New Coordination Mode for the Porphyrin Ligand in the Boron Porphyrin Complex B₂OF₂(TTP)

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The predominant mode of porphyrin ligand to metal coordination involves the interaction of all four pyrrolic nitrogen atoms with a single metallic element to form four-, five-, or six-coordinate complexes. The central element either lies in the N_4 plane or is displaced from it by only a small distance. Well-characterized complexes containing a porphyrin ligand complexed to nonmetallic elements (where coordination implies interaction of an element with more than one pyrrole nitrogen) are rare, especially for the smaller, lighter elements. Currently, examples are limited to silicon,[1] phosphorus,[2] and carbon.[3] Despite the small size of the P^V ion, it coordinates to the porphyrin through all four N atoms to form octahedral six-coordinate cationic complexes.[2] Porphyrins complexed to a carbene fragment (CR_2), on the other hand, do so through only two N atoms with marked out-of-plane geometry.[3] A single report in the literature describes an attempt to prepare a boron porphyrin complex from the reaction of $BCl_3 \cdot MeCN$ with H_2TPP in chlorobenzene followed by chromatography of the product on alumina.[4] While the formulation of the complex was proposed on the basis of elemental analysis and mass spectrometry to be $B_2(OH)_4(TPP)$, the data available were not sufficient to deduce the coordination geometry of the complex.

We re-examined this reaction using H_2TTP (tetra-*p*-tolylporphyrin) and isolated a product with the formula $B_2O(OH)_2(TTP)$. The ^1H and ^{13}C NMR data indicate that the complex has low symmetry.[5] Using $BF_3 \cdot OEt_2$ as the reagent we have prepared a second example of a boron porphyrin complex, $B_2OF_2(TTP)$.[6] Elemental analysis and measurement of an accurate mass by FAB-MS confirm this formulation, and an extensive NMR study was conducted on the complex comprising ^1H, ^{13}C, ^{11}B, and ^{19}F experiments. The ^1H and ^{13}C spectra were completely and uniquely assigned by the use of COSY (H,H and H,C), FLOCK,

NOESY, and ROESY experiments.[7] In the ^1H spectrum the β-pyrrolic signals appear as two AB quartets and the tolyl methyl groups appear as three singlets with a 2:1:1 ratio. This indicates that the complex has a single plane of symmetry (C_s) containing one set of opposite *p*-tolyl groups and two meso carbon atoms. The spectra at room temperature indicate free rotation of the two inequivalent *p*-tolyl groups, while rotation of the two symmetry-related *p*-tolyl groups is restricted. Variable temperature ^1H, ^{13}C, and ^{19}F NMR experiments (218–323 K) confirmed the existence of only one porphyrin isomer or conformation over this temperature range. The ^{11}B and ^{19}F NMR spectra each show two signals, indicating that the two B and two F atoms in the molecule are chemically inequivalent.[8] The more upfield ^{11}B resonance has a significantly larger half-width, suggesting that this boron atom occupies an electronically less symmetrical site.

The spectroscopic evidence suggested that the molecule contains a $B_2OF_2^{2+}$ moiety coordinated to the porphyrin such that the B and F atoms are inequivalent and the overall complex attains C_s symmetry. Two models were considered, both containing an F–B–O–B–F group lying in the single plane of symmetry through the molecule, and with each B atom coordinated to only two of the porphyrin nitrogen atoms. In one arrangement both F atoms are on the same face of the porphyrin (*cis*) while in the other they are on opposite sides (*trans*). Calculations on these two models using the simpler porphine ligand were performed using the AM1 semiempirical molecular orbital theory.[9] Both starting structures were fully optimized to acceptable minima with respect to all atom coordinates. The optimized *trans* structure (II) was found to be 8.2 kcal mol⁻¹ lower in energy than the *cis* structure I.

