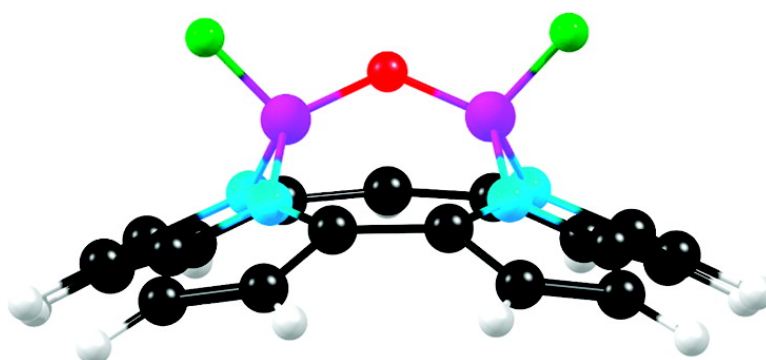


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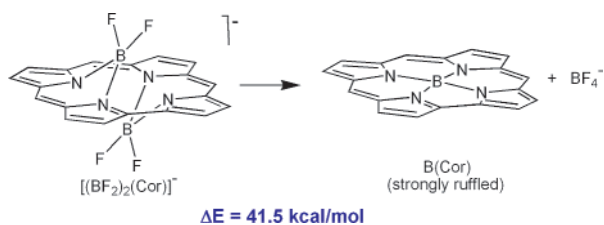
Corrole as a Binucleating Ligand: Preparation, Molecular Structure and Density Functional Theory Study of Diboron Corroles

Amelia M. Albrett,[†] Jeanet Conradie,^{‡,§} Peter D. W. Boyd,[†] George R. Clark,[†] Abhik Ghosh,^{*,‡} and Penelope J. Brothers^{*,†}

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand, Department of Chemistry and Center for Theoretical and Computational Chemistry, University of Tromsø, N-9037 Tromsø, Norway, and Department of Chemistry, University of the Free State, 9300 Bloemfontein, South Africa

Received October 10, 2007; E-mail: p.brothers@auckland.ac.nz

Since the development of one-pot syntheses of corrole a few years ago, the chemistry of corroles has grown by leaps and bounds.^{1,2} Indeed, both the coordination chemistry and range of applications of corroles promise to be just as diverse as those of porphyrins.³ There are major differences between the two classes of ligands, of course. Unlike porphyrins, corroles, as trianionic ligands, readily form stable, formally high-valent transition metal complexes.³ One interesting limitation of corrole chemistry is that all transition metal and main group corrole complexes known to date contain a single coordinated heteroelement. This is in contrast to our work on boron porphyrin complexes, which shows that coordination of two boron atoms per porphyrin is possible and leads to unusual chemistry at both the boron and the porphyrin.^{4–7} A study of boron corroles was undertaken not only to pursue novel coordination chemistry, but also to investigate the development of new boron reagents for neutron capture therapy, sugar sensing, and other applications.^{3a} Might the binucleating behavior of porphyrins extend to corroles and will further unusual chemical reactivity be stimulated? No experimental precedence is available that allows an answer to this question; the only reported boronated corrole complexes contain carboranyl groups covalently attached to the macrocycle peripheries.⁸



A density function theory (DFT) study of the isodesmic reaction shown above indicates that the diboron starting material is favored by over 40 kcal mol⁻¹ relative to the monoboron products. Moreover, the optimized structures of a variety of diboron corrole derivatives revealed no evidence of undue structural strain, prompting us to undertake the syntheses reported herein. The reaction of BF₃·OEt₂ with *meso*-triarylcorroles and diisopropylethylamine in dichloromethane has resulted in the first boron corrole complexes. Elemental analysis and mass spectrometry data indicate that the anionic complexes comprise a corrole trianion (Cor³⁻) coordinated to an FBOBF moiety and a diisopropylethylammonium counteranion. Oxygen in the product derives from partial hydrolysis at boron by adventitious water, as observed in the related reactions of free-base porphyrins with BF₃·OEt₂.^{4,6} Four [HNⁱPr₂Et][B₂OF₂-

