ΔG value (ca. $-25\,\mathrm{kcal\,mol^{-1}}$ to ca. $-35\,\mathrm{kcal\,mol^{-1}}$), so a photoinduced electron-transfer mechanism is apparently favored for these photochemical cycloaddition reactions.

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A Porphyrin as a Binucleating Ligand: Preparation and Crystal Structure of a Porphyrin Complex Containing a Coordinated B_2O_2 Ring

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The enormously wide utility of the porphyrin ligand in coordination chemistry derives in part from the fact that there is a distance of 2 Å from the center of the square-planar N_4 coordination site to one nitrogen atom; a broad range of elements in various oxidation states can be accommodated. Even larger elements can be coordinated as out-of-plane complexes, and to some extent smaller elements can be accommodated by ruffling of the ligand and compression of the porphyrin core. We recently demonstrated that boron can form a porphyrin complex[1] which contains two boron atoms as an F-B-O-B-F moiety threaded through the cavity in the porphyrin, such that each boron atom is coordinated to two different porphyrin nitrogen donor atoms. One boron atom lies approximately in the plane of the ligand, while the other is displaced significantly out of this plane (overall C_s symmetry). This compound, $[B_2OF_2(ttp)]$ (**1**, ttp = dianion of 5,10,15,20-tetra-*p*-tolylporphyrin), was prepared by the reaction of $BF_3\cdot OEt_2$ with the free base porphyrin $H_2(ttp)$ in the presence of a trace of water. The structure of **1** was confirmed by an X-ray crystal structure determination of $[B_2OF_2(TpClpp)]$ (**2**, T*p*Clpp = dianion of 5,10,15,20-tetra-*p*-chlorophenylporphyrin).[1]

The corresponding reaction of $BCl_3\cdot MeCN$ with $H_2(ttp)$ in chlorobenzene containing a trace of water[2] is more complex than that of $BF_3\cdot OEt_2$. Initially a blue-green precipitate forms which is highly reactive and releases the bound boron atoms to provide the free base porphyrin if dissolved in a neutral or acidic solvent. When the precipitate is dissolved in dichloromethane and subjected to chromatography on basic alumina, $[B_2O(OH)_2(ttp)]$ (**3**) is formed. This compound is analogous to the fluoroboron complex $[B_2OF_2(ttp)]$ but contains hydroxo groups in place of the fluorine substituents.[1]

The blue-green precipitate formed in the reaction of $BCl_3\cdot MeCN$ with $H_2(ttp)$ persists in solution for a few minutes, which is long enough to obtain its ^1H NMR spectrum in $CDCl_3$. The spectrum shows the compound to have higher symmetry than $[B_2OX_2(ttp)]$ (X = F, OH), and the tolyl methyl groups appear as two singlets in a 1:1 ratio. By careful control of the reaction conditions and use of $H_2(TpClpp)$ as the porphyrin and benzene as the solvent, it proved possible to isolate crystals of the blue-green compound following recrystallization from $CHCl_3$ saturated with $BCl_3\cdot MeCN$. X-ray crystallography revealed a second structural type for a boron porphyrin and a new coordination mode for the porphyrin ligand.[3]

The compound $[B_2O_2(BCl_3)_2(TpClpp)]$ (**4**) contains a four-membered B_2O_2 ring coordinated in the cavity of the porphyrin; the plane of the B_2O_2 ring is perpendicular to the ligand plane (Figure 1). Two porphyrin nitrogen atoms coordinate to each boron atom, and the two boron atoms are essentially coplanar with the porphyrin. Each bridging oxygen atom is coordinated to a BCl_3 molecule. The crystals contain two independent half-molecules that are related through a center of symmetry. Each B_2O_2 ring has two unique B–O distances which are almost the same (av 1.49(2) Å), and the $B1\cdots B1'$ distance across the ring is close to 2.1 Å. The B2–O1 distances involving the coordinated BCl_3 molecules average 1.49(2) Å.

To accommodate two boron atoms in the same plane as the porphyrin, the macrocycle has undergone an elongation along one axis to result in a rectangular rather than a square core. The $N1\cdots N2$ distance parallel to the $B\cdots B$ axis averages 3.63 Å, over 1.1 Å longer than the $N1\cdots N2'$ distance within the N-B-N chelate rings (2.49 Å). This elongation is reflected in the bond angles at C4, C5, and C6, which have opened

