for the tetragonal distortions is more complex to calculate for the lower symmetry corrole, but is less than observed for the porphyrin complexes, a consequence of the smaller hole size and more constrained macrocycle, and it may be these features that result in the differences between the preferred geometry for the corrole and porphyrin complexes.[38]

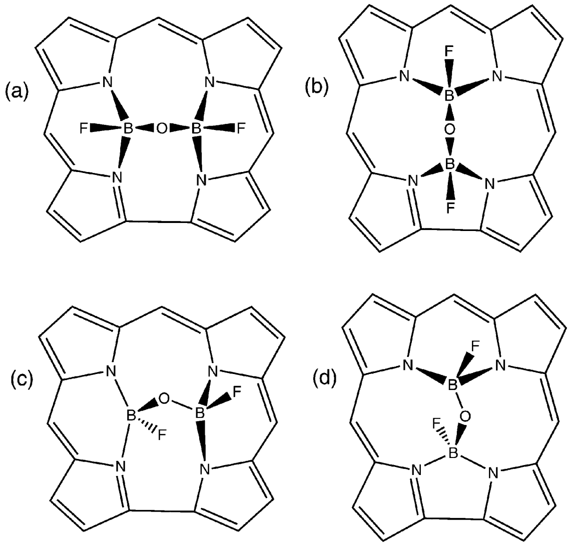


Chart 4 Sketches of structures computed (OLYP/TZ2P) for $[B_2OF_2(corrole)]^-$ in (a) cisoid dipyrromethene/dipyrromethene (most stable), (b) cisoid dipyrromethene/dipyrrole (+16.1 kcal mol^{-1}), (c) transoid dipyrromethene/dipyrromethene (+18.4 kcal mol^{-1}), and (d) transoid dipyrromethene/dipyrrole (+32.3 kcal mol^{-1}) binding sites.[38]

Preliminary results from studies on the reactions of other boron halides with corroles have yielded several examples of mono-boron corroles, indicating that further differences between boron porphyrin and corrole chemistry can be expected.

4. Boron complexes of expanded porphyrins

There is a wide range of macrocyclic ligands containing more than the four pyrrole rings observed in porphyrins, known collectively as expanded porphyrins.[39] Coordination of boron to expanded porphyrins has been recently demonstrated for amethyrin and [32]octaphyrin.[17] Amethyrin is a hexapyrrole ligand comprising two terpyrroles linked by two methine bridges, while [32]octaphyrin is an octapyrrole in which two tetrapyrroles are linked by two methine bridges.[40] The reactions of amethyrin and [32]octaphyrin with $BF_3\cdot OEt_2$ each yielded two products, containing one and two coordinated BF_2 groups (Scheme 5). Although there are several potential bidentate coordination sites within both expanded porphyrins,

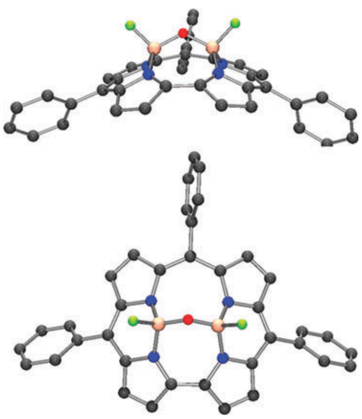
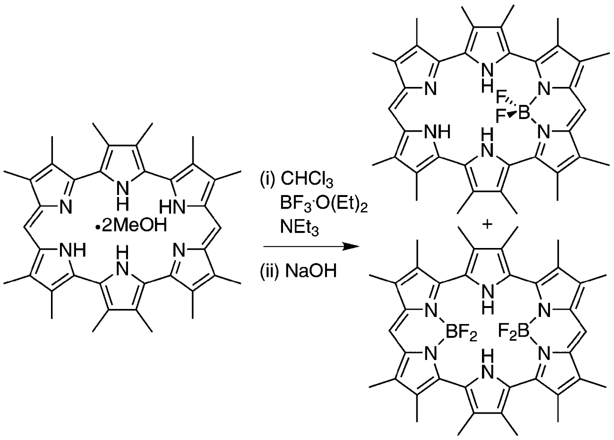


