A Ni(II) 10-Boracorrole: An Antiaromatic Porphyrinoid Containing A Boron Atom at the *meso*-Position

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Supporting Information

ABSTRACT: A Ni(II) 10-boracorrole (**2**) was obtained from the transmetallation of the corresponding 10-silacorrole with BBr$_3$. The antiaromaticity of **2** was examined by ^{1}H NMR spectroscopy and theoretical calculations. The antiaromatic character of **2** is reflected in a very narrow HOMO–LUMO gap that results in weak and broad absorption bands in the NIR region up to 1800 nm. Furthermore, titration experiments revealed a high Lewis acidity of **2** toward pyridines. Theoretical calculations on **2** indicated the presence of p–π* conjugation, which significantly stabilizes the energy level of its LUMO.

Boron-containing π-conjugated molecules are a fascinating class of compounds due to their unique optoelectronic properties and reactivity.[1] In these systems, the vacant p orbital of the boron atom endows the compounds with high Lewis acidity. In addition, the interaction between the p orbital of the boron atom and the π* orbital (p–π* conjugation) significantly lowers their LUMO levels, thus enhancing their electron-accepting ability. Borole, a five-membered heterocycle with a boron atom, is particularly interesting,[2,3] as it is isoelectronic to the cyclopentadienyl cation and exhibits distinct antiaromaticity due to the cyclic 4π-electron system. This unusual electronic structure endows boroles with unique reactivity, which includes the formation of borates with Lewis bases,[3d,3f,3h,3l] one- and two-electron reduction,[3g,3i] Diels–Alder reactions with alkynes,[3a,3b,3d,3j] and metal-free H$_2$ activation reactions.[3k] Other boron-containing antiaromatic macrocycles are also expected to show such intriguing properties. However, reports on such molecules remain elusive due to the difficulties associated with their synthesis, which arise predominantly from the intrinsically high reactivity of antiaromatic molecules.

Porphyrinoids are macrocycles with a porphyrin-like polypyrrole skeleton. Recently, the introduction of heteroatoms into the π-conjugation circuits of such porphyrinoids has received much attention. Bröring and co-workers have reported the synthesis of 10-heterocorroles containing oxygen, sulfur, and selenium.[4] Our group has independently developed 10-aza, 10-oxa, 10-thia, 10-sila, and 10-phosphacorroles.[5] Despite

these accomplishments, the synthesis of porphyrinoids containing boron atoms at the *meso*-positions has not yet been accomplished. Considering the attractive properties that can be expected from boron-containing π-conjugated molecules, 10-boracorrole represents a fascinating research target in the context of porphyrin and boron chemistry. Furthermore, based on a theoretical study, Foroutan-Nejad and Ghosh have recently predicted a distinct antiaromaticity for 10-boracorroles.[6]

A promising method to construct boron-containing heterocycles is the transmetallation of the corresponding metallacycles containing silicon or tin.[3a,3c,3d,3f-h,3l,7] Accordingly, a previously reported 10-silacorrole[5f] would be a promising potential precursor for 10-boracorrole. Herein, we report the synthesis of a Ni(II) complex of 10-boracorrole (henceforth: Ni(II) 10-boracorrole) as well as the examination of its antiaromaticity, reactivity, and Lewis acidity.

Scheme 1. Synthesis of Ni(II) 10-boracorrole 2.
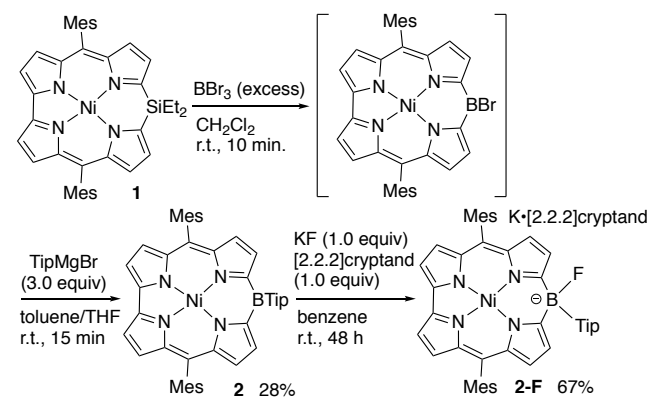
The synthesis of this Ni(II) 10-boracorrole was achieved from the corresponding Ni(II) 10-silacorrole via a transmetallation of the silicon atom with BBr$_3$ as the key step (Scheme 1). Treatment of Ni(II) 10-silacorrole **1** with BBr$_3$, followed by the introduction of a triisopropylphenyl (Tip) group using the corresponding Grignard reagent, provided Ni(II) 10-boracorrole **2** in 28% yield over two steps. As **2** is stable in air, it was purified by standard column chromatography on silica gel. Conversely, the corresponding analogue with a mesityl group on boron was less stable and underwent rapid decomposition

within a few hours under ambient conditions. The stability of such Ni(II) 10-boracorroles thus seems to depend on the steric bulk of the substituent on the boron atom.

