Synthesis, Characterization, and Complexation of Tetraarylborates with Aromatic Cations and Their Use in Chemical Sensors

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Abstract: Five aromatic borate anions, namely tetrakis(4-phenoxyphenyl)borate (**1**), tetrakis(biphenyl)borate (**2**), tetrakis(2-naphthyl)borate (**3**), tetrakis(4-phenylphenol)borate (**4**), and tetrakis(4-phenoxy)borate (**5**), have been prepared and tested as ion-recognition sites in chemical sensors for certain aromatic cations and metal ions. To gain further insight into the complexation of the cations, some complexes have been prepared and structurally characterized. The complexation behavior of **1** and **2** towards *N*-methylpyridinium (**6**), 1-ethyl-4-(methoxycarbonyl)pyridinium (**7**), tropylium (**8**), imidazolium (**9**), and 1-methylimidazolium (**10**) cations has been studied, and the stability constants of the complexes of **1** with cations **6** and **8** have been measured to compare them with the values for the previously studied complexes of tetraphenylborate. The structures of the borate anions and their complexes have been characterized by NMR and mass spectrometric methods. X-ray crystal structures have been determined for potassium tetrakis(4-phenoxyphenyl)borate (K^+·**1**), *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6**·**1**), 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate (**7**·**1**), tropylium tetrakis(4-phenoxyphenyl)borate (**8**·**1**), and imidazolium tetrakis(biphenyl)borate (**9**·**2**). The results show that borate derivatives are potential candidates for a completely new family of charged carriers for use in cation-selective electrodes.

Keywords: aromatic cations · borates · charged carrier · ion-selective electrode · molecular recognition · noncovalent interactions

Introduction

Tetraphenylborate was introduced in analytical chemistry in the 1940s, when it was used for the precipitation of monocations such as those of potassium, rubidium, cesium, and quaternary ammonium compounds.[1] Tetraphenylborate is an example of a simple organic precipitating reagent, but there have also been numerous studies of other substituted borates that form saltlike precipitates.[2] The investigation of borate complexes containing organic cations as guest molecules has not attracted a great deal of interest, although a variety of substituted borates bearing aryl groups have been synthesized.[3,4] Electrochemical sensors constitute an important group of chemical sensors that are attractive for practical applications allowing the use of small-size, portable, and low-cost instrumentation.[5,6] Potentiometric ion sensors (ion-selective electrodes, ISEs) based on neutral or charged carriers (receptors, ionophores) are one of the oldest and most successful types of chemical sensors in routine use today, especially in clinical analysis.[7] These ion sensors are normally based on plasticized polymer membranes containing specific ionophores and ionic additives.[8]

Tetraphenylborate derivatives have been used as ionic additives in ISEs, initially just to reduce the anionic interference observed in the presence of lipophilic anions (Donnan exclusion).[8] They cannot form specific, strong ion pairs due to their shielded negative charge, but they nevertheless seem to play an active role as complexing agents, in addition to bringing negative charge to the sensor surface. For example, it has recently been shown that the Hg^{2+} interference on Ag^+-ISEs can be reduced by six orders of magnitude when replacing tetrakis(4-chlorophenyl)borate by a weakly

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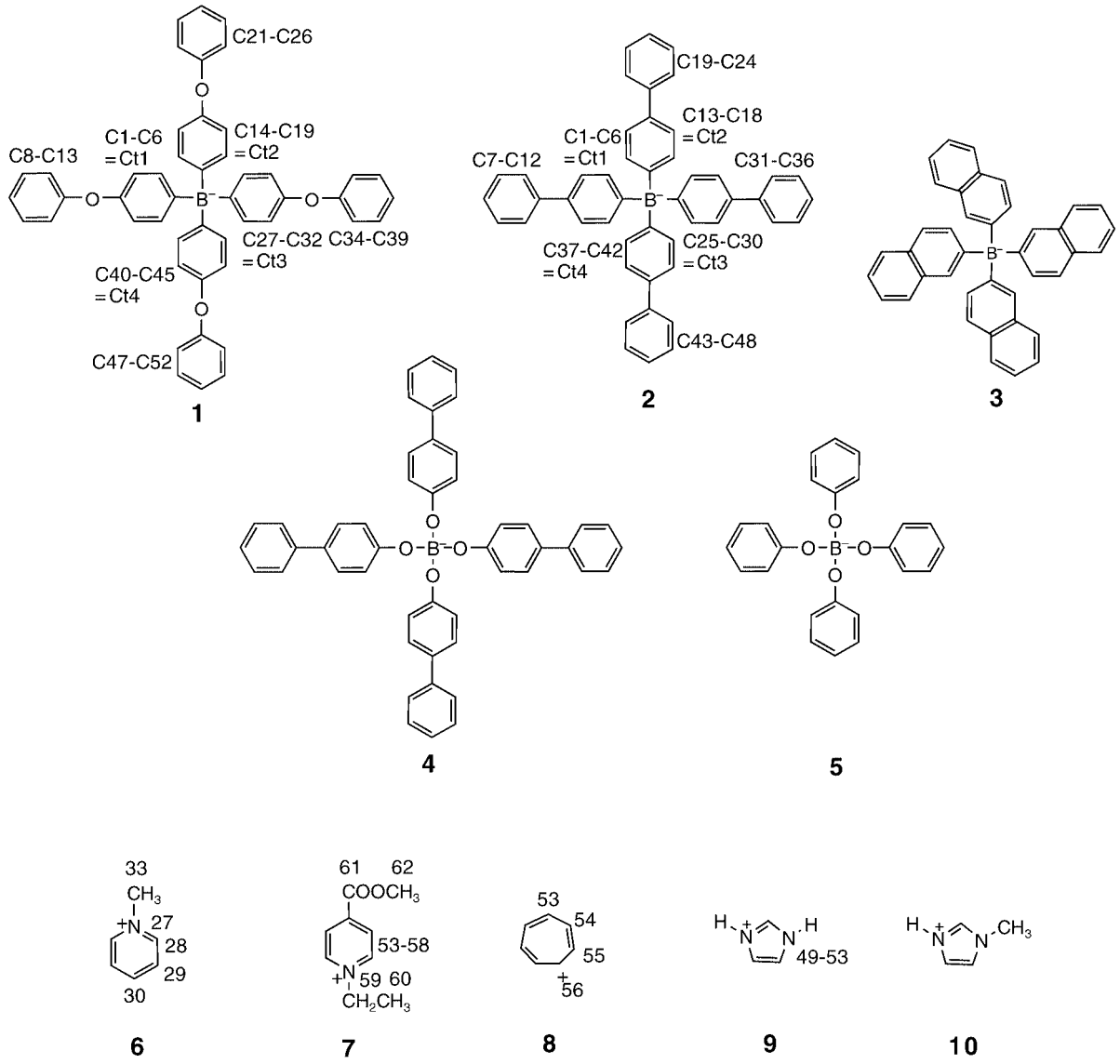
coordinating carborane as the anionic additive in the ion-selective membrane.[9] In the complexes of borates, hydrogen-bonding, π-π, and cation-π interactions are the principal attractive forces.[4,10,11] Complexation of the organic cations is an important field in supramolecular chemistry, having applications in synthetic, analytical, as well as in industrial fields.