I   II
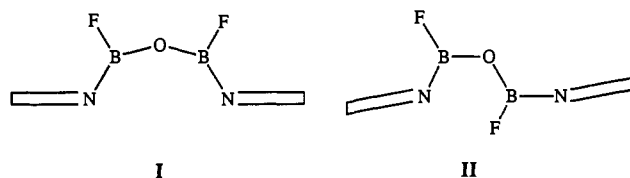
Further investigations using force field[10] and more elaborate density functional theory calculations[11] are in qualitative agreement with these findings. The calculations support a model, structure II, which is completely consistent with all the NMR data and has the following unusual features: (i) one plane of symmetry in the complex which contains the B, O, and F atoms; (ii) different environments for the two B and two F atoms; (iii) close contacts between protons on two of the peripheral tolyl rings with the adjacent pyrrole protons, leading to restricted rotation; and (iv) distortion of the porphyrin ring in an unusual step-shaped arrangement. The structure of the diboron porphyrin complex was confirmed by an X-ray crystal structure determination of the tetrakis-(*p*-chlorophenyl)porphyrin (T*p*ClPP) derivative $B_2OF_2(TpClPP)$ (Figure 1, Table 1). The structure is

(1) (a) Boyan, D. B.; Calvin, M. *J. Am. Chem. Soc.* **1967**, *89*, 5472. (b) Gouterman, M.; Schwarz, F. P.; Smith, P. D.; Dolphin, D. *J. Chem. Phys.* **1973**, *59*, 676.
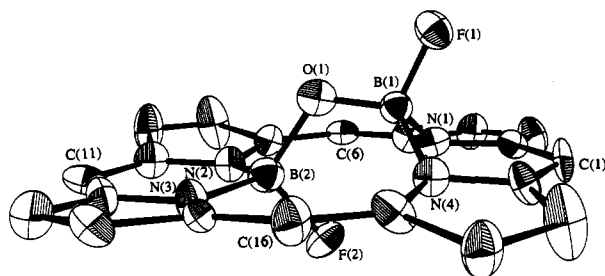
(2) (a) Mangani, S.; Meyer, E. F., Jr.; Cullen, D. L.; Tsutsui, M.; Carrano, C. J. *Inorg. Chem.* **1983**, *22*, 400. (b) Barbour, T.; Belcher, W. J.; Brothers, P. J.; Rickard, C. E. F.; Ware, D. C. *Inorg. Chem.* **1992**, *31*, 746.

(3) (a) Wisnieff, T. J.; Gold, A.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 5616. (b) Callot, H. J.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1982**, *104*, 1272.

(4) Carrano, C.; Tsutsui, M. *J. Coord. Chem.* **1977**, *7*, 125.

(5) $B_2O(OH)_2(TTP)$ was prepared as described in ref 6 using $BCl_3 \cdot MeCN$ as the reagent. ^1H NMR ($CDCl_3$, 400 MHz): 8.95 (m, 4H, H_β), 8.67 (d, 2H, H_β), 8.63 (d, 2H, H_β), 8.37 (dd, 2H, H_o), 8.20 (d, 2H, H_o), 8.17 (d, 2H, H_o), 8.05 (dd, 2H, H_o), 7.65 (m, 6H, H_m), 7.53 (d, 2H, H_m), 2.77 (s, 6H, CH₃), 2.70 (s, 3H, CH₃), 2.68 (s, 3H, CH₃), −9.10 (brs, 2H, OH) ppm. UV/vis (CH_2Cl_2): λ_{max} (log ε), 430 (5.54), 573 (4.28), 623 (4.38) nm.