The formation of **2** was confirmed by NMR spectroscopy and mass spectrometry. The ^{11}B NMR spectrum of **2** exhibited a peak at 29.9 ppm, suggesting the presence of a tri-coordinated boron atom.[8] In the ^{1}H NMR spectrum, the β-pyrrolic protons were observed as four relatively high-field-shifted doublets (3.62, 3.51, 3.45, and 3.42 ppm). These high-field shifts clearly reflect the paratropic ring-current effect, and thus the antiaromatic character of Ni(II) 10-boracorrole **2** under magnetic criteria.[9] The parent mass ion peak of **2** appeared at m/z = 790.37566 (calcd for $(C_{51}H_{53}N_4{}^{11}B^{58}Ni)^+$ = 790.37198), and the isotope pattern matched the theoretical expectations.

The solid-state structure of **2** was determined by a single-crystal X-ray diffraction analysis (Figure 1a,b). In the solid state, **2** adopts a highly planar conformation with a mean plane deviation of 0.057 Å. The endocyclic C–B bond in **2** (1.536(5) Å) is shorter than typical C–B single bonds and the exocyclic C–B bond (1.588(4) Å) in **2**, indicating the presence of macrocyclic π-conjugation through the boron atom.
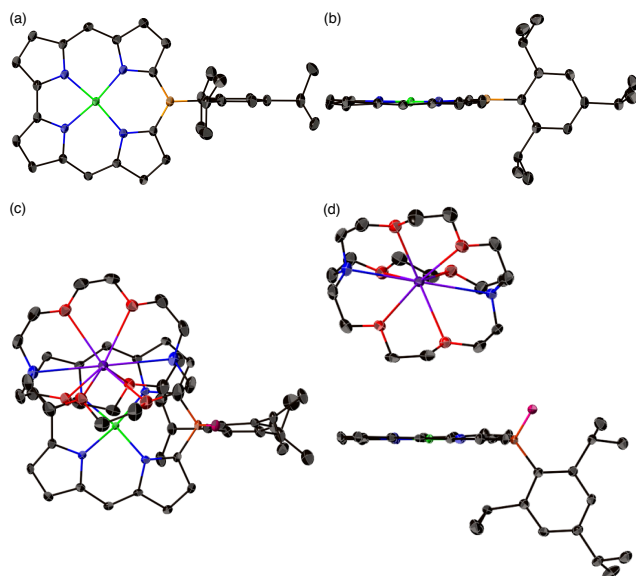

Figure 1. X-ray crystal structures of **2** and **2-F**. (a) Top view and (b) side view of **2**. (c) Top view and (d) side view of **2-F**; thermal ellipsoids are shown at 50% probability; *meso*-mesityl groups and hydrogen atoms are omitted for clarity.

The antiaromaticity of boracorrole **2** was corroborated by the large positive values obtained from the nucleus independent chemical shift (NICS(0)) calculations on the optimized crystal structure (Figure S12).[10] The ring current effect was evaluated by ACID calculations.[11] The counter-clockwise orientation of the current confirmed the distinct antiaromaticity of **2** (Figure 2).
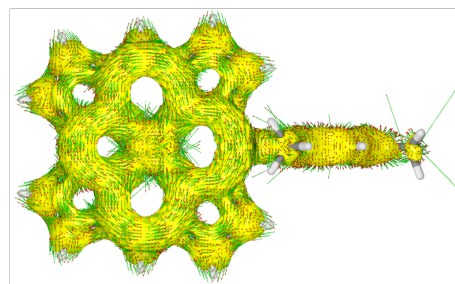

Figure 2. ACID plot of **2** (isovalue: 0.05), calculated at the CSGT-B3LYP/def2-TZVP level of theory.

Figure 3 displays the electronic absorption spectrum of **2** in dichloromethane. The shape of the spectrum is significantly different from that of normal porphyrins and other 10-heterocorroles. Notably, **2** exhibits considerably weak and broad absorption bands from 900 to 1800 nm, which is typical for antiaromatic porphyrinoids.[12] To gain further insights into the electronic structure of **2**, we conducted DFT calculations at the B3LYP/6-31G(d)+SDD level of theory (Figure S10). While the distribution of the HOMO is almost identical to that in 10-silacorroles,[5f] the LUMO is delocalized over the boron atom and the neighboring carbon atoms, similar to the LUMO of borole. This result suggests effective conjugation between the vacant p orbital of the boron atom and the π^* orbital of the porphyrinic skeleton. This interaction should play an important role to lower the energy level of the LUMO of **2**. Moreover, the shapes of the HOMO and LUMO are similar to those in 16π-electron antiaromatic norcorrole. TD-DFT calculations revealed that the weak long-wavelength absorption of **2** is derived from the forbidden HOMO–LUMO transition (f = 0.0031), which is a diagnostic feature of antiaromatic porphyrinoids (Figure S11).