We have previously reported the complexation of tetraphenylborate with organic *N*-heterocyclic cations.[11] Weak, noncovalent interactions such as C–H···π and N–H···π hydrogen bonds or π-stacking were identified as the principal intermolecular forces between the aromatic π-systems of tetraphenylborate and the organic cations in the crystalline state. Stability constants measured by ^{1}H NMR titrations of the tetraphenylborate complexes were relatively low.

In this work, we have prepared five different borates (**1**–**5**; Scheme 1) to study their properties in chemical sensors. Of these, tetrakis(4-phenylphenol)borate (**4**) has not been characterized previously, whereas tetrakis(4-phenoxyphenyl)borate[12,13] (**1**), tetrakis(biphenyl)borate[14] (**2**), tetrakis(2-naphthyl)borate[15] (**3**), and tetrakis(4-phenoxy)borate[16] (**5**) were prepared by modification of the literature procedures. Additionally, we have studied the complexation of the *N*-methylpyridinium (**6**), 1-ethyl-4-(methoxycarbonyl)pyridinium (**7**), tropylium (**8**), imidazolium (**9**), and 1-methylimidazolium (**10**) cations with borates **1** and **2** (Scheme 1) by means of NMR and mass spectrometry and in some cases also by X-ray crystallography. Stability constants of complexes of *N*-methylpyridinium (**6**) and 1-ethyl-4-(methoxycarbonyl)pyridinium (**7**) with **1** have been measured by ^{1}H NMR titration in a mixture of [D_3]acetonitrile and [D_4]methanol (1:1, *v*/*v*).



Scheme 1. Structural formulae and crystallographic numbering of tetrakis(4-phenoxyphenyl)borate (**1**), tetrakis(biphenyl)borate (**2**), tetrakis(2-naphthyl)-borate (**3**), tetrakis(4-phenylphenol)borate (**4**), tetrakis(4-phenoxy)borate (**5**), *N*-methylpyridinium (iodide) (**6**), 1-ethyl-4-(methoxycarbonyl)pyridinium (iodide) (**7**), tropylium (tetrafluoroborate) (**8**), imidazolium (perchlorate) (**9**), and 1-methylimidazolium (perchlorate) (**10**).

Results and Discussion

Synthesis of borates: Lithium tetrakis(2-naphthyl)borate was originally prepared by Williams et al.[15] in 1968 according to the general method described by Wittig and Raff.[17] A modification of this procedure was used in the preparation of sodium tetrakis(2-naphthyl)borate (**3**) and sodium tetrakis(biphenyl)borate[14] (**2**). Sodium tetrakis(4-phenoxy)-borate (**5**) was synthesized by a modification of the procedure reported by Cole et al.,[16] in which sodium borohydride in THF was reported to react with three equivalents of phenol to give $NaBH(OPh)_3$. In our studies, this method produced $NaB(OPh)_4$, and we used an analogous procedure to prepare the new compound sodium tetrakis(4-phenylphenol)borate (**4**). The synthesis of tetrakis(4-phenoxyphenyl)-borate (**1**) from bromodiphenyl ether and potassium tetrafluoroborate in THF has been described previously.[12]

Ion-selective electrodes: We find it of particular interest to vary the aryl substituents on boron in tetraarylborates to determine their influence on the sensitivity and selectivity of ion-selective electrodes (ISEs). The tetraarylborates **1**–**4** were incorporated as ion receptors (charged carriers) in plasticized poly(vinyl chloride) (PVC) membranes by using 2-nitrophenyl octyl ether (*o*-NPOE) as plasticizer. The ion-selective membranes contained around 30 $\mu mol\,g^{-1}$ of the respective tetraarylborate. Borate **5** could not be evaluated due to its limited solubility in THF, the solvent used to dissolve the membrane components. The distinguishing structural features of the borate anions used here in comparison with BPh_4^- are the nature of the aromatic units (**1**–**3**) and the oxygen bridge between boron and the aromatic moiety (**4**, **5**). In borates **1** and **4**, the oxygen bridges impart flexibility to the structure, which could have an effect on the complex formation.

The ISEs were constructed by using poly(3,4-ethylenedioxythiophene) (PEDOT) as the solid contact material, following the same procedure as described earlier.[9] The ISEs were investigated as potentiometric sensors for the *N*-methylpyridinium cation, which was used as a model aromatic cation.

Typical potentiometric responses of the ISEs in *N*-methylpyridinium iodide solutions (10^{-2}–10^{-6} M) are shown in Figure 1. ISEs based on the tetraarylborates **1**, **2**, and **3** show Nernstian responses in the concentration range 10^{-5}–10^{-2} M, with a detection limit of about $10^{-5.4}$ M. The responses of these ISEs based on borates **1**–**3** are similar to that previously observed for BPh_4^-.[12] On the contrary, the ISE based on tetraarylborate **4** shows only a slight response to *N*-methylpyridinium. The potentiometric selectivity coefficients estimated by using the separate solution method are summarized in Table 1. It can be seen that all the ISEs are more selective towards *N*-methylpyridinium than to the other cations tested ($\log K_{N\text{-MePy},j} < 0$), except for the ISE based on borate **4**, which is more selective towards pyridinium than towards *N*-methylpyridinium ($\log K_{N\text{-MePy, Py}} > 0$). For example, ISEs based on borates **1**–**3** are 2–3 orders of magnitude more selective towards *N*-methylpyridinium than towards alkali metal ions. The selectivity obtained by using tetraarylborate **4** clearly deviates from that seen with borates **1**–**3**. Results obtained previously with BPh_4^- are included in Table 1 for comparison.[12]

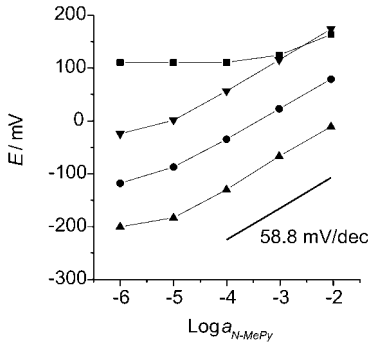


Figure 1. Calibration plots for ISEs based on tetraarylborates **1** (●), **2** (▲), **3** (▼), and **4** (■) in 10^{-6}–10^{-2} M *N*-methylpyridinium iodide.

Table 1. Potentiometric selectivity coefficients for ISEs based on the tetraarylborates **1**–**4** using *N*-methylpyridinium as primary ion.

	$\log K_{N\text{-MePy},j}$				
j	**1**	**2**	**3**	**4**	BPh_4^-[b]
Li^+	−3.0	−3.4	−3.1	−0.7	−2.8
Na^+	−3.1	−3.3	−3.1	−0.7	−2.7
K^+	−2.6	−2.4	−2.7	−0.7	−2.9
NH_4^+	−2.6	−3.0	−3.0	−0.5	−2.9
Ca^{2+}	−4.2	−4.9	−4.5	−1.7	−4.0
Mg^{2+}	−4.1	−4.7	−4.6	−1.6	−4.0
Py^+	−0.6	−1.1	−0.6	0.8	−1.5
TMA^+[a]	−0.4	−0.7	−0.1	−0.4	−0.4

[a] TMA^+ = tetramethylammonium. [b] Data from reference [12].