Fig. 14 Two views of the molecular structure of the $[B_2OF_2(tpc)]^-$ anion.[38]



Scheme 5 Preparation of boron amethyrin complexes.

the BF_2 groups are found in the dipyrromethene-like sites, bonded to two pyrrole groups linked by a methine bridge, rather than in the dipyrrole sites in which two pyrrole groups are linked by a direct C_α–C_α bond. X-Ray crystal structures were obtained for the mono-BF_2 and bis-BF_2 amethyrin complexes and $(BF_2)_2$(octaphyrin) (Fig. 15).[17]

Some notable differences can be observed between the porphyrin and expanded porphyrin BF_2 complexes. $(BF_2)_2$(ttp) and $(BF_2)_2$(oep) readily hydrolyse to B_2OF_2(por), whereas no hydrolysis is seen for $(BF_2)_2$(amethyrin) or $(BF_2)_2$(octaphyrin) even under reflux in the presence of NaOH. Formation of a B–O–B link is probably precluded by the larger size of the macrocycle. The ready hydrolysis of the porphyrin complex may be explained by the sterically strained environment and the close proximity of the two boron atoms. In the porphyrin case, only a bis-BF_2 complex is formed, and a porphyrin with only one BF_2 (or other halide) has never been observed. Amethyrin and octaphyrin appear to behave chemically as if they contain two independent dipyrromethene units each forming a BF_2 complex and the unusual features seen for the porphyrin system do not occur.

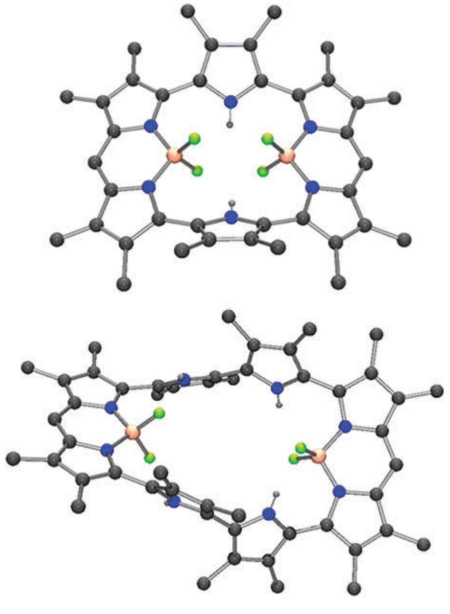


Fig. 15 Molecular structures of $(BF_2)_2$(amethyrin) and $(BF_2)_2$-(octaphyrin).[17]

Heptaphyrin(1.1.1.1.1.1.1) contains seven pyrroles linked by seven methine carbons bearing C_6F_5 groups. The macrocycle adopts a distorted figure-of-eight structure in which one loop comprises a tetrapyrrolic segment and the other a tripyrrolic segment. Thermal activation of the macrocycle leads to fusing of one or two of the peripheral aryl groups across one, two or four of the pyrrole nitrogens in the tetrapyrrole loop giving singly, doubly and quadruply N-fused heptaphyrins. The tripyrrolic loop in the quadruply N-fused macrocycle remains intact and coordinates boron upon treatment with BBr_3 and N^iPr_2Et. The coordination environment of boron is similar to that in a contracted porphyrinoid (see section 5), with three B–N(pyrrolyl) bonds and a fourth, anionic ligand (OH or OR), and in fact resembles the long-elusive subporphyrin.[41] In a remarkable reaction sequence, metallation of heptaphyrin(1.1.1.1.1.1.1) using copper acetate suppresses the N-fusion reactions and produces the Cu(II) heptaphyrin in which the copper ion occupies the tetrapyrrolic site. Subsequent reaction of the copper complex with BBr_3 resulted not in the copper–boron bismetallated heptaphyrin, but in cleavage of the ligand to produce copper porphyrin and a boron subporphyrin.[41] The chemistry of the subporphyrins is discussed in more detail in section 5.