(Cor)] complexes were prepared, containing 5,10,15-triphenylcorrole (TPC), 5,10,15-tris(4-methylphenyl)corrole (T(4-Me-P)C), 5,10,15-tris(4-fluorophenyl)corrole (T(4-F-P)C), and 5,10,15-tris-[4-(trifluoromethyl)phenyl]corrole (T(4-CF₃-P)C). However, although the synthesis appears to be quite general, it did not work for 5,10,15-tris(4-methoxyphenyl)corrole (T(4-MeO-P)C), presumably because the methoxy groups react competitively with BF₃. In the related porphyrin complexes B₂OF₂(Por) (Por = octaethylporphyrin, OEP; 5,10,15,20-tetrakis(4-chlorophenyl)-porphyrin, T(4-Cl-P)P) each boron atom is bonded to two adjacent pyrrole nitrogens.^{4,6} A similar coordination mode might be expected for the corrole complexes, but the lower symmetry of the corrole and the presence of both dipyrromethene and bipyrrrole sites implies that multiple isomers are possible.

Full assignment of the ¹H NMR spectrum of each analogue was achieved using COSY and NOESY experiments (see Supporting Information for details). The molecular structure of the TPC complex (Figure 1) confirms the presence of a [B₂OF₂(TPC)]⁻ anion and a [HNⁱPr₂Et]⁺ cation. Each boron atom in the FBOBF unit is coordinated to two adjacent nitrogen atoms in the dipyrromethene sites indicating that coordination of boron in the bipyrrrole site is less favored.

Furthermore, the FBOBF group occupies one face of the corrole in a *cisoid* arrangement (**1**), in contrast to the corresponding porphyrin complexes B₂OF₂(Por), which adopt an asymmetric *transoid* geometry with the FBOBF group threaded through the porphyrin core such that the F atoms lie on opposite sides of the porphyrin plane (**2**).^{4,6} The corrole macrocycle is domed with each pyrrole ring tilted toward a coordinated boron.

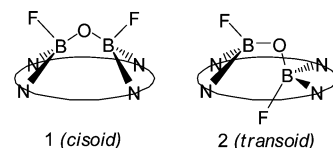


Figure 2 depicts selected DFT (OLYP⁹/TZ2P, ADF 2006 program system¹⁰) geometry parameters for four alternative isomers of the peripherally unsubstituted [B₂OF₂(Cor)]⁻ anion. The observed *cisoid* arrangement with both boron atoms in the dipyrromethene sites (Figure 2a) is 16.1 kcal mol⁻¹ more stable than the isomer with one boron in the dipyrromethene site and the other in the bipyrrrole site (Figure 2b). This is consistent with the coordination mode observed for the mono- and bis-BF₂ complexes of amethyrin (a macrocyclic hexapyrrole containing two dipyrromethene and four bipyrrrole sites) in which the BF₂ groups bond to two adjacent nitrogens in the dipyrromethene sites only.⁶ Figure 2 structures b and d show large variations between the BNC_α angles at the bipyrrrole nitrogens, indicating that these isomers are highly strained.

[†] The University of Auckland.

[‡] University of Tromsø.

[§] University of the Free State.

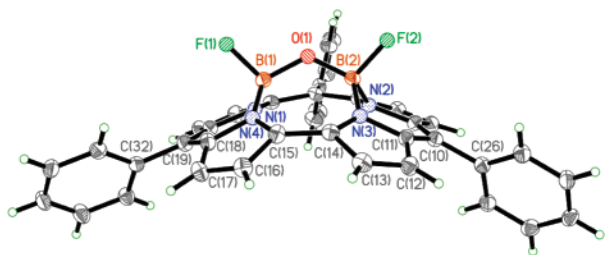


Figure 1. Molecular structure of the $[B_2OF_2(TPC)]^-$ anion. Selected average bond lengths (Å): B–N, 1.551; B–F, 1.432; B–O, 1.395. Average bond angles (deg) FBO, 107.30; NBN, 102.45; FBN, 107.03; OBN, 116.20; BOB, 126.13.