In compounds **1**–**3**, the boron center is bound to four aryl groups, while in compound **4**, the boron center is bound to four oxygen atoms, which obviously has a large effect on the ion sensitivity. When the oxygen centers are located further away from the boron center, as in compound **1**, they have only a small effect on the ion-recognition process. These results indicate that the substituents closest to boron play a determining role in ion recognition of *N*-methylpyridinium by tetraarylborates. A detailed comparison of borates **1**–**3**, and BPh_4^- (Table 1) clearly shows that the nature of the aromatic unit bound to the boron center also has some effect on the selectivity.

The ISE based on tetraarylborate **4** was further studied by using the local anaesthetic bupivacaine as the primary ion, yielding a linear response in the concentration range 10^{-2}–10^{-4} (slope = 53 mV/dec) and a detection limit of about $10^{-4.4}$ M. Here again, the selectivity coefficients for the ISE based on **4** differ from those obtained with ISEs based on **1** and **2**, as shown in Table 2.

It is noteworthy that the ISE based on **4** shows a significantly higher selectivity towards pyridinium than towards *N*-methylpyridinium (Table 1 and Table 2), despite the greater lipophilicity of the latter. This indicates some specific inter-

Table 2. Potentiometric selectivity coefficients for ISEs based on the tetraarylborates **1**, **2**, and **4** using bupivacaine as primary ion.

	$\log K_{\text{Bupivacaine},j}$		
j	**1**	**2**	**4**
Li^+	−3.1	−3.0	−2.2
Na^+	−3.1	−2.9	−2.2
K^+	−3.0	−2.9	−2.2
NH_4^+	−2.6	−2.3	−1.9
Ca^{2+}	−4.0	−3.8	−3.2
Mg^{2+}	−4.1	−3.9	−3.2
Py^+	−1.8	−1.7	−0.6
N-$MePy^+$	−1.6	−1.6	−1.8
lidocaine	−1.1	−1.1	−0.8
procaine	−1.2	−1.2	−0.9
TMA^+[a]	−2.0	−2.0	−1.9

[a] TMA^+ = tetramethylammonium.

actions between **4** and pyridinium cations. Furthermore, a "dummy" membrane containing only PVC and *o*-NPOE without any borate showed a significantly lower selectivity towards pyridinium ($\log K_{\text{Bupivacaine,Py}} = -3.0$) compared to the membrane containing borate **4** ($\log K_{\text{Bupivacaine,Py}} = -0.6$). These results show that substituted borates offer interesting possibilities for the design of new charged carriers for use in cation-selective electrodes.

Complexation studies: The complexation of borates **1** and **2** with selected aromatic cations was studied to gain further information about the nature of the complexes. Delocalized π systems were chosen on the basis of our previous studies,[11] in which these five selected cations were found to form complexes with tetraphenylborate.

The complexes of cations **6–8** with borate **1** and of cation **9** with borate **2** could be prepared in a straightforward manner. In a suitable solvent (methanol, ethanol, or acetonitrile), the formation of a 1:1 complex was observed in each case by NMR spectroscopy and later verified by X-ray crystallography. The complexes precipitated immediately upon mixing of the warm solutions, and X-ray quality single crystals could be grown direct from the reaction solutions by slow evaporation of the solvent. The complex formation of cations **9** and **10** with borate **1** and of cations **7**, **8**, and **10** with borate **2** was detected by mass spectrometry and NMR spectroscopy, but the crystal structures of these five complexes could not be determined due to the poor quality of the crystals.

The stability constants of the complexes of *N*-methylpyridinium (**6**) and 1-ethyl-4-(methoxycarbonyl)pyridinium (**7**) with borate **1** were measured by ^{1}H NMR titration in [D_3]acetonitrile/[D_4]methanol solution (Table 3). This mixture of solvents was chosen because methanol increases the solubility of the tetrakis(4-phenoxyphenyl)borate (**1**), thereby allowing comparison with the previously studied tetraphenylborate systems.[11] No precipitation occurred during the stability constant measurements. Tropylium, however, decomposes in the presence of alcohols,[18] so the stability constant of the tropylium complex could not be measured in [D_3]acetonitrile/[D_4]methanol solution.

Table 3. Stability constants (K_a) of the complexes of borate **1** with two six-membered aromatic cations in [D_3]acetonitrile/[D_4]methanol solution at 30 °C determined by ^{1}H NMR titration. Tetraphenylborate complexes are included for comparison.

Complex	K_a [$dm^3 mol^{-1}$]	$\Delta\delta_C$ [ppm]	r^{2}[a]
6·**1**	12 ± 2	−0.35 ± 0.03	0.997
7·**1**	13 ± 1	−0.37 ± 0.03	0.999
6·BPh_4[b]	17 ± 2	−0.43 ± 0.05	0.998
7·BPh_4[b]	10 ± 1	−1.4 ± 0.1	0.997

[a] Regression correlation for Benesi–Hildebrand plot. [b] Data from reference [11].

When borate was added to a solution of the respective cation in [D_3]acetonitrile/[D_4]methanol, an upfield shift was observed in the proton resonance. The stability constants for the complexation were calculated directly from the chemical shift differences of the cation protons in the borate complexes and in the free form using the Benesi–Hildebrand equation. The errors in K_a and $\Delta\delta_C$ were evaluated numerically based on the standard deviations of single K_a and $\Delta\delta_C$ values, usually obtained from measurements. In each case, the differences in the chemical shifts of the free and complexed cations proved to be a linear function of the inverse of the borate concentration ($[\text{borate}]^{-1}$), indicating 1:1 stoichiometry. The regression values for the least-squares fitting were generally better than 0.99, reflecting also the goodness of the fitting. The measurements would not have been reliable had there been prominent deviations from linearity. Deviations from linearity would also have indicated the formation of higher aggregates than 1:1 complexes. The stability constant determined for *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6**·**1**) was 12 ± 2 $dm^3 mol^{-1}$, while that for 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate (**7**·**1**) was 13 ± 1 $dm^3 mol^{-1}$. These values are similar to the stability constants determined for the previously studied tetraphenylborate complexes (17 ± 2 and 10 ± 1 $dm^3 mol^{-1}$, respectively[11]). In our previous studies, corresponding measurements were also made for imidazolium and 1-methylimidazolium tetraphenylborates (19 ± 4 and 46 ± 2 $dm^3 mol^{-1}$, respectively[11]), and the stability constants of these complexes were also of similar magnitude. As a polar solvent, methanol was also studied, which has a marked effect on the complexation environment. It increases the solubility of the charged species, decreasing the degree of association of the complexes and thereby lowering the stability constants.

As a complexing agent, tetrakis(4-phenoxyphenyl)borate (**1**) differs from tetraphenylborate in that the additional phenyl rings may also take part in the binding and even encapsulate the cation. The anion also contains electronegative oxygens, which make the structure flexible and provide hydrogen-bonding sites for suitably predisposed guests. However, the stability constants do not indicate any significant positive impact of these two structural features on the complexation. In addition, the crystal structures show that the cations are situated between the inner aromatic rings, closer to the boron, while the outer phenyl rings have no interac-

tions with the cations, as might be expected in view of the similarity of the stability constants to those of the tetraphenylborate complexes.