5. Boron subporphyrin and subphthalocyanine complexes

Phthalocyanines are well-known 18 π electron macrocycles closely related to porphyrins, comprising isoindole groups linked by sp^2 nitrogens rather than pyrroles linked by methine carbons.[42] Subphthalocyanines (subpc), first discovered in 1972,[43] contain only three diiminoisoindole groups linked through nitrogen atoms in the *meso* positions around a core boron atom. They are formed from the cyclotrimerisation of phthalonitrile in the presence of a boron trihalide (BCl_3 or BBr_3) or, less commonly, a substituted boron precursor ($PhBCl_2$). Unlike phthalocyanines and porphyrins, the free-base subphthalocyanines are unknown, and all examples to date are stabilised by the core boron atom. Subphthalocyanines are dianionic ligands and the boron is typically four-coordinate, bonded to three isoindole nitrogen atoms and an anionic axial substituent (Chart 5). Subphthalocyanines contain a 14-electron, non-planar aromatic core and their structures exhibit a bowl shape with the axial substituent at the apex (Fig. 16a).[44] Several recent, comprehensive reviews discuss all aspects of subphthalocyanines,[45,46] and only an overview will be given here, particularly to highlight the relationship between boron subphthalocyanines and boron porphyrins. Subphthalocyanines have attracted a lot of attention, particularly as the field of materials chemistry has grown, because of their unusual second-order nonlinear optical properties, their potential applications as inks, dyes, or photosensitisers, and as curved, aromatic building blocks for molecular materials.[42] In this respect, they have been incorporated into larger aromatic systems by fusing two or more subphthalocyanines together[47] or by extending the indole groups as in naphthalocyanine.[46]

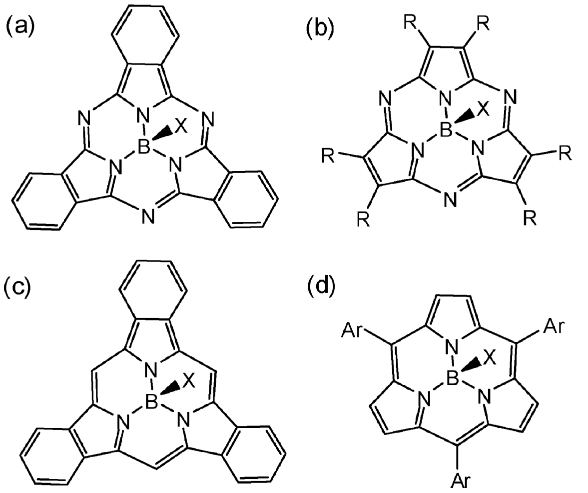


Chart 5 Sketches of (a) subphthalocyanine, (b) octalkylsubazaporphyrin, (c) subbenzoporphyrin and (d) triarylsubporphyrin.

The unusual spectral and electronic features of subphthalocyanines arise from the presence of a non-planar aromatic system. Derivatives can be obtained by substitution at the periphery of the macrocycle, or by changing the axial substituent at boron. The spectral and redox properties tend to be driven by the aromatic core with some effect from the peripheral substituents but little from the axial substituent at boron. Recent, novel derivatives are the three-coordinate, cationic subphthalocyanine $[B(subpc)]^+$ isolated by the use of a weakly coordinating carborane anion[48] and a diboranyl bissubphthalocyanine (subpc)BB(subpc) prepared by reductive coupling of B(subpc)Cl.[49] Subphthalocyanines have also been used as precursors to unsymmetrically substituted phthalocyanines by addition of a fourth diiminoisoindole group, a reaction in which the templating boron atom is lost.[46]

