Cation–π Interactions

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# Exclusive π Encapsulation of Light Alkali Metal Cations by a Neutral Molecule

*Rüdiger Bertermann, Holger Braunschweig,* Philipp Constantinidis, Theresa Dellermann, Rian D. Dewhurst, William C. Ewing, Ingo Fischer, Thomas Kramer, Jan Mies, Ashwini K. Phukan, and Alfredo Vargas*

*Dedicated to Professor Dr. F. Ekkehardt Hahn on the occasion of his 60th birthday*

**Abstract:** *Cation–π interactions are one of the most important classes of noncovalent bonding, and are seen throughout biology, chemistry, and materials science. However, in almost every documented case, these interactions play only a supporting role to much stronger covalent or dative bonds, thus making examples of exclusive cation–π bonding exceedingly rare. In this study, a neutral diboryne molecule is found to encapsulate the light alkali metal cations $Li^+$ and $Na^+$ in the absence of a net charge, covalent bonds, or lone-pair donor groups. The resulting encapsulation complexes are, to our knowledge, the first structurally authenticated species in which a neutral molecule binds the light alkali metals exclusively through cation–π interactions.*

The predominantly electrostatic interaction of cations with neutral π-electron systems, known as cation–π interactions, is a key concept in the increasingly important field of noncovalent bonding.[1] Such cation–π (neutral) interactions are a common feature of biology, a prime example being those found between alkali metal cations and sodium and potassium channels.[2–5] Although the concept of alkali metal cation–π interactions was developed in a biological context, it is becoming clear that this phenomenon is also of great importance to materials science and supramolecular chemistry.[6,7] Cation–π interactions have been demonstrated between alkali metal cations and carbon nanotubes (CNTs),[8–10] and have been used to improve the dispersion stability of CNTs[11] and graphene sheets.[12] Very recently, stacks of graphene oxide membranes that select alkali metal cations using cation–π interactions have been developed for water desalination and molecular sieve applications.[13] Similarly, boron-nitride nanotubes exhibit cation–π interactions with ionic liquids,[14] and can act as permeable channels for alkali metal cations.[15] The intercalation of lithium ions into graphite in common (discharged) lithium-ion batteries does not involve cation–π interactions, as the carbon material is negatively charged; however, a small amount of residual $Li^+$ ions remain in the neutral carbon material after charging of the battery.[16,17] As this is a common source of performance loss in lithium-ion batteries, a better understanding of the interactions of $Li^+$ ions with neutral carbon-based materials is highly desirable.

Despite the clear importance of alkali metal cation–π interactions throughout biology and materials chemistry, there is limited unequivocal structural evidence for such interactions,[18] and even fewer structurally authenticated molecules or materials in which alkali metal cations are bound exclusively to neutral π systems (without lone pairs of electrons). Molecular systems in which cation–π interactions exist alongside stronger interactions with Lewis donor groups[19,20] or strong covalent bonds[21,22] are very common in the literature, but almost none exist in the absence of these stronger interactions. Although mass-spectrometric data exist for neutral molecules that bind alkali metal cations exclusively through cation–π interactions,[23] only a handful of structurally authenticated examples are known, namely fullerenes with intercalated cations (**I** and **II**, Figure 1),[24] and four alkyne and arene complexes of potassium and cesium cations (**III**–**VI**, Figure 1).[25] Apart from fullerene complexes **I** and **II**, in which the cations are kinetically trapped, to our knowledge no complexes exist in the condensed phase in which the lighter alkali metal cations $Li^+$ and $Na^+$ bind exclusively to neutral π systems.[26] This is even more surprising given that cation–π interactions with the lighter alkali metals have been calculated to be more energetically favorable than those with the heavier cations in the $M^+$-benzene model.[27]

We recently prepared a neutral molecule with a boron–boron triple bond (diboryne $B_2IDip_2$, Figure 2),[28] which has subsequently been shown to possess remarkable reactivity and strong reducing properties.[29] Given the interest in boron-