X-ray crystallographic studies: The crystal structures of potassium tetrakis(4-phenoxyphenyl)borate (K^+·**1**), *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6**·**1**), 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate (**7**·**1**), tropylium tetrakis(4-phenoxyphenyl)borate (**8**·**1**), and imidazolium tetrakis(biphenyl)borate (**9**·**2**) were determined.

The starting compound, potassium tetrakis(4-phenoxyphenyl)borate (K^+·**1**), was crystallized from a mixture of benzene and ethanol. Potassium cations and the borate anions form a beautiful complex, in which each potassium cation is packed between two hosts with strong cation–π interactions (Figure 2) (potassium–centroid distances are K···Ct1 2.917(1), K···Ct2 3.020(1), K···Ct3* 2.932(1), and K···Ct4* = 2.997(1) Å), forming continuous chains of potassium tetrakis(4-phenoxyphenyl)borate. An interesting feature is that, as noted above, the potassium is situated between the inner aromatic rings, that is, between the rings closer to boron, while the outer phenyl rings have no interactions with the cation. This can be attributed to the more electronegative nature of the closer rings, and also to the packing efficiency: potassium fits perfectly into the cavity formed by the inner aromatic rings. The outer aromatic rings point outwards, allowing ethanol solvent molecules to occupy interstitial sites in the crystal lattice.

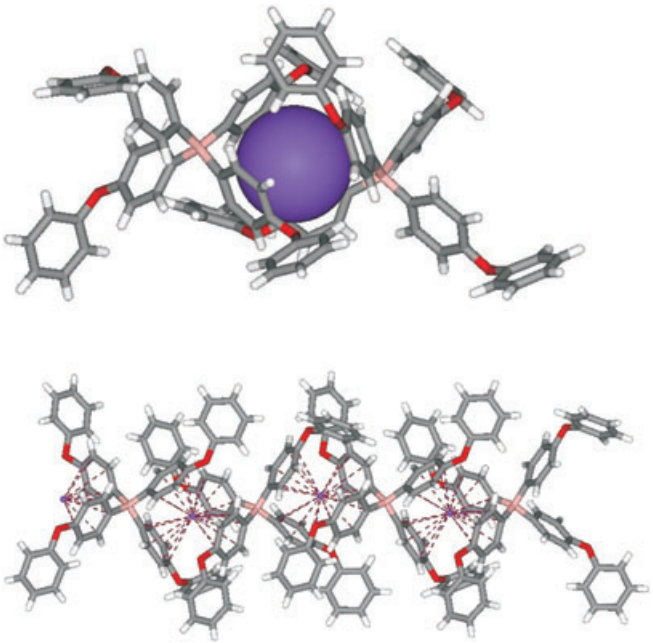


Figure 2. Top: Crystal structure of potassium tetrakis(4-phenoxyphenyl)-borate (K^+·**1**) showing potassium with VDW radius. Potassium fits perfectly into the cavity formed by the inner aromatic rings of two adjacent borate anions. Bottom: Crystal packing reveals continuous chains of anions connected by strong cation···π interactions.

In the crystal structures of planar aromatic cations with tetrakis(4-phenoxyphenyl)borate (**1**) and tetrakis(biphenyl)-borate (**2**), the significance of π-interactions in the complex formation is obvious. They all show relatively short face-to-face π···π contacts and also edge-to-face-type C–H···π interactions. In all of the complexes, most of the interactions between the anion and cation involve the inner, more electronegative aromatic rings.

The crystal structure of *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6**·**1**) was somewhat problematic to determine because the crystals decomposed at low temperatures and to some extent also at room temperature. The data collection was performed at two temperatures (173 K and 263 K), giving the same result in both cases, with almost equal R values (R = 0.127 at 173 K and 0.115 at 263 K). Due to the instability of the crystals, the resulting structure is not excellent but still good enough to give information about the solid-state structure of the complex.

N-Methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6**·**1**) also forms continuous chains, in which each cation is located between two hosts (Figure 3). The complexation stems from the sandwich-type of face-to-face packing of the cation and the aromatic rings of the adjacent anions (centroid-to-centroid distances between the cation and the anion are 3.63(1) Å) and, on the other hand, from the edge-to-face interactions between the cation and other aromatic rings of the anion (edge-to-face distances between C29 of the cation and the centroid of the aromatic ring are 3.82(1) Å). As in the potassium structure, the cation is located between the inner rings while the outer rings do not interact with the cation. Instead, the outer aromatic units are edge-to-face connected to nearby anions, thereby connecting the adjacent chains together.

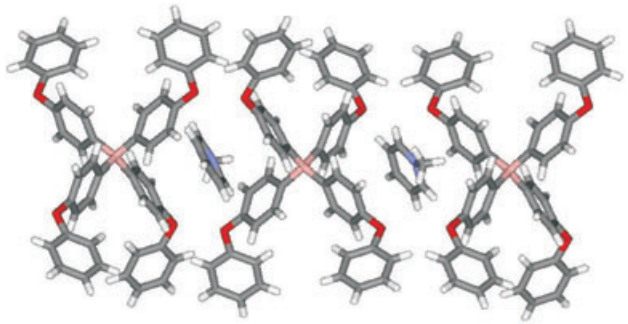


Figure 3. Crystal structure of *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6**·**1**). The cation and anion are in face-to-face π···π contact forming infinite chains.

The 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate complex (**7**·**1**) shows the greatest deviation from the structures of the other complexes since the cation interacts with more than two anions and even slightly with the outer aromatic units of the anion owing to the interactions of the extended side chains of the larger cation. However, the most important and the strongest intermolecular interactions are still the slightly offset face-to-face-type

π···π interactions between the cation and two adjacent anions (centroid-to-centroid distances are 3.647(2) Å and 4.122(2) Å) and edge-to-face interactions (C58···Ct1 3.434(2) Å) (Figure 4). No clear chain or column type of packing pattern can readily be discerned in this case.

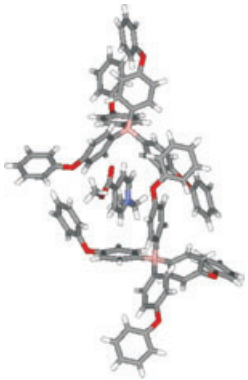


Figure 4. 1-Ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate complex (**7·1**) with offset face-to-face-type π···π interaction.

The crystal data for tropylium tetrakis(4-phenoxyphenyl)-borate (**8·1**) were obtained from a weakly diffracting crystal crystallized from acetonitrile. The tropylium cation is disordered so that it can only be described as an eight-membered ring. Even though the formation of continuous chains of anions mediated by the cations is again observed in this case, the anions also interact with each other forming a substructure which could be described as two facing "tweezers". The cation–anion interactions are very similar to those observed in *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**6·1**). Thus, tropylium is "sandwiched" between two aromatic rings of the adjacent hosts, and there are additional edge-to-face π···π interactions with two other rings (Figure 5). The centroid-to-centroid distances between the cation and the anions are 3.653(3) Å and the closest edge-to-face distance, C54···Ct2, is 3.431(3) Å.