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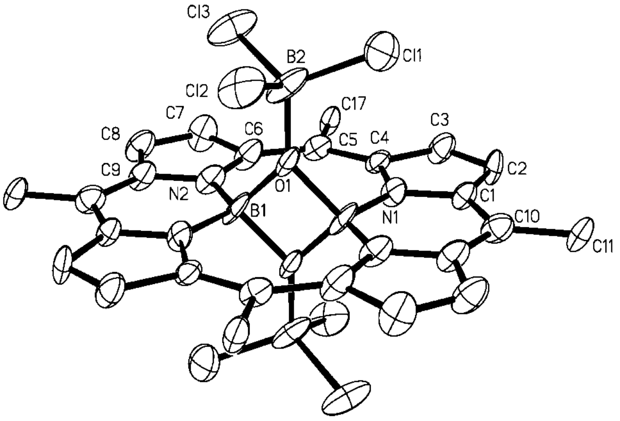
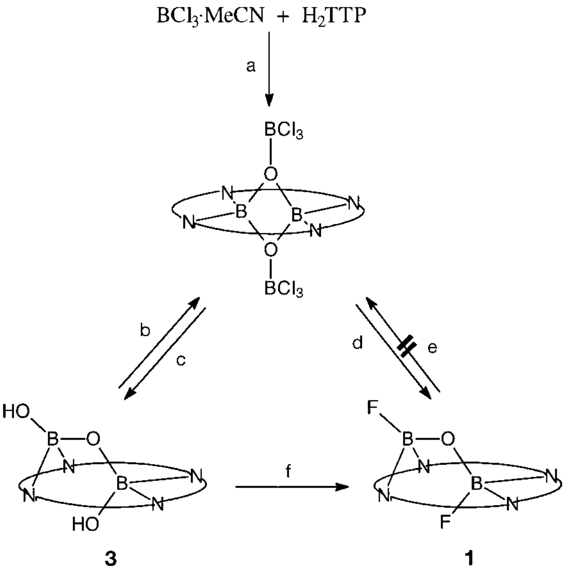


Figure 1. Molecular structure of **4** (*p*-chlorophenyl groups omitted for clarity). Selected bond lengths [Å] and angles [°] for one of the two independent molecules in the unit cell: B1–O1 1.508(12), B1–O1′ 1.498(13), B2–O1 1.496(13), B1–N1 1.455(14), B1–N2 1.47(2), N2–C6 1.382(13), C6–C5 1.432(14), C5–C4 1.429(13), C4–N1 1.358(12), N1–C1 1.393(11), C1–C10 1.396(14), C10–C9′ 1.420(14), C9–N2 1.383(12); B1-O1-B1′ 88.8(7), O1-B1-O1′ 91.2(7), B1-O1-B2 136.2(7), B1′-O1-B2 134.9(7), N1-C4-C5 132.1(9), C4-C5-C6 136.8(10), C5-C6-N2 132.6(9), N1-C1-C10 120.5(9), C1-C10-C9′ 121.3(8), C10′-C9-N2 119.5(9).



Scheme 1. Chemical interconversions of **1**, **3**, and $[B_2O_2(BCl_3)_2(ttp)]$ (all shown schematically). a) C_6H_5Cl, trace H_2O, reflux; b) $BCl_3 \cdot MeCN$, reflux; c) basic Al_2O_3; d) $n$$Bu_4NF$, THF; e) $BCl_3 \cdot MeCN$, reflux; f) $BF_3 \cdot OEt_2$.

considerably to greater than 130°, whereas the corresponding angles at C1, C10, and C9 are all close to the expected 120° (Figure 1). However, the bond lengths in the N1-C4-C5-C6-N2 and N1-C1-C10-C9′-N2′ portions of the porphyrin are quite similar, indicating that only the bond angles are significantly affected by the elongation. The porphyrin itself remains essentially planar, with deviations of 0.02 Å or less from the mean plane formed by the 24 atoms. The rectangular distortion of a planar porphyrin has been observed previously in free base porphyrins bearing sterically crowded substituents on the periphery.[4] The rectangular distortion observed in **4** is unusual. Firstly, it results from steric crowding within the cavity rather than on the periphery of the ligand. Secondly, the magnitude of the distortion is large for the diboron complex ($\delta(N \cdots N) = 1.1$ Å, compared to about 0.4 Å in decasubstituted porphyrins[4]).

Although six-membered and larger rings containing alternating boron and oxygen atoms are very well known, particularly for the inorganic borates,[5] only three crystal structures of compounds containing four-membered B_2O_2 rings have been reported.[6–8] Of these, the dimer $[(Me_2BOBMe_2)_2]$[6] is the most closely related to the porphyrin compound reported here; it contains a B_2O_2 ring involving four-coordinate boron and three-coordinate oxygen atoms (B–O 1.580(1), B ··· B 2.31 Å). Of all four structures,[6–8] **4** has the shortest B–O and B ··· B distances within the B_2O_2 ring, presumably a result of the steric constraint imposed by the porphyrin cavity.