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[*] Dr. R. Bertermann, Prof. Dr. H. Braunschweig, T. Dellermann, Dr. R. D. Dewhurst, Dr. W. C. Ewing, Dr. T. Kramer, Dr. J. Mies
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: h.braunschweig@uni-wuerzburg.de

P. Constantinidis, Prof. Dr. I. Fischer
Institut für Physikalische und Theoretische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)

Prof.Dr. A. K. Phukan
Department of Chemical Sciences, Tezpur University
Napaam 784028, Assam (India)

Dr. A. Vargas
Department of Chemistry, School of Life Sciences
University of Sussex
Brighton BN1 9QJ, Sussex (UK)

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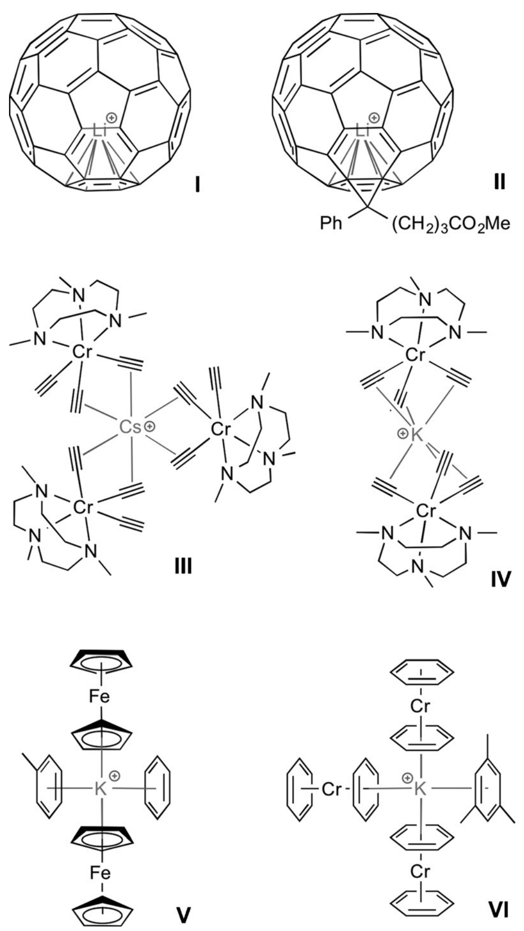

*Figure 1.* Structurally authenticated complexes in which alkali metal cations bind exclusively to π systems of neutral molecules.

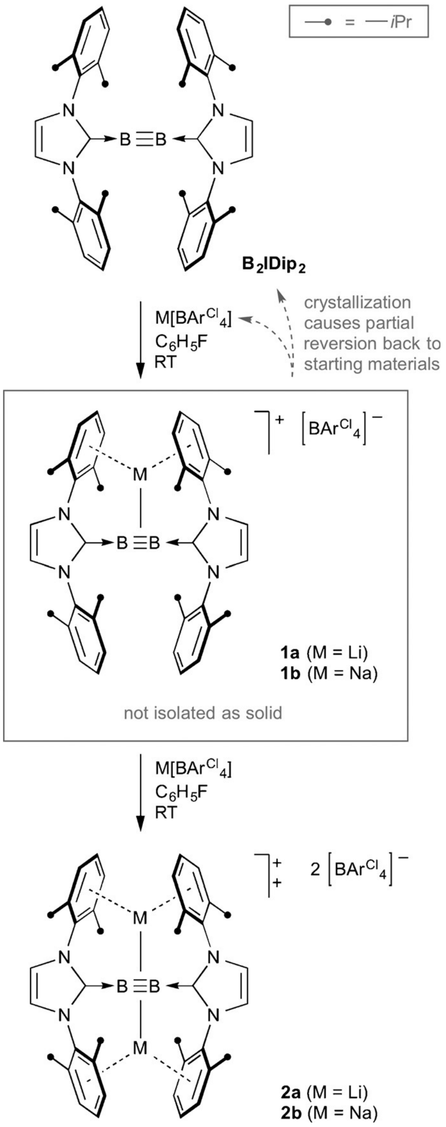

*Figure 2.* Synthesis of **2a** and **2b**.

containing materials and cation–π interactions, and the high reactivity of our neutral boron–boron triple-bond system, we were interested in attempting to bind this molecule to alkali metal cations. Herein we report the reaction of the neutral diboryne $B_2IDip_2$ with light alkali metal salts of weakly coordinating anions, which leads to encapsulation of two alkali metal cations in the diboryne molecule. To our knowledge, these are the first authenticated examples in which cations of the light alkali metals lithium and sodium are bound solely through π interactions with neutral molecules, excluding those trapped in fullerenes.