The only tetrakis(biphenyl)borate (**2**) structure that we succeeded in crystallizing was imidazolium tetrakis(biphenyl)borate (**9·2**), which was obtained from ethanol solution. Imidazolium is a somewhat smaller cation than the other cations used in this study and tetrakis(biphenyl)borate is a more rigid anion than tetrakis(4-phenoxyphenyl)borate (**1**), hence the properties and interactions of this structure are slightly different. Imidazolium is also complexed by π-interactions, but instead of the sandwich-type of face-to-face π···π interactions, the cation here is offset face-to-face stacked with one of the inner phenyl rings (C50 of imidazolium is directly above the center of the inner phenyl ring C37–C42; C50···Ct4 3.296(7) Å) and edge-to-face (C–H···π) connected to three other aromatic units (C50···Ct3 3.277(6) Å, C52···Ct1* 3.397(6) Å, and C53···Ct2* 3.602(7) Å; Figure 6). There are also some π-interactions with the outer aromatic rings of the anion owing to the shorter distance and rigid bridge between the two aromatic

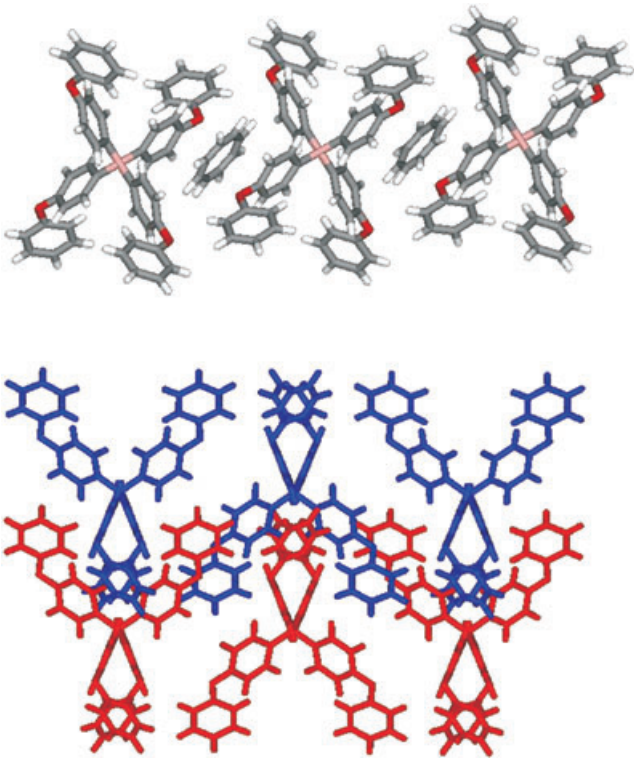


Figure 5. Top: Infinite chains of anions and cations of tropylium tetrakis(4-phenoxyphenyl)borate complex (**8·1**) with face-to-face π···π interaction. Bottom: Adjacent chains of tweezer-like borate anions depicted in red and blue. Cations have been omitted for clarity.

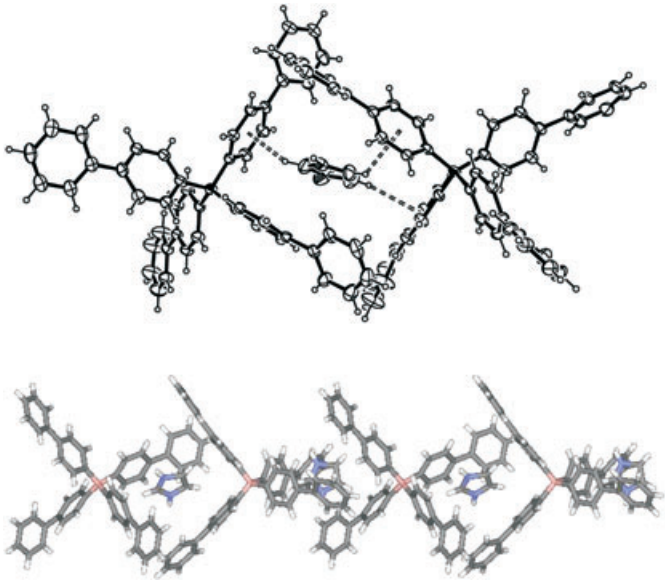


Figure 6. Top: Imidazolium tetrakis(biphenyl)borate complex (**9·2**). The complexation involves both offset face-to-face π···π interactions and edge-to-face C–H···π interactions. Bottom: The packing of the anion–cation complexes is similar to that of tetrakis(4-phenoxyphenyl)borate complexes, that is, chainlike.

moieties. Owing to the rigid nature of the anion and the small size of the cation, the packing of the anion–cation ad-

ducts is not as efficient as with tetrakis(4-phenoxyphenyl)-borate. Consequently, there is space in the crystal lattice for ethanol solvent molecules, which occupy interstitial sites between the anions and cations and are hydrogen-bonded to the N–H groups of the imidazolium, thus preventing the latter from participating in NH–π interactions. The packing, however, is still similar to that of the other complexes, being also a chain-like assembly of anions and cations.

Conclusion

The present results indicate that the synthesized borate structures can form complexes with aromatic cations and metal ions. This has been shown by the stability constant measurements, as well as by spectroscopic and crystallographic methods. The complexation involves weak, noncovalent interactions between the aromatic cation and the aromatic rings closest to the boron atom. We directed our studies with a view to highlighting the influence of borate structure modification on the sensitivity and selectivity of ion-selective electrodes. Borates were used as ion receptors for certain selected organic cations and metal ions. The research described in this paper has shown that borate structure modification influences the selectivity of potentiometric ion sensors. The borates gave different results when incorporated into chemical sensors, indicating that they play an active role. Thus, they show potential for the future development of anionic receptor molecules in chemical sensors. The results strongly indicate that borate derivatives may give rise to a new family of charged carriers for cation-selective electrodes.

Experimental Section

General procedures: The basic ^{1}H and ^{11}B NMR measurements were carried out at room temperature on a 200 MHz Bruker Avance DPX200 spectrometer and the ^{13}C NMR measurements on a Bruker DRX500 spectrometer. Complex formation was also studied by MS analysis. Electrospray ionization mass spectra (ESI-MS) were recorded on an LCT (Micromass, Ltd.) time-of-flight mass spectrometer equipped with an OpenLynx 3 data system. Exact mass peaks of the borates were determined on a Micromass LCT using ESI^- or ESI^+ methods. ESI mass spectra showed 2:1 complexation in the gas phase, where two cation molecules formed a complex with one borate molecule. No 1:1 complexes were observed in ESI-MS.

All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques. 2-Bromonaphthalene, 4-bromobiphenyl, phenol, boron trifluoride diethyl etherate, sodium tetrahydroborate, potassium tetrafluoroborate, 1-ethyl-4-(methoxycarbonyl)pyridinium iodide (**7**), and tropylium tetrafluoroborate (**8**) were obtained from commercial sources and were used without further purification or drying. The compositions of the products were verified crystallographically and by NMR and MS analyses. Chemical shifts in the ^{11}B NMR spectra are reported in ppm with respect to external $BF_3{\cdot}Et_2O$ (with CD_3CN as solvent).

Synthesis

Potassium tetrakis(4-phenoxyphenyl)borate (1): The synthesis of potassium tetrakis(4-phenoxyphenyl)borate has been described previously.[12] X-ray quality crystals of this compound were grown by slow evaporation of the solvents from a solution in a benzene/ethanol mixture.