The chemical interconversion of the three boron porphyrin complexes **1**, **3**, and $[B_2O_2(BCl_3)_2(ttp)]$ is shown in Scheme 1. $[B_2O_2(BCl_3)_2(ttp)]$ and **3** can be interconverted, and **1** can be produced from either compound. However, the reaction of **1** with $BCl_3 \cdot MeCN$ provides unchanged starting material, reflecting the difficulty of disrupting the stronger B–F bonds.

The two derivatives of $[B_2O_2(BCl_3)_2(por)]$ (por = ttp or T*p*Clpp) are the only examples of porphyrin compounds containing a small ring coordinated in the cavity. A porphyrin-like macrocycle containing a similar motif bears a four-membered Cu_2Cl_2 ring coordinated in the cavity with the plane of the Cu_2Cl_2 ring perpendicular to that of the macrocycle. However, in this case the macrocycle is an expanded porphyrin containing six pyrrole rings.[9] The diboron porphyrin complex reported here shows that a conventional porphyrin can act as a binucleating ligand which can coordinate two elements in the plane of the macrocycle. The key features are the incorporation of the very small element boron and the remarkable tetragonal elongation of the porphyrin ligand.

Experimental Section

$[B_2O_2(BCl_3)_2(ttp)]$: $BCl_3 \cdot MeCN$ (5.00 g, 31.6 mmol) was added to a solution of $H_2(ttp)$ (2.00 g, 3.0 mmol) in undried chlorobenzene (25 mL). The reaction mixture was heated under reflux for 6 h under a flow of dry N_2 to remove $HCl_{(g)}$. The color of the solution changed from dark purple to blue-green, and a dark solid began to precipitate. The reaction mixture was cooled to room temperature and then to 4 °C for 18 h. The dark purple crystals were collected and washed with hexane (2.36 g, 83 %). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 9.12$ (AB q, 8H, β-pyrrolic), 8.31 (d, 4H, $^3J =$ 7.7 Hz, *ortho*), 8.25 (d, 4H, $^3J = 7.7$ Hz, *ortho*), 7.73 (d, 4H, $^3J = 7.7$ Hz, *meta*), 7.59 (d, 4H, $^3J = 7.7$ Hz, *meta*), 2.79 (s, 6H, CH_3), 2.72 (s, 6H, CH_3); ^{11}B NMR ($CDCl_3$, 128 MHz): $\delta = -15.12$; UV/Vis (CH_2Cl_2): λ_{max} ($\lg \varepsilon$) = 425 (5.58), 559 (4.36), 610 nm (4.42).

4: Compound **4** was prepared as described for $[B_2O_2(BCl_3)_2(ttp)]$. H_2(T*p*Clpp) (1.5 g, 2.0 mmol) and $BCl_3 \cdot MeCN$ (4 g, 25.3 mmol) in undried benzene (60 mL) were heated under reflux for 12 h. The dark green precipitate was collected by filtration and redissolved in $CHCl_3$ saturated with $BCl_3 \cdot MeCN$. The solution was filtered into a Schlenk tube, and the volume of the solvent reduced until crystallization was imminent. The tube was cooled at 4 °C for three weeks, after which time dark green-red dichroic crystals suitable for X-ray analysis were isolated. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 9.17$ (AB q, 8H, β-pyrrolic), 8.42 (d, 4H, $^3J = 7.8$ Hz, *ortho*), 8.30 (d, 4H, $^3J = 8.2$ Hz, *ortho*), 7.94 (d, 4H, $^3J = 7.9$ Hz, *meta*), 7.82 (d, 4H, $^3J = 7.6$ Hz, *meta*); UV/Vis (CH_2Cl_2): $\lambda_{max} = 422$, 556, 600 nm.

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[3] Crystal structure analysis of **4** $\cdot 2\,CHCl_3 \cdot C_6H_6$: $C_{44}H_{24}B_4Cl_{10}N_4O_2 \cdot 2\,CHCl_3 \cdot C_6H_6$: $M_r = 1355.26$, triclinic, space group $P\bar{1}$, $T = 193$ K, $a = 10.238(12)$, $b = 10.272(3)$, $c = 27.865(7)$ Å, $\alpha = 97.33(2)$, $\beta = 97.64(5)$, $\gamma = 96.18(5)^\circ$, $V = 2857(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.575\ g\,cm^{-3}$, $F(000) = 1360$. Suitable crystals were grown from a solution in $CHCl_3$ saturated with $BCl_3 \cdot MeCN$. The crystals were small ($0.20 \times 0.12 \times 0.12$ mm), of poor quality, and only weakly diffracting, which limited the data quality and hence the final precision. Enraf-Nonius CAD-4 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Total of 9008 reflections to $2\theta = 50^\circ$. Semi-empirical absorption correction (Ψ scans, $\mu = 0.81\ mm^{-1}$, $A_{min}/A_{max} = 0.907/0.922$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 with all data. The unit cell contains two independent half-molecules, each related through a center of symmetry, as well as one benzene and two chloroform molecules per porphyrin molecule. All atoms were allowed to refine anisotropically, and hydrogen atoms were included with a riding model. Refinement converged to $R = 0.0937$ for the 4249 observed data ($I > 2\sigma I$) and $wR2 = 0.2924$ for all data. Goodness of fit on $F^2 = 0.973$. Programs used: SHELXS (structure solution) and SHELXL (structure refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100798 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Topochemical Conversion of a Hydrogen-Bonded Three-Dimensional Network into a Covalently Bonded Framework[**]