The addition of a solution of the diboryne $B_2IDip_2$ in fluorobenzene to two equivalents of solid lithium or sodium salts of tetrakis(3,5-dichlorophenyl)borate ($[BAr^{Cl}{}_4]^-$) followed by trituration with ultrasound led to homogeneous solutions and a color change from dark green to either pink or violet, respectively (Figure 3, bottom). The $^{11}B$ NMR spectra of the reaction mixtures at this point indicated an upfield shift of the diboryne boron signal from $\delta = 39$ ppm ($B_2IDip_2$)[28] to $\delta = 17.6$ (M = Li) and $\delta = 17.3$ ppm (M = Na). However, after some time, pink (M = Li, **2a**; Figure 2) and purple (M = Na, **2b**; Figure 2) solids precipitated from these mixtures. These isolated precipitates were subsequently found to be highly insoluble, and do not even color the supernatant liquid when the original reaction solvent fluorobenzene is added to them, which significantly limits possibilities for their characterization.[30] The differences in solubility between the pink/purple compounds present in the reaction mixtures and the isolated solids leads us to assume that the solution compounds are the single-cation addition products (**1a**/**b**, Figure 2), which eventually encapsulate a second cation, thereby forming the highly insoluble salts **2a**/**b** and precipitating from solution. When these monocation species were specifically targeted by equimolar addition of alkali metal salts, the same $^{11}B$ NMR signals ($\delta =$ ca. 17 ppm) were observed. However, all attempts to isolate the compounds as solids led to crystallization of the alkali metal salt $M[BAr^{Cl}{}_4]$ (M = Li or Na) and green coloration of the supernatant solution by free $B_2IDip_2$, which is indicative of partial reversion back to the starting materials.

Elemental analysis of the solids **2a** and **2b** suggested the presence of two $[BAr^{Cl}{}_4]^-$ counterions per diboryne $B_2IDip_2$.