Sodium tetrakis(biphenyl)borate (2): One-fifth of a solution of 4-bromobiphenyl (3.78 g, 16.2 mmol) in THF (20 mL) was slowly added to Mg turnings (0.39 g, 16.0 mmol) containing an I_2 crystal. The mixture was stirred under nitrogen and warmed until the reaction started. The rest of the solution was then slowly added, and the mixture was stirred for 1.5 h with occasional warming. A solution of boron trifluoride diethyl etherate (0.45 g, 3.2 mmol) in THF (10 mL) was added to the aryl Grignard reagent thus produced over a period of about 30 min. The reaction mixture was stirred for an additional 45 min, warming occasionally. It was then poured into a solution of Na_2CO_3 (1.7 g) in distilled water (40 mL), and the resulting mixture was stirred vigorously for 20 min, during which the inorganic material separated, which could be filtered off. The aqueous filtrate was extracted with THF (3×25 mL) and the combined THF fractions were dried over Na_2CO_3 overnight. The solution was then filtered and the solvent was removed under reduced pressure, whereupon a precipitate formed. The crude product was redissolved in acetone (20 mL), and benzene (60 mL) was added. The mixture was concentrated to a quarter of its original volume and the precipitated product was collected by filtration and dried in vacuo. ^{11}B NMR (200 MHz, CD_3CN): $\delta = -6.30$ ppm; ^{1}H NMR (200 MHz, CD_3CN): $\delta = 7.2$–7.6 ppm (m, arom.); ^{13}C NMR (500 MHz, CD_3CN): $\delta = 125.62$ and 125.63 (arom., 3C), 127.3 (arom., 1C), 127.6 (arom., 2C), 129.8 (arom., 2C), 135.7 (arom., 1C), 137.3 (arom., 2C), 143.6 ppm (arom., 1C); ESI-MS: m/z: 622 [$^-$B(-Ph-Ph)$_4$], 669 [$^-$B(-Ph-Ph)$_4$+2Na$^+$]; exact mass: 669.2715 [M+2Na]$^+$ (calcd. for $C_{48}H_{36}BNa_2$, 669.2705).

Sodium tetrakis(2-naphthyl)borate (3): The procedure used for the preparation of sodium tetrakis(2-naphthyl)borate was similar to that described for the synthesis of sodium tetrakis(biphenyl)borate (**2**). The reaction set-up was identical. One-fifth of a solution of 2-bromonaphthalene (3.40 g, 16.4 mmol) in THF (20 mL) was slowly added to Mg turnings (0.39 g, 16.0 mmol). The mixture was stirred under nitrogen and warmed until the reaction started. The rest of the solution was added and the reaction mixture was stirred. A solution of boron trifluoride diethyl etherate (1.89 g, 13.3 mmol) in THF (10 mL) was slowly added to the Grignard reagent. The reaction mixture was stirred for 45 min and then poured into a solution of Na_2CO_3 (1.7 g) in distilled water (40 mL), and the resulting mixture was stirred, filtered, and extracted. The combined organic layers were dried and purified. The product was dried in vacuo. ^{11}B NMR (200 MHz, CD_3CN + THF): $\delta = -5.68$ ppm; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.8$–6.6 ppm (m, arom.); ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 125.9$ (arom., 1C), 126.2 (arom., 1C), 126.3 (arom., 1C), 126.6 (arom., 1C), 127.9 (arom., 1C), 128.4 (arom., 1C), 128.7 (arom., 1C), 132.7 (arom., 1C), 133.8 (arom., 1C), 138.5 ppm (arom., 1C); ESI-MS: m/z: 565.5 [$^-$B(-2-naphthalene)$_4$+2Na$^+$]; exact mass: 519.2286 [M]$^-$ (calcd. for $C_{40}H_{28}B$, 519.2284).

Sodium tetrakis(4-phenylphenol)borate (4): A solution of 4-hydroxybiphenyl (1.37 g, 8.0 mmol) in THF (25 mL) was slowly added to a solution of sodium tetrahydroborate (0.08 g, 2.1 mmol) in THF (10 mL). The reaction mixture was warmed and then stirred for 24 h at room temperature. The solvent was evaporated and the product was dried under vacuum with heating by means of a water bath for 6 h. The crude product was dissolved in acetone and three times the volume of benzene was added. The mixture was concentrated to a quarter of its original volume under reduced pressure and the precipitate formed was collected by filtration. The product was washed with cyclohexane and dried in vacuo. ^{11}B NMR (200 MHz, CD_3CN + THF): $\delta = 3.21$ ppm; ^{1}H NMR (200 MHz, CD_3CN): $\delta = 6.9$ (d, arom., 8H), 7.3–7.6 ppm (m, arom., 28H); ^{13}C NMR (500 MHz, CD_3CN): $\delta = 116.7$ (arom., 2C), 127.5 (arom., 2C), 127.7 (arom., 1C), 129.2 (arom., 2C), 130.0 (arom., 2C), 133.5 (arom., 1C), 141.8 (arom., 1C), 157.9 ppm (arom., 1C); ESI-MS: m/z: 687 [$^-$B(-O-Ph-Ph)$_4$]; exact mass: 687.2723 [M]$^-$ (calcd for $C_{48}H_{36}O_4B$, 687.2707).

Sodium tetrakis(4-phenoxy)borate (5): A solution of phenol (0.75 g, 8.0 mmol) in THF (15 mL) was slowly added to a solution of sodium tetrahydroborate (0.0767 g, 2.1 mmol) in THF (10 mL). The reaction mixture was stirred for 24 h at room temperature. The solvent was removed and the product was dried under vacuum with heating by means of a

water bath for 6 h. ^{11}B NMR (200 MHz, CD_3CN): $\delta = -3.06$ ppm; ^{1}H NMR (200 MHz, CD_3CN): $\delta = 6.6$–7.3 ppm (m, arom.); ^{13}C NMR (500 MHz, CD_3CN): $\delta = 116.7$ (arom., 2C), 119.6 (arom., 1C), 130.6 (arom., 2C), 159.6 ppm (arom., 1C); ESI-MS: m/z: 429 [$^-$B(-O-Ph)$_4$+2 Na$^+$]; exact mass: 429.1245 [M+2 Na]$^+$ (calcd for $C_{24}H_{20}O_4BNa_2$, 429.1250).

Synthesis of the complexes

***N*-Methylpyridinium tetrakis(4-phenoxyphenyl)borate (6·1)**: The cation was prepared according to the literature procedure.[16] The complex was prepared by mixing equimolar amounts of solutions of *N*-methylpyridinium iodide (**6**) and borate **1** in acetonitrile (no precipitate). X-ray quality crystals were grown from acetonitrile by slow evaporation. ^{1}H NMR (200 MHz, CD_3CN + TMS): $\delta = 4.3$ (s, 3H; N-CH_3), 6.7–7.2 (m, 36H; borate), 8.0 (m, 2H; Me-pyridinium), 8.5 (t, 1H; Me-pyridinium), 8.6 ppm (d, 2H; Me-pyridinium); ESI-MS: m/z: 876 [2·(**6**)+$^-$B(-Ph-O-Ph)$_4$]; exact mass: 875.4012 [M+2·**6**]$^+$ (calcd. for $C_{60}H_{52}O_4N_2B$, 875.4020).