Contracted examples of other porphyrin relatives, azaporphyrins (also known as porphyrazines) and benzoporphyrins,[50] are also very recent additions to the family of contracted porphyrinoids (Chart 5, Fig. 16). Subazaporphyrins were first unequivocally characterised in 2005[51] while the first example of a tribenzosubporphyrin was reported in 2006,[52] as was a novel subpyriporphyrin containing two pyrrole and one pyridine groups.[53] Unlike the dianionic subphthalocyanine, subazaporphyrin and tribenzosubporphyrin macrocycles, the subpyriporphyrin could be obtained as both the monoprotic free base and the cationic phenylboron complex, possibly because with only one internal proton the repulsion that would occur in the diprotic free-base subporphyrinoid macrocycles is not an issue.

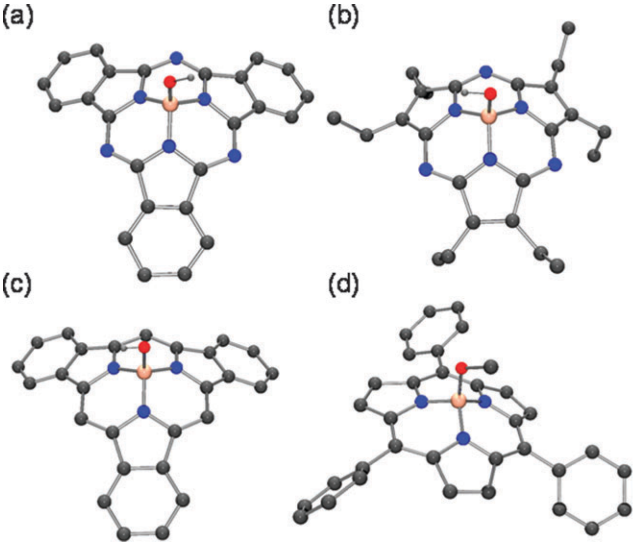


Fig. 16 Molecular structures of (a) B(OH)(subphthalocyanine),[44] (b) B(OH)(hexaethylsubazaporphyrin),[51] (c) B(OH)(subtribenzoporphyrin)[52] and (d) B(OMe)(triphenylsubporphyrin).[56]

The tribenzoporphyrin and subpyriporphyrin represented the closest approaches to the final member of the contracted porphyrin family, subporphyrin (subpor) itself (Chart 5, Fig. 16).[54] This was finally realised in 2007 when two groups independently prepared the first examples of boron triarylsubporphyrins, by the reaction of tripyrrolyl borane[55] or its pyridine adduct[56] with an arylaldehyde under Adler-type condensation conditions. Both groups reported that the Lindsey-type conditions were unsuccessful. A range of complexes containing different peripheral aryl groups were isolated as (HO)B(subpor)[55] or (MeO)B(subpor)[56] and one example of $(CF_3OCO)B(subpor)$[56] after lengthy chromatographic purification processes, in yields ranging from 1–8%. By-products included the tetraarylporphyrins and a boron dipyrromethene.[55] The subporphyrin containing C_6F_5 peripheral aryl groups could not be prepared by this method, but was achieved by extrusion from the Cu(II) heptaphyrin(1.1.1.1.1.1.1) complex (section 4).[41]

Several examples of boron subporphyrins were characterised by X-ray crystallography and show the bowl shape typical of the other boron contracted porphyrinoid species (Fig. 16). The synthesis and structure were supported by spectroscopic, electrochemical and MO computational studies. The availability of examples with a range of aryl groups containing both electron-withdrawing and electron-donating substituents showed that the *meso*-phenyl rings have much larger influences on the electronic properties of the subporphyrin than are observed for the corresponding porphyrin complexes.