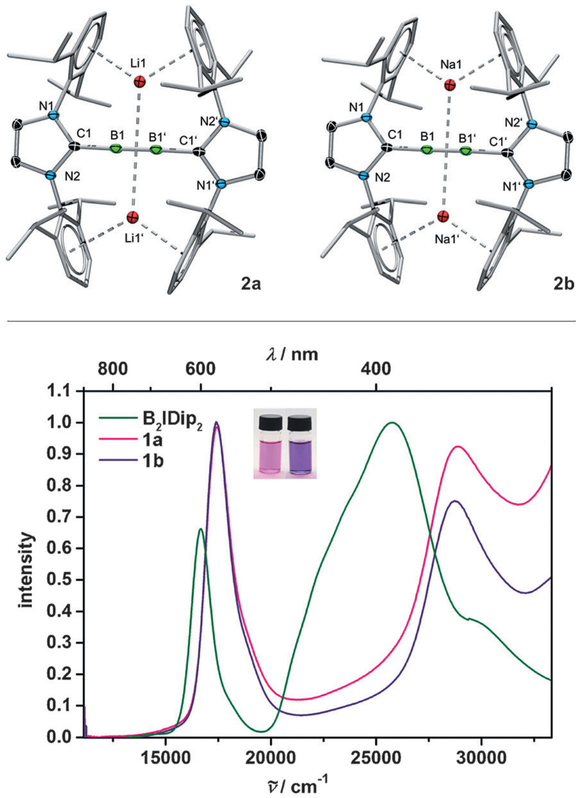

***Figure 3.*** Top: Structures of the dicationic parts of **2a** and **2b** as derived from single-crystal X-ray diffraction studies. Thermal ellipsoids in the structures depict the 50% probability level. For clarity, hydrogen atoms have been removed and the aryl groups are not shown. Selected distances [Å] for **2a**: B1-B1′ 1.452(6), B1-C1 1.516(4), B-Li 2.514(5), 2.522(5), Li-C (avg.) 2.806, 2.978. Selected distances [Å] for **2b**: B1-B1′ 1.459(4), B1-C1 1.523(3), B-Na 2.764(2), 2.768(2), Na-C (avg.) 2.863, 2.933. Bottom: UV/Vis/NIR spectra of $B_2IDip_2$, **1a** and **1b** in fluorobenzene at 25 °C. The colors of the lines approximate the colors of the respective complexes. Insets: photographs of solutions of **1a** (left) and **1b** (right) in fluorobenzene.

Solid-state $^{11}$B MAS NMR spectroscopy showed broad diboryne $B_2$ signals, along with attendant sharp high-field signals corresponding to the $BAr^{Cl}_4$ counterions (**2a**: $\delta(^{11}B) = 2.6$ (broad), $-6.5$ ppm (sharp); **2b** $\delta(^{11}B) = 1.9$ (broad), $-6.5$ ppm (sharp), see the Supporting Information). The upfield nature of these diboryne $^{11}$B NMR signals relative to those found in the solution $^{11}$B NMR spectra of the reaction mixture are in line with our hypothesis of the sequential addition of cations to the diboryne, where the signals move from 39 ppm in $B_2IDip_2$ to about 17 ppm in the monocations **1a**/**b**, to approximately 2 ppm in the dications **2a**/**b**. The solid-state $^{7}$Li MAS NMR spectrum of **2a** showed two signals of approximately equal intensity ($\delta_{iso} = -3.7$, $-4.1$ ppm), while the solid-state $^{23}$Na MAS NMR spectrum of **2b** showed a central resonance of a second-order quadruploar powder pattern, which could be fitted to two nearly coincident and equal-intensity signals ($\delta_{iso} = -8.7$, $-10.3$ ppm). The two signals of equal intensity in each of these spectra can be attributed to inequivalent cation sites in **2a** and **2b**.

As a consequence of the insolubility of the salts **2a** and **2b**, single crystals thereof could only be obtained by slow evaporation of the initial reaction solutions. Single-crystal X-ray diffraction study of the respective salts revealed that the alkali metal cations were bound astride the boron–boron triple bond of the neutral diboryne molecule (Figure 3, top). The dications in each crystal of **2a**/**b** contained two alkali metal cations either side of the B≡B bond (**2a**: $d$(B-Li) = 2.514(5), 2.522(5) Å; **2b**: $d$(B-Na) = 2.764(2), 2.768(2) Å) and between two roughly eclipsed phenyl rings of the N-heterocyclic carbene (NHC) donor groups (**2a**: $d(\text{Li-C})_{av} = 2.806$, 2.978 Å; **2b**: $d(\text{Na-C})_{av} = 2.863$, 2.933 Å). The binding of alkali metal cations is also presumably responsible for the completely coplanar NHC donor groups in **2a** and **2b**, in marked contrast to the tilted arrangement of those in precursor $B_2IDip_2$ (angle between NHC planes: 56.7°).[28] It should also be noted that the boron–boron distances in the dication (**2a**: 1.452(6) Å; **2b**: 1.459(4) Å) were found to be identical to that of the alkali-metal-free precursor $B_2IDip_2$ (1.449(3) Å)[28] within experimental uncertainty, thus suggesting little covalent interaction between the alkali metals and the B≡B bond π system. Additionally, the Raman-active $\nu_{B\equiv B}$ stretching frequency was found to change very little from its initial value of 1628 cm$^{-1}$[31] upon the addition of the cations (**2a**: 1594 cm$^{-1}$; **2b**: 1554 cm$^{-1}$), which is indicative of small distortions in the shape of the π system comprising the B≡B bond rather than wholesale changes in the bonding environment (Figure S12, Table S3). It should be noted that small amounts of two perpendicular, crystallographically superimposed orientations of the alkali metals were found to be cocrystallized in the crystals of **2a** and **2b**, which differed only in the position of the alkali metals (see the Supporting Information for more details). Solid-state NMR signals for these minor isomers were not observed, presumably because of the inherent broadness and coincidence of the signals. However, the existence of the alternative isomers, wherein the $M^+$ cations are separated from the π systems of the phenyl rings, indicates the predominance of the electrostatic interaction of the cations with the $B_2$ unit.