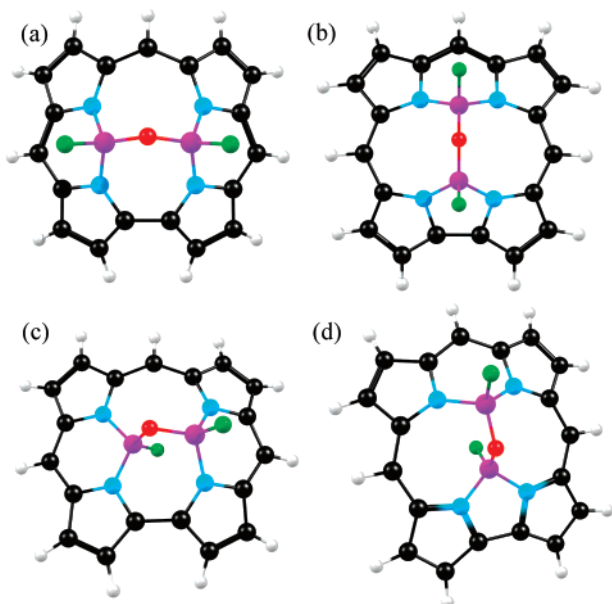


Figure 2. Optimized (OLYP/TZ2P) structures of $[B_2OF_2(Cor)]^-$ for (a) *cisoid* dipyrromethenes-only (0 kcal mol⁻¹ relative energy), (b) *cisoid* dipyrromethene/bipyrrole (+16.1 kcal mol⁻¹), (c) *transoid* dipyrromethenes-only (+19.5 kcal mol⁻¹), and (d) *transoid* dipyrromethene/bipyrrole (+32.3 kcal mol⁻¹) coordination modes. See Supporting Information for metrical data.

All calculated metrical parameters for the lowest energy structure (Figure 2a) are in reasonable agreement with those observed experimentally. The *transoid* geometry for $[B_2OF_2(Corr)]^-$ was computed to be 19.5 and 32.3 kcal mol⁻¹ less stable for the dipyrromethene (Figure 2c) and bipyrrole (Figure 2d) arrangements, respectively. This is in contrast to porphyrin analogues $B_2OF_2(Por)$ for which the observed *transoid* geometry was calculated to be 15.9 kcal mol⁻¹ lower in energy than the *cisoid* arrangement.^{4,6}

Diboron porphyrin complexes undergo a marked tetragonal distortion of the macrocycle to accommodate the two boron atoms. For example, in $B_2OF_2(T(4-Cl-P)P)$ the nonbonded $N\cdots N$ distance parallel to the $B\cdots B$ axis is 1.06 Å longer than the perpendicular $N\cdots N$ distance.⁴ A similar effect is also seen for $[B_2OF_2(TPC)]^-$, where the $N\cdots N$ distances parallel to the bipyrrole $C_\alpha-C_\alpha$ bond (and $B\cdots B$ axis) are 2.919 and 3.282 Å, and the perpendicular $N\cdots N$ distance is 2.420 Å. In other words, the distances between adjacent N's in the boron corroles span a slightly shorter range (0.86 vs 1.06 Å) than in boron porphyrins. The range, however, is still impressive, considering the inherently smaller N_4 core of corroles. The *transoid* isomers (Figure 2c,d) have more pronounced distortions than the *cisoid* isomers (Figure 2a,b) and this may contribute to the higher energy of these isomers.

Although the metrical parameters of the pyrrole rings are essentially the same as in common corrole derivatives, the bond angles at the central *meso* carbon in the FBOBF complexes flex and expand to accommodate the tetragonal distortion. Thus, in $[B_2OF_2(TPC)]^-$ the $C_\alpha-C_{meso}-C_\alpha$ angles are only ca. 119° at C₅ and C₁₅ but ca. 130° at C₁₀. The corresponding angles for free-base and mononuclear corrole derivatives all hover around 125°.

Unlike many transition-metal corrole derivatives whose Soret maxima are exceedingly sensitive to peripheral substituents,¹¹ the four FBOBF derivatives studied exhibit nearly identical UV–vis spectra (see Supporting Information, p S21), a scenario similar to that found for free-base *meso*-triarylcorrole derivatives.^{11a} DFT studies indicate that the substituent sensitivity of the Soret bands of many transition-metal corroles reflects charge-transfer transitions to low-lying empty metal d orbitals or ligand holes.¹¹ Clearly, a similar situation is out of the question for the electronically saturated boron complexes studied here.

Overall, the rich chemistry observed for both boron and the porphyrin ligand in boron porphyrin complexes^{4–7} may extend to corroles as well. In particular, the corrole ligand, despite its smaller N_4 core size, can accommodate two coordinated boron atoms. The sterically driven spontaneous reductive coupling in the reaction of BBr_3 and BI_3 with porphyrins to give a product containing a B–B bond⁷ may be even more facile for the corresponding corrole complexes.

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Supporting Information Available: Details of the syntheses, elemental analyses, spectroscopic data (UV–vis, MS, ¹H NMR including COSY and NOESY experiments), DFT calculations and CIF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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