All four types of boron contracted porphyrinoids (subporphyrins, tribenzosubporphyrins, subazaporphyrins, subphthalocyanines) are 14 π electron systems which show blue shifted spectra (shorter wavelengths) relative to their 18 π electron tetrapyrrolic relatives and interesting fluorescence properties. The degree of curvature of the π systems can be measured by the "depth" of the bowl, taken as the distance between the central boron atom and the mean plane through the six β carbon atoms of the pyrrole (or indole) rings. Within each class of macrocycles, the curvature can vary depending on the substituents on the periphery of the ring and on the boron atom. For example, for the subporphyrins the depth ranges from 1.18–1.43 Å.[55,56] The curvature also varies between classes of macrocycles, with the least and greatest curvature shown by the tribenzosubporphyrins and subazaporphyrins, respectively (Fig. 17). The addition of the long sought-after subporphyrin to this family of macrocycles means that the area is maturing and that opportunities exist for further

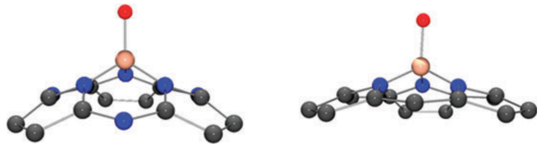


Fig. 17 Molecular structures showing the relative curvature of the tripyrrolyl cores of (left) B(OH)(subazaporphyrin)[51] (bowl depth 1.76 Å) and (right) B(OH)(subbenzoporphyrin)[53] (bowl depth 1.41 Å).

development of applications of these novel non-planar aromatic systems. For example, the first non-covalent interactions involving subporphyrins have recently been reported.[57] The role of the boron in the compounds is almost entirely structural, and unlike the boron porphyrins, the novel chemistry and features arise from the properties of the macrocycles themselves rather than the presence of a boron centre. To date no subporphyrinoid complexes templated by any atom other than boron have been reported.

6. Boron dipyrromethene complexes

The most widely utilised class of pyrrolyl boron complexes are the boron difluoride dipyrromethenes, containing the conjugated, monoanionic dipyrromethene ligand, also known as a dipyrrin ligand (Fig. 18).[58] This family of compounds occurs with a wide range of substituents on the pyrrole and central methine carbons. First prepared in 1968,[59] they are most notable for their fluorescence properties and have been developed as laser dyes[60] and as fluorescent labels for biological systems,[61] and examples tailored for both applications are marketed commercially. For laser applications they are known as 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene dyes, and as BODIPY dyes for molecular probes applications.[62] Two recent reviews give a comprehensive summary of boron dipyrromethenes, the first dealing with dipyrromethene complexes in general, with a good discussion on boron complexes,[63] and the second focuses on the structure, photophysical and lasing properties of boron dipyrromethene dyes.[64]

The compounds are highly fluorescent, very stable, insensitive to solvent polarity and pH, and have a high tolerance for functional groups. In more recent applications they have been investigated as building blocks for donor–acceptor energy cassettes and light-harvesting arrays, either through linking of aryl or alkynyl chromophores to the methine position,[65] or in a small number of examples, directly to the boron.[66] These latter examples are among the few boron dipyrromethenes which do not contain fluoride substituents on boron.[67] A further modification is replacement of the methine carbon by nitrogen, forming aza-BODIPY dyes, which also have excellent fluorescent properties.[68] A representative example of a boron dipyrromethene structure is shown in Fig. 18.[58]

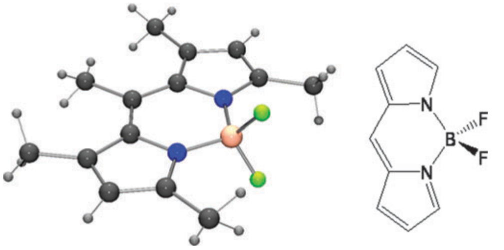


Fig. 18 Molecular structure of 1,3,5,7,9-pentamethyldipyrromethene boron difluoride.[58]

Conceptually, linking two dipyrromethenes through methine bridges will produce the aromatic porphyrin macrocycle; in this sense a dipyrromethene can be considered to be "half" a porphyrin. Dipyrromethene groups occur within a wide range of other molecules (expanded, contracted and isomeric porphyrins) but, despite the importance of the BODIPY dyes, the boron chemistry of these other macrocycles has not been widely investigated. Exceptions are the small number of examples of expanded porphyrin complexes described above, in which the boron prefers to bind in the dipyrromethene rather than bipyrrole sites, echoing the stability of the BODIPY moiety.