Geometry optimizations of **2a** and **2b** by using Kohn–Sham density functional theory (DFT) were carried out at the ωB97XD/6-31+G* level of theory. In contrast to the experimentally observed boron–boron distances, which show no statistically significant variation between alkali-metal-bound **2a**/**b** and free diboryne $B_2IDip_2$, the calculations showed that metalation results in a variation of the B–B bond distance. This difference could be ascribed to the different environment parameters for the solid state (X-ray crystal structure) versus the gas phase, in which packing effects are absent. The binding of $Li^+$ and $Na^+$ cations to the diboryne results in a modest decrease and increase in the B–B distances, respectively (Table S1). However, in both cases, significant increases in the negative charges on the boron atoms and the B–B Wiberg bond indices are witnessed upon cation coordination, thus indicating that complexation with the metal cations induces a $C{:}\rightarrow B\rightarrow M^+$ charge flow and also polarizes the $\pi_{BB}$ orbital. These two effects act independently, and principally dictate the observed trends regarding the B–B distances and bond orders, but both imply point and chargecloud interactions. Overall, the calculated variations in the structure, bond order, and partial charge upon complexation to a cation strongly suggest that the interactions of the alkali metal cations with the neutral diboryne molecule are mainly through electrostatics and not through dispersion interactions with the phenyl moieties. In addition, the $^{11}$B NMR shifts of **2a** and **2b** were calculated using the GIAO method and found to match the solid-state NMR data quite well (**2a**: $\delta_{calcd} = -0.5$; $\delta_{solid} = 2.6$; **2b**: $\delta_{calcd} = 0.5$; $\delta_{solid} = 1.9$ ppm). The calculated $^{7}$Li NMR data of **2a** also match the solid-state NMR data ($\delta_{calcd} = -4.9, -5.3$ ppm; $\delta_{solid} = -3.7, -4.1$ ppm) well; however, the calculated $^{23}$Na NMR signals of **2b** are found at lower field than those in the solid-state NMR spectrum ($\delta_{calcd} = 0.17, 0.43$ ppm; $\delta_{solid} = -8.7, -10.3$ ppm). The solid-state and calculated NMR data agree that the two cations are magnetically inequivalent in **2a** and **2b**. However, this is in contrast to the crystallographically derived structures, which are centrosymmetric and have equivalent cation sites. The calculated $^{11}$B NMR data of the presumed monocations **1a/b** also fit those observed in the solution NMR spectra of the reaction mixtures (**1a**: $^{11}$B $\delta_{calcd} = 12.6$; $\delta_{solution} = 17.6$; **1b**: $^{11}$B $\delta_{calcd} = 12.5$; $\delta_{solution} = 17.3$ ppm), as do the $^{7}$Li NMR data of **1a** ($\delta_{calcd} = -2.1$; $\delta_{solution} = -3.3$ ppm).

Alkali metal cation–π interactions, vitally important in biology and materials science, are almost exclusively observed in the presence of stronger supporting donor groups or anionic, covalently bound ligands. Aside from fullerenes containing trapped alkali metal cations, the complexes **2a** and **2b** presented herein are the only confirmed examples of complexes in which light alkali metal cations are bound to neutral molecules without a Lewis donor group. The results show that cation–π interactions alone can support the binding of the light alkali metal cations and that such interactions can induce dramatic structural and electronic changes of the host π system without strong covalent interactions. Moreover, these systems show that even in the absence of a net charge, boron atoms can bind very strongly to alkali metal cations, a finding that may have implications on the use and noncovalent functionalization of boron-containing materials, such as those based on boron nitride or boron-doped carbon nanostructures.

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