1-Ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate (7·1): The complex was prepared by mixing equimolar amounts of solutions of **7** and borate **1** in methanol. The solid complex formed immediately upon mixing of the solutions. X-ray quality crystals were grown from a solution in acetonitrile by slow evaporation. ^{1}H NMR (200 MHz, CD_3CN): $\delta = 1.6$ (t, 3H; N-CH_2CH_3), 4.0 (s, 3H; OCH_3), 4.6 (q, 2H; N-CH_2CH_3), 6.8–7.4 (m, 36H; borate), 8.4 (m, 2H; arom. cation), 8.8 ppm (d, 2H; arom. cation); ESI-MS: m/z: 1020 [2·(**7**)+$^-$B(-Ph-O-Ph)$_4$]; exact mass: 1019.4431 [M+2·**7**]$^+$ (calcd for $C_{66}H_{60}O_8N_2B$, 1019.4443).

Tropylium tetrakis(4-phenoxyphenyl)borate (8·1): The complex was prepared by mixing equimolar amounts of solutions of **8** and borate **1** in acetonitrile. The crystalline complex formed immediately. ^{1}H NMR (200 MHz, CD_3CN): $\delta = 6.7$–7.4 (m, 36H; borate), 9.2 ppm (s, 7H; tropylium); ESI-MS: m/z: 869 [2·(**8**)+$^-$B(-Ph-O-Ph)$_4$]; exact mass: 869.3832 [M+2·**8**]$^+$ (calcd for $C_{62}H_{50}O_4B$, 869.3802).

Imidazolium tetrakis(4-phenoxyphenyl)borate (9·1): The cation was prepared according to the literature procedure.[20] The complex was prepared by mixing equimolar amounts of solutions of imidazolium perchlorate (**9**) and borate **1** in acetonitrile (no precipitate). ^{1}H NMR (200 MHz, CD_3CN): $\delta = 6.7$–7.4 (m, 36H; borate + 2H; imidazolium), 8.4 ppm (s, 1H; imidazolium); ESI-MS: m/z: 826 [2·(**9**)+$^-$B(-Ph-O-Ph)$_4$]; exact mass: 825.3588 [M+2·**9**]$^+$ (calcd. for $C_{54}H_{46}O_4N_4B$, 825.3612).

1-Methylimidazolium tetrakis(4-phenoxyphenyl)borate (10·1): The cation was prepared according to the literature procedure.[20] The complex was prepared by mixing equimolar amounts of solutions of 1-methylimidazolium perchlorate (**10**) and borate **1** in acetonitrile (no precipitate). ^{1}H NMR (200 MHz, CD_3CN): $\delta = 3.8$ (s, 3H; N-CH_3), 6.7–7.3 (m, 36H; borate), 8.3 ppm (s, 1H; 1-Me-imidazolium); ESI-MS: m/z: 854 [2·(**10**)+$^-$B(-Ph-O-Ph)$_4$]; exact mass: 853.3959 [M+2·**10**]$^+$ (calcd for $C_{56}H_{50}O_4N_4B$, 853.3925).

***N*-Methylpyridinium tetrakis(biphenyl)borate (6·2)**: The complex was prepared by mixing equimolar amounts of solutions of *N*-methylpyridinium iodide (**6**) and borate **2** in acetonitrile. The solid complex formed immediately upon mixing of the solutions. Crystals were grown from acetonitrile by slow evaporation. ^{1}H NMR (200 MHz, CD_3CN + CD_3OD): $\delta = 4.3$ (s, 3H; N-CH_3), 7.3–7.6 (m, 36H; borate), 8.0 (m, 2H; Me-pyridinium), 8.5 (t, 1H; Me-pyridinium), 8.6 ppm (d, 2H; Me-pyridinium); ESI-MS: m/z: 812 [2·(**6**)+$^-$B(-Ph-Ph)$_4$]; exact mass: 811.4194 [M+2·**6**]$^+$ (calcd for $C_{60}H_{52}N_2B$, 811.4224).

1-Ethyl-4-(methoxycarbonyl)pyridinium tetrakis(biphenyl)borate (7·2): The complex was prepared by mixing equimolar amounts of solutions of **7** and borate **2** in acetonitrile. The yellow solid complex formed immediately upon mixing of the solutions. ^{1}H NMR (200 MHz, CD_3CN): $\delta = 1.6$ (t, 3H; N-CH_2CH_3), 4.0 (s, 3H; OCH_3), 4.6 (q, 2H; N-CH_2CH_3), 7.2–7.7 (m, 36H; borate), 8.4 (m, 2H; arom. cation), 8.9 ppm (d, 2H; arom. cation); ESI-MS: m/z: 956 [2·(**7**)+$^-$B(-Ph-Ph)$_4$]; exact mass: 955.4621 [M+2·**7**]$^+$ (calcd for $C_{66}H_{60}O_4N_2B$, 955.4646).

Tropylium tetrakis(biphenyl)borate (8·2): The complex was prepared by mixing equimolar amounts of solutions of tropylium tetrafluoroborate (**8**) and borate **2** in acetonitrile (no precipitate). Black crystals formed within a few hours. ^{1}H NMR (200 MHz, CD_3CN): $\delta = 6.9$–7.9 (m, 38H; borate), 9.2 ppm (s, 7H; tropylium); ESI-MS: m/z: 806 [2·(**8**)+$^-$B(-Ph-Ph)$_4$]; exact mass: 805.3981 [M+2·**8**]$^+$ (calcd for $C_{62}H_{50}B$, 805.4006).

Imidazolium tetrakis(biphenyl)borate (9·2): The complex was prepared by mixing equimolar amounts of solutions of imidazolium perchlorate (**9**) and borate **2** in ethanol (no precipitate). X-ray quality crystals were grown from ethanol by slow evaporation. ^{1}H NMR (200 MHz, CD_3CN): $\delta = 7.2$–7.7 (m, 36H; borate + 2H; imidazolium), 8.5 ppm (s, 1H; imidazolium); ESI-MS: m/z: 761 [2·(**9**)+$^-$B(-Ph-Ph)$_4$]; exact mass: 761.3792 [M+2·**9**]$^+$ (calcd for $C_{54}H_{46}N_4B$, 761.3816).

1-Methylimidazolium tetrakis(biphenyl)borate (10·2): The complex was prepared by mixing equimolar amounts of solutions of 1-methylimidazolium perchlorate (**10**) and borate **2** in acetonitrile (no precipitate). ^{1}H NMR (200 MHz, CD_3CN): $\delta = 3.6$ (s, 3H; N-CH_3), 7.2–7.6 (m, 36H; borate + 2H; 1-Me-imidazolium), 8.2 (s, 1H; 1-Me-imidazolium); ESI-MS: m/z: 790 [2·(**10**)+$^-$B(-Ph-Ph)$_4$]; exact mass: 789.4108 [M+2·**10**]$^+$ (calcd for $C_{56}H_{50}N_4B$, 789.4129).