(6) $BF_3 \cdot OEt_2$ (4 mL) was added to a solution of H_2TTP (2 g) in chlorobenzene (25 mL) containing 2 drops of H_2O under an N_2 atmosphere. The reaction mixture was stirred for 12 h and was monitored by UV/vis spectroscopy until no further insertion was observed. The reaction mixture was evaporated to dryness and chromatographed on silica gel. Elution with CH_2Cl_2 removed a red band containing H_2TTP; then elution with CH_2Cl_2/THF (9:1) removed a green band of the desired product. Chromatography was repeated to obtain a pure product. Recrystallization from CH_2Cl_2/hexane resulted in the product as a purple powder (0.41 g, 18%). MS (FAB⁺): *m/z* 744 (M⁺, 100%). ^1H NMR ($CDCl_3$, 400 MHz): 9.07 (d, 2H, H_β), 9.04 (d, 2H, H_β), 8.68 (d, 2H, H_β), 8.64 (d, 2H, H_β), 8.34 (d, 2H, H_o), 8.19 (m, 6H, H_o), 7.67 (m, 6H, H_m), 7.58 (d, 2H, H_m), 2.79 (s, 6H, CH₃), 2.72 (s, 3H, CH₃), 2.70 (s, 3H, CH₃) ppm. ^{11}B NMR ($CDCl_3$, ppm *vs* $BF_3 \cdot OEt_2$): −15.07 (1B), −16.80 (1B). ^{19}F NMR ($CDCl_3$, ppm *vs* $CFCl_3$): −146.56 (1F), −167.90 (1F). UV/vis (CH_2Cl_2): λ_{max} (log ε), 427 (5.60), 569 (4.29), 619 (4.42) nm.

(7) ^{13}C NMR data and complete assignments are given in the supplementary data.

(8) BF coupling is not observed although the peaks in the ^{19}F NMR spectrum show fine structure. Each resonance appears as two peaks in a 20:80 ratio due to the ^{10}B and ^{11}B isotopes.

(9) AM1 semiempirical molecular orbital theory implemented in the program AMPAC 4.0 (Semichem, 7128 Summit, Shawnee, KS 66216, 1993).

(10) Force field calculations using the program CERIUS 2.0 (Molecular Simulations, Inc.) with the Universal Force Field and the Q_{Eq} charge equilibration scheme (Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024) gave a result qualitatively in agreement with the AM1 model, with II lying 10.3 kcal mol⁻¹ lower than I.

(11) Density functional theory calculations using the program DMOL (version 2.3) (Biosym Technologies, San Diego) with the DN basis set with Hedin–Lundqvist/Janak–Morruzi–Williams local correlation functional. Structure II is computed to be 15.9 kcal mol⁻¹ more stable then structure I.

Figure 1. ORTEP diagram of $B_2OF_2(TpClPP)$, with the *meso-p*-chlorophenyl groups omitted for clarity. C(1) and the eight pyrrole carbon atoms associated with N(1) and N(4) are displaced 0.12–0.56 Å below the mean plane through the four N atoms, while C(11) and the pyrrolyl carbon atoms associated with N(2) and N(3) lie 0.07–0.52 Å above the mean plane.

Table 1. Bond Lengths and Angles for $B_2OF_2(TpClPP)$

	AM1[a]	DMOL[b]	X-ray[c]
B(1)–F(1)	1.336	1.44	1.38(2)
B(1)–O(1)	1.385	1.38	1.26(2)
B(2)–F(2)	1.340	1.46	1.45(2)
B(2)–O(1)	1.452	1.41	1.53(2)
B(1)–N (av)	1.65	1.55	1.60(2)
B(2)–N (av)	1.60	1.51	1.54(3)
B(1)–O(1)–B(2)	115.5	119.7	115.8(13)
F(1)–B(1)–O(1)	108.9	113.4	108(2)
N(1)–B(1)–N(4)	104.1	104.0	100.8(12)
F(2)–B(2)–O(1)	121.7	114.8	108(2)
N(2)–B(2)–N(3)	108.5	108.3	109(2)

[a] Calculated using AM1 semiempirical molecular orbital theory (ref 9). [b] Calculated using density functional theory (ref 11). [c] Data for one of the two half-weighted F–B–O–B–F fragments in the disordered X-ray crystal structure determination. F(2) and O(1) could not be resolved due to the disorder (ref 12).

disordered such that the bridging oxygen and one fluorine atom (F(2)) could not be resolved crystallographically.[12]