7. Conclusions

The benchmark for boron pyrrole species are the well-known and stable difluoroboron dipyrromethenes, containing a chelating ligand comprising, formally, one neutral and one anionic pyrrole donor (although they are in fact fully delocalised). The boron atom completes the six-membered, planar BNCCCN chelate ring. Among the polypyrrole macrocycle ligands surveyed in this article, where a dipyrromethene motif occurs within the macrocycle, it is the preferred binding site for boron, as observed in all of the diboron porphyrin, corrole and expanded porphyrin complexes, and the monoboron N-confused porphyrin. Another mode of coordination occurs for the subporphyrinoid ligands, the N-fused porphyrin and heptaphyrin(1.1.1.1.1.1.1) which contain three pyrrolic nitrogen donors in close enough proximity that all three can coordinate to boron. Even in these ligands, the boron still effectively occupies dipyrromethene-type binding sites. The difluoroboron moiety, with its exceptionally strong B–F bonds, also predominates, and very few examples of boron dipyrromethenes containing other substituents on boron are known. In contrast, the boron subporphyrinoid complexes contain a range of anionic ligands occupying the fourth coordination site. In all complexes, where boron is four-coordinate (which is the case for all but a small number of the diboron porphyrins), the geometry at boron is the expected distorted tetrahedral.

In summary, the chemistry of boron pyrrolyl species follows a consistent pattern dominated by the stability of the boron dipyrromethene moiety and the strong B–F bonds. In the subporphyrinoid complexes the role of boron is purely structural, while in the expanded porphyrins, the boron dipyrromethene moieties show little effect from being incorporated into a macrocycle. The exceptions are the diboron porphyrin complexes, and early indications are that boron corrole complexes will also show unusual features. The coordination site in a porphyrin or corrole is essentially too small to accommodate two boron atoms, but the energy gained from the formation of two boron dipyrromethene chelate rings must outweigh the necessary energy cost of the consequent distortions in the porphyrin ring. The poor fit and enforced close proximity of two boron atoms within the porphyrin stimulates unusual chemistry, notably the sterically induced spontaneous reductive coupling to give compounds with direct B–B bonds and the much higher propensity of B–F (or other B–halide) bonds to undergo hydrolysis and formation of B–O–B links. This unusual chemistry also extends to the porphyrin ring, with the marked tetragonal distortions and the isolation and characterisation of a rare example of a doubly reduced 20 π electron isophlorin complex. A surprising range of complexes are accessible, including three- and four-coordinate boron, a selection of substituents on boron (halide, oxo, alkoxide, alkyl and aryl), a variety of geometries in terms of the position of the boron atoms in or above the mean porphyrin plane, and a high degree of conformational flexibility in the porphyrin ligand itself.

Still to be explored are the possibilities for tuning the unusual redox chemistry by varying the peripheral substituents on the porphyrin, more detailed spectroscopic studies of the boron porphyrin and corrole species, the chemistry of boron hydrides with porphyrin and porphyrin-like macrocycles, the coordination chemistry of boron with the steadily increasing availability of new expanded and contracted porphyrins, and finally, with this rich variety available, to develop new potential applications of the boron porphyrin complexes.

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23 Abbreviations: dpm, dipyrromethene; cor, unspecified corrole trianion; por, unspecified porphyrin dianion; oep, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; tpp, dianion of 5,10,15,20-tetraphenylporphyrin; ttp, dianion of 5,10,15,20-tetra-*p*-tolylporphyrin; t*p*Clpp, 5,10,15,20-tetra-*p*-chlorophenylporphyrin; tpc, trianion of triphenylcorrole; pc, phthalocyanine; subpc, subphthalocyanine; subpor, subporphyrin.

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