Subsequently, we transformed **2** into fluoroborate **2-F** (Scheme 1). The reaction of **2** with potassium fluoride in the presence of [2.2.2]cryptand afforded **2-F** in 67% yield. The ^{1}H NMR spectrum of **2-F** showed four doublets for the β-pyrrolic protons at 6.03, 5.90, 5.82, and 5.61 ppm. These values reflect the non-aromatic character of **2-F**, indicating the loss of anti-aromaticity upon coordination of fluoride. A single-crystal X-ray diffraction analysis unambiguously confirmed the formation of fluoroborate **2-F** (Figure 1c,d), wherein the boron atom adopts a tetrahedral geometry upon coordination of the fluoride ion. The interatomic distance between potassium and boron (> 8 Å) suggests negligible interactions between these atoms. The endocyclic C–B bonds in **2-F** (1.610(3)/1.614(3) Å) are elongated due to the loss of the partial double-bond character of the C–B bonds in **2**. Furthermore, fluorination of **2** results in a drastic change of the absorption spectrum, specifically the disappearance of the lower-energy absorption bands (1000–1800 nm) (Figure 3). The shape of the absorption spectrum of **2-F** resembles to that of 10-isocorrole,[13] which is isoelectronic to **2-F**. Consequently, the disruption of the cyclic π-conjugation of **2** upon sp^3-hybridization of the boron center changes its electronic properties.
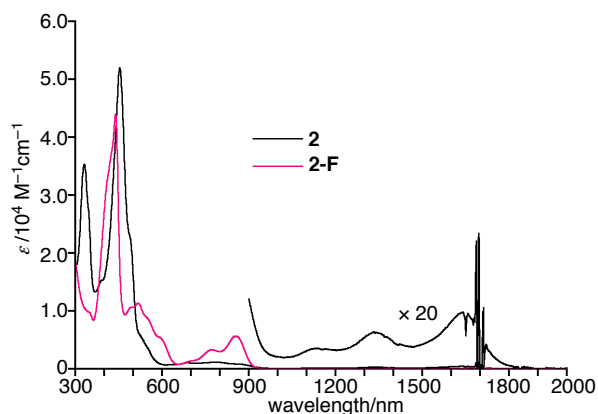
Figure 3. UV/vis/NIR absorption spectra of **2** and **2-F** in CH_2Cl_2.

Subsequently, we conducted an electrochemical analysis of **2** and **2-F** by cyclic voltammetry (Figures S8 and S9). While two reversible reduction waves were observed for **2**, the oxidation wave was irreversible. The first reduction potential of **2** (−0.932 V) is substantially higher than those of normal porphyrins (−1.75 V)[14] or other 10-heterocorroles (−2.01~−1.42 V),[5] which indicates a high electron-accepting ability for **2**. The narrow HOMO–LUMO gap of **2** (1.22 V), electrochemically determined by the difference between the first oxidation potential and the first reduction potential, is a typical feature of antiaromatic porphyrinoids. In contrast, fluoroborate **2-F** showed a considerably lower oxidation potential (−0.323 V), which reflects its anionic character. The electrochemically determined HOMO–LUMO gap of **2-F** (1.657 V) is larger than that of **2**, which supports the anticipated loss of antiaromaticity.

We also investigated the Lewis acidity of the boron atom of **2** by addition of *N,N*-dimethyl-4-aminopyridine (DMAP) to a solution of **2** in CH_2Cl_2, which induced a significant change in its absorption spectrum (Figure S6). The shape of the spectrum after addition of DMAP is identical to that of **2-F**, which clearly suggests the coordination of DMAP to the boron atom under concomitant sp³-hybridization. The same spectral change was also observed in the case of the addition of pyridine (Figure S7). The calculated association constants for **2** and DMAP (1.4×10^4 M^{-1}) or pyridine (11 M^{-1}) stand in contrast to the behavior of *B*-triisopropylphenyldibenzoborepin, which does not interact with pyridine.[15] On the basis of these results, we conclude that the loss of antiaromaticity upon coordination of pyridine is an important factor for the Lewis acidity.[3d,3f,3h,3l,7a] This notion is further corroborated by density functional theory (DFT) calculations (Scheme S1 and Table S2), which suggest that the complexation of antiaromatic *B*-mesitylboracorrole with pyridine is exergonic (ΔG = −4.2 kcal mol^{-1}), while the complexation of pyridine with aromatic *B*-mesitylborepine is endergonic (ΔG = 7.2 kcal mol^{-1}).

In summary, we have synthesized a Ni(II) complex of a 10-boracorrole (**2**). The ^{1}H NMR analysis of **2** revealed its distinct antiaromatic character, which was corroborated by theoretical calculations. Optical and electrochemical analyses of **2** revealed a narrow HOMO–LUMO gap and weak NIR absorption bands. Theoretical calculations on **2** suggested effective p–π* conjugation, which significantly lowers the energy level of the LUMO. Moreover, **2** showed substantial Lewis acidity toward pyridines. Upon coordination of pyridines under concomitant sp³-hybridization of the boron center, the disruption of the cyclic π-conjugation of **2** results in dramatic changes to its absorption features. The results of the present study demonstrate that the characteristic features of boron prevail in macrocyclic π-conjugation systems and allow fine-tuning the optoelectronic properties of such boron-containing porphyrinoids.

ASSOCIATED CONTENT

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16π antiaromatic