The X-ray structure and the calculated structure are in good agreement, particularly in the coordination environment about the N_2–B(F)–O–B(F)–N_2 moiety. In the X-ray structure B(2) is only 0.03 Å above the mean N_4 plane, while B(1) lies 0.93 Å above this plane. F(2) lies over the center of the porphyrin ring while F(1) is directed toward the periphery; thus the two atoms are in different regions of the porphyrin ring current. Significant steric interactions exist between the *ortho* protons on the two

symmetry-related *p*-chlorophenyl rings (on C(6) and C(16)) and the adjacent β-pyrrolic protons. This is consistent with the restricted rotation observed for these aryl rings. Close contacts are not found between the *ortho* protons of the nonequivalent aryl rings (on C(1) and C(11)) and the adjacent β-pyrrolic protons, and these rings are observed to rotate freely on the NMR time scale.[14] The porphyrin ring is distorted in an unusual step fashion such that the two pyrrole rings containing N(1) and N(4) are tilted below the mean N_4 plane while those containing N(2) and N(3) are tilted above (see Figure 1). The deviation of the carbon atoms on the periphery of the porphyrin from the mean N_4 plane is less marked in the X-ray structure than in the calculated structure which features the simpler porphine ligand. Curiously both the X-ray and computed structures maintain an almost centrosymmetric porphyrin ligand in spite of the asymmetric coordination of the FBOBF moiety. This type of step-shaped distortion is also evident but less pronounced in the structures of other out-of-plane complexes such as $(PdCl_2)(CHOCH_2Ph)$-$(TPP)^{3b}$ and $[Rh(CO)_2]_2(OEP)$.[13] The similarity of the NMR data for $B_2O(OH)_2(TTP)$ and $B_2OF_2(TTP)$ indicates that the former probably adopts the same structure as the latter.[5,6]

In summary, we have described the first fully characterized boron porphyrin complex. A new coordination mode for the porphyrin ligand is demonstrated where the F–B–O–B–F moiety is essentially threaded through the center of the porphyrin ligand with each B atom coordinated to only two pyrrole nitrogen atoms in an unsymmetrical fashion. The complex was initially characterized through a detailed NMR study in concert with structure calculations by three independent computational methods[9–11] and was subsequently confirmed by an X-ray crystal structure which showed excellent agreement with the calculated structure. The results indicate that boron porphyin complexes can be prepared which have a rich new structural chemistry.

Supplementary Material Available: Elemental analysis data, complete ^1H and ^{13}C NMR assignments for $B_2OF_2(TTP)$, details of structure solution and refinement, atom labeling scheme, and tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and deviations from mean N_4 plane for $B_2OF_2(TpClPP)$, and tables of calculated coordinates (AM1 and DMOL) for the computed structure (19 pages); listing of observed and calculated structure factors for $B_2OF_2(TpClPP)$ (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(12) Purple crystals of $B_2OF_2(TpClPP)$, prepared as described in ref 6 using $H_2TpClPP\cdot2(CH_3C_6H_5)$, were grown by diffusing xylene into a CHCl$_3$/toluene solution of the complex. Crystal data: $a = 7.767(1)$ Å, $b = 10.607(2)$ Å, $c = 15.928(7)$ Å, $\alpha = 71.84(2)°$, $\beta = 82.65(2)°$, $\gamma = 81.13(1)°$, $Z = 1$, $d(\text{calc}) = 1.367$ g cm^{-3}, space group $P1$. A total of 3605 reflections ($I > 2\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at 193 K using Mo Kα radiation ($\lambda = 0.710$ 69Å). Least-squares refinement on F^2 converged to $R(F) = 0.070$ and $R_w(F^2) = 0.19$. The FBOBF group was disordered and occupied two sites related by an approximate inversion center. The structure was refined using two half-weighted FBOBF groups. O(1) from one group and F(2) from the other were close to overlapping and could not be resolved; accordingly, they were refined with the same coordinates, leading to uncertainty in the geometric parameters associated with these atoms.

(13) Takenaka, A.; Sasada, Y.; Ogoshi, H.; Omura, T.; Yoshida, Z. *Acta Crystallogr.* **1975**, *B31*, 1.

(14) The β-pyrrolic H···H distances flanking the aryl rings on C(6) and C(16) are 5.01 (average) Å compared to 5.68 (average) Å for the H···H distance flanking the nonequivalent aryl rings on C(1) and C(11). The corresponding values for the calculated structure (based on porphine) are 4.8 and 5.6 Å, respectively.