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The design and construction of supramolecular, three-dimensional networks has been an area of increasing interest over recent years with respect to engineering crystal packing at will.[1] Strategies for crystal engineering include the use of various intermolecular forces, from weak van der Waals forces, hydrogen and covalent bonding,[2, 3] to ionic interactions.[4] Most of the reported three-dimensional architectures are formed as a result of self-assembly from solution.[5] An exciting, yet little explored area of supramolecular chemistry, is the reversible interconversion between monomers and oligomers initiated by the input of external information (e.g. protons, electrons, photons). Such materials may have functional use due to their switching ability and the possibility to sequester and release guest molecules. Recently a proton-dependent monomer–oligomer interconversion in solution was reported.[6] Here we report the topochemical thermal conversion of a novel, three-dimensional network held together by strong hydrogen bonding into a covalent, supramolecular framework by dehydration of coordinated water. This unexpected transformation of hydrogen-bonded to covalent network appears to be assisted by strong NH···O hydrogen bonds and irreversible.

$[\{Zn(sala)(H_2O)\}_2] \cdot 2\,H_2O$ (**1**) was prepared by the reaction of $Zn(ClO_4)_2 \cdot 6\,H_2O$ with $Li_2(sala)$ in aqueous solution and characterized by single-crystal X-ray diffraction techniques[7] ($H_2(sala)$ = *N*-(2-hydroxybenzyl)-L-alanine). Figure 1 shows the structure of the basic dimeric building block,

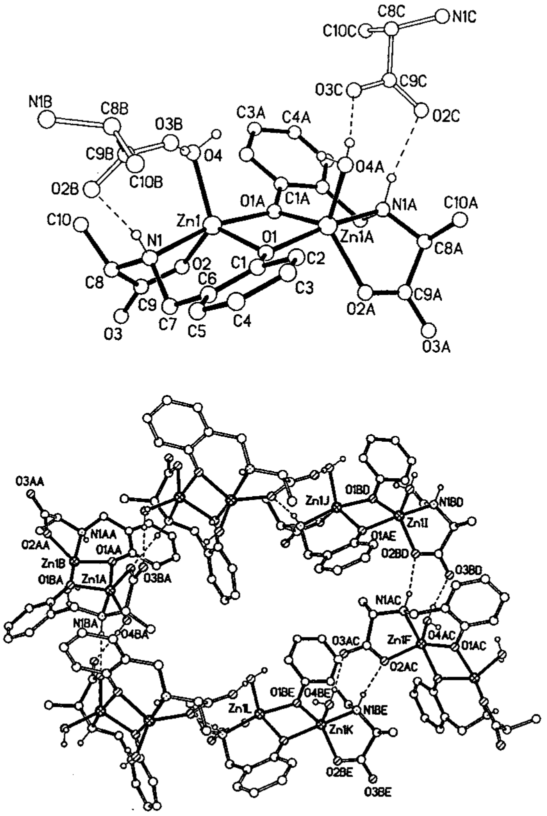

Figure 1. Top: Structure of the binuclear complex **1**. Hydrogen bonds are drawn with dotted lines. The hydrogen atoms attached to carbon atoms are omitted for clarity. Selected fragments of neighboring molecules involved in hydrogen bonding are shown with open bonds. Selected bond distances [Å] and angles [°]: Zn1···Zn1 A 3.092(1), Zn1–O1 2.009(2), Zn1–O1 A 2.040(2), Zn1–O2 2.027(2), Zn1–O4 2.030(2), Zn1–N1 2.140(2), C9–O2 1.270(4), C9–O3 1.246(4); Zn1-O1-Zn1 A 99.58(7), O1-Zn1-N1 93.00(8), O1-Zn1-O1 A 79.56(8), O2-C9-O3 124.1(3). Bottom: The hydrogen bonds link the dimers together to form hexagonal rings.

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