Ion-selective electrodes: Plasticized polymer membrane-based ion-selective electrodes (ISEs) were prepared by using poly(3,4-ethylenedioxythiophene) (PEDOT) as a solid contact material.[12] PEDOT was deposited on a glassy carbon (GC) disk electrode (area = 0.07 cm^2) by galvanostatic electrochemical polymerization (current = 0.014 mA, time = 714 s) from a deaerated aqueous solution containing 0.01 M 3,4-ethylenedioxythiophene and 0.1 M sodium poly(sodium 4-styrenesulfonate). The electropolymerization was performed by using an Autolab General Purpose Electrochemical System (Eco Chemie B.V., The Netherlands) connected to a conventional one-compartment, three-electrode electrochemical cell. The GC disk electrode was used as the working electrode, a GC rod as an auxiliary electrode, and an Ag/AgCl (3 M KCl) electrode as the reference electrode. Prior to electropolymerization, the GC disk electrode was polished with 0.3 μm alumina, rinsed with deionized water, and cleaned ultrasonically. After electropolymerization, the GC/PEDOT electrodes were rinsed with deionized water and conditioned for at least 24 h in 0.01 M *N*-methylpyridinium iodide solution. The GC/PEDOT electrodes were then coated with ion-selective membranes of the following composition (*w*/*w*): tetraarylborate (1.6–2.2 %), PVC (32–33 %), and *o*-NPOE (65–66 %). The components of the membrane were dissolved in THF and applied by means of a micropipette onto the GC/PEDOT electrode. After evaporation of the THF, the resulting ion-selective membrane covered the underlying PEDOT film completely. The resulting ISEs were conditioned in 0.01 M *N*-methylpyridinium iodide for at least 24 h. Potentiometric measurements were performed with a home-made multichannel mV meter, using an Ag/AgCl (3 M KCl) electrode as the reference electrode. Activity coefficients were calculated by using the extended Debye–Hückel equation.[21] Selectivity coefficients were estimated by the separate-solution method (SSM) employing 0.01 M concentrations of different cations (chloride or iodide salts).[22] The measurements were conducted at room temperature (23 ± 2 °C). Selected ISEs were also studied by using bupivacaine as the primary ion. Bupivacaine (1-butyl-*N*-[2,6-dimethylphenyl]-2-piperidinecarboxamide) is an aromatic cation that is used as a local anaesthetic and is commercially available (Sigma Chemical Co.) in the form of a hydrochloride salt. Two other local anaesthetics, namely lidocaine (2-diethylamino-*N*-[2,6-dimethylphenyl]acetamide) and procaine (*p*-aminobenzoic acid diethylaminoethyl ester), in the form of their hydrochloride salts (Sigma Chemical Co.), were used for comparison purposes.

Stability constant determination by ^{1}H NMR titration: A standard solution of the guest in [D_3]acetonitrile/[D_4]methanol (1:1, v/v) was prepared at a concentration of 2×10^{-3} M, just sufficient to give an observable NMR signal. A series of donor solutions (0.01–1.0 M) were prepared by weighing out appropriate amounts of the donor. A 2-mL portion of the standard solution was then added and the flask was re-weighed. The solutions were thoroughly mixed and the spectrum was measured immediately; 5 mm NMR tubes sealed with Parafilm to avoid evaporation were used. The temperature (303 K) was held constant during the measurements. The stability constant K_a for the complexation was calculated from NMR chemical shifts using the Benesi–Hildebrand least-squares line-fitting procedure.[23]

Table 4. Crystal data for the complexes.

Compound	$K^+ \cdot$**1**	**6**·**1** at 263.0 K	**6**·**1** at 173.0 K	**7**·**1**	**8**·**1**	**9**·**2**
formula	$C_{48}H_{36}O_4B^- \cdot K^+ \cdot 0.5\,CH_3CH_2OH$	$C_{48}H_{36}O_4B^- \cdot C_6H_8N^+$	$C_{48}H_{36}O_4B^- \cdot C_6H_8N^+$	$C_{48}H_{36}O_4B^- \cdot C_9H_{12}NO_2^+$	$C_{48}H_{36}O_4B^- \cdot C_7H_7^+$	$C_{48}H_{36}B^- \cdot C_3H_4N_2^+ \cdot 2\,CH_3CH_2OH$
formula weight	749.71	781.71	781.71	853.77	778.70	784.80
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	*Pcnb* (no. 60)	*Pcnb* (no. 60)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)
a [Å]	15.9719(4)	8.4500(4)	8.000(2)	16.3291(3)	27.7530(9)	16.2123(7)
b [Å]	15.4125(5)	20.666(1)	19.957(6)	13.5383(3)	8.2586(3)	13.5315(7)
c [Å]	16.7234(5)	24.704(2)	25.614(6)	20.6400(3)	21.4186(5)	22.2775(8)
β [°]	106.976(2)	90	90	99.946(1)	120.598(2)	101.248(3)
volume [Å^3]	3937.3(2)	4314.0(5)	4089(2)	4494.3(1)	4225.6(2)	4793.3(4)
Z	4	4	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.265	1.204	1.270	1.262	1.224	1.088
absorption coefficient [mm^{-1}]	0.182	0.075	0.079	0.081	0.075	0.065
F(000)	1572	1648	1648	1800	1640	1672
refl. collected/unique	17898/6893	15132/3768	9199/1788	22303/7943	11372/3707	21436/5476
data/restraints/parameters	6893/0/499	3768/0/256	3092/0/276	7943/0/588	3707/0/276	8247/0/581
GooF	1.030	1.123	1.134	1.052	1.088	1.067
final R indices [$I > 2\sigma(I)$]	0.044/0.104	0.115/0.224	0.127/0.213	0.044/0.093	0.053/0.122	0.110/0.294
R indices (all data)	0.057/0.1094	0.172/0.249	0.210/0.245	0.072/0.104	0.067/0.129	0.152/0.326
largest diff. peak and hole [e Å^{-3}]	0.571/−0.257	0.594/−0.417	0.377/−0.280	0.129/−0.193	0.319/−0.385	0.788/−0.362

Crystal structures: X-ray crystallographic data for the complexes were recorded with a Nonius Kappa CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) at a temperature of 173.0 ± 0.1 K, except for the structure of **6**·**1**, which was measured both at 173 ± 0.1 and 263.0 ± 0.1 K due to the decay of the crystals at low temperatures. The CCD data were processed with the Denzo-SMN v.0.93.0 program[24] and all reflections were corrected for Lorentz and polarization effects. An absorption correction was not applied. The structures were solved by direct methods (SHELXS-97[25]) and refined against F^2 (SHELXL-97[26]). The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the carbon temperature factor) and refined as riding atoms. The solvent ethanol in K^+·**1** was found to be disordered over two positions with site occupancies of 0.5. The hydrogen of the hydroxy group could not be determined for disordered ethanol. N27, C30, and C33 of the *N*-methylpyridinium molecule of **6**·**1** were found to be disordered over two positions with occupancies of 0.50. The tropylium cation of **8**·**1** proved to be disordered as an eight-membered ring, with C56 having a site occupancy of 0.50. The -CH_2- unit of one of the ethanol molecules in **9**·**2** was found to be disordered over two positions (0.702:0.298), and two other ethanols have occupancies of 0.5. The hydroxy hydrogen of one of the ethanol molecules could not be reliably determined. Detailed crystal data for the complexes are presented in Table 4. CCDC-250232–250237 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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