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Anion Receptors

Gem-Diboronic Acids: A Motif for Anion Recognition in Competitive Media

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Abstract: *Gem*-diboronic acid derivatives have previously been demonstrated to facilitate substrate binding within a metal's secondary coordination sphere, but their use as an anion recognition motif has not been explored. Here, we introduce the *gem*-diboronic acid motif as a highly effective group for recognition of oxoanions in aqueous solution. Anion receptors based on this motif demonstrate higher binding affinities than other common neutral motifs such as amides and (thio)ureas, and display a unique selectivity profile. Studies with a receptor bearing two *gem*-diboronic acid groups, receptor 2, indicate that the interaction with anions is highly directional. Despite its simplicity, receptor 2 represents one of the most selective receptors for malonate reported to date.

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Anionic species are involved in a wealth of biological processes, including metabolism and cellular signaling, as structural elements in biology, as industrial by-products, and as environmental contaminants.[1] As such, the development of selective receptors for anions is of broad interest. However, selective recognition of anionic species is a challenge due to the plethora of closely related anionic analytes, the large size of anions in comparison to cations, and strong hydration energies that inhibit high-affinity interactions in aqueous media.[2–5] For example, sulfate and phosphate have the same geometry, are nearly identical in size (r = 0.230 nm; *c.f.*: 0.238 nm), and display hydration energies that are comparable with divalent cations that are nearly 10 times more charge dense.[6] Biological systems contain hundreds of phosphate and carboxylate species.[7] The citric acid cycle alone contains nine distinct carboxylate species, many of which differ from each other by only a single heavy atom.[8] Consequently, receptors suitable for analysis of these anions must display exquisite selectivity and shape complementarity while also out-competing interactions of both the anion and receptor with water.[5]

Advances in the fields of supramolecular chemistry, anion transport, and catalysis have led to the development of a range of anion recognition motifs.[2,9–12] Each of these motifs possesses inherent benefits and disadvantages for selective anion recognition. Metal cations display the strongest affinities.[5] However, the isotropic nature of the cation–anion interaction means that complex architectures must be used, both as a ligand to hold the cation in place and to direct the approach of interacting anions, to achieve selectivity.[5] As an alternative approach, hydrogen-,[13] C–H–,[14] and halogen-bonding[15] motifs are highly directional—leading to selectivity benefits—but typically display weaker binding that is insufficient for recognition in competitive aqueous-containing media. Thus, the most effective examples of anion receptors capable of selective binding in aqueous-containing media are typically highly preorganized macrocyclic or caged structures and require many recognition units to increase the anion affinity.[16,17] The synthesis of such complex structures is often multistep and low-yielding. Hence, there remains a need for anion recognition motifs—and in particular neutral motifs—that are simple to prepare, and exhibit high-binding affinity and selectivity. Neutral motifs are of particular interest, due to their potential to offer more directional interactions compared to charged motifs, providing improved ability to discriminate between anions.[17]

Receptors containing boronic acids enable recognition of a range of sugars, α-hydroxy carboxylic acids such as tartaric,

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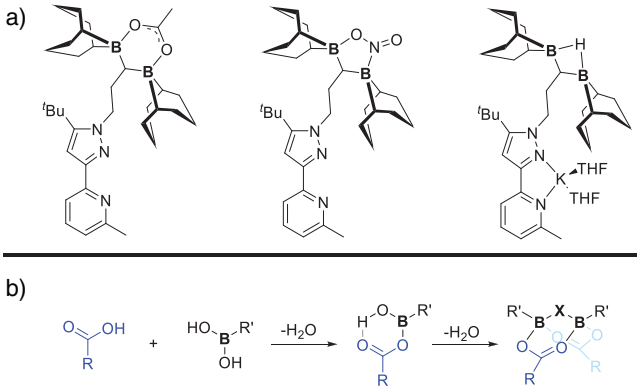


Figure 1. a) Anion-coordinated *gem*-diboranes reported previously by our group to form 4, 5 and-6 membered heterocycles. b) Mechanism of boronic acid-mediated amidation catalysis proposed by Whiting and Sheppard. An initial dehydration step leads to formation of an acyloxyboronate complex. Further dehydration leads to a bridged "B-X-B" species that interacts with carboxylates.

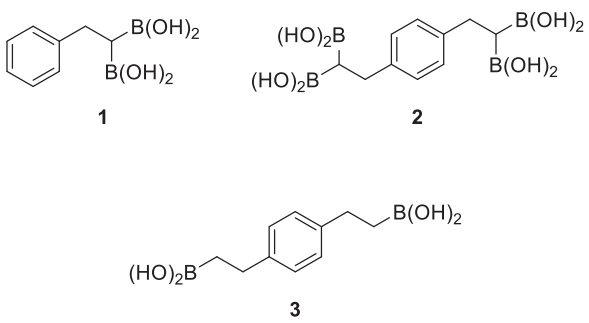


Figure 2. *Gem*-diboronic acid receptors (1, 2) and control compound (3) explored in this work.

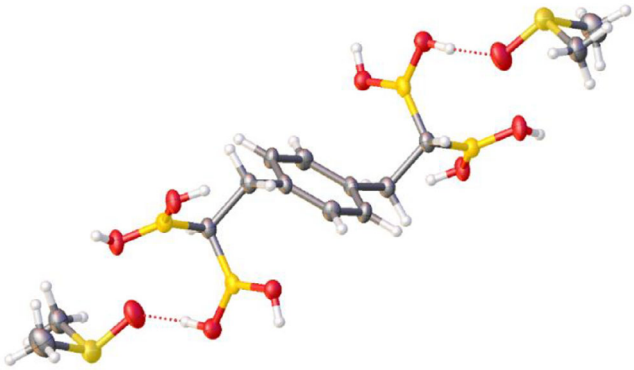


Figure 3. Crystal structure of receptor 2. The receptor is bound to DMSO via hydrogen bonding interactions and forms an extended hydrogen-bonded network with other receptor molecules.

gluconic, and malic acids, and catechol-containing compounds such as dopamine.[18–20] These analytes form covalent bonds to the boron center to generate stable boronates, even in aqueous media. A handful of examples of anion binding by boronic acids have recently been reported,[21–25] but the use of boronic acids in anion recognition is not well established. This may be due, in part, to the tendency of boronic acids to form complex mixtures of anhydrides and cyclic boroximes.

Recently, we reported a bidentate ligand containing a *gem*-diborane motif to facilitate substrate binding within a metal's secondary coordination sphere (Figure 1a).[26] This motif formed stable adducts with acetate, nitrite, and hydride in anhydrous THF solution, and selectively bound ditopic bases in the presence of excess fluoride (a base that typically forms strong B─F bonds). Additionally, we established an additive effect for the ditopic boranes compared to the monotopic analogues. *Gem*-diboronic acids have also been recently developed as catalysts for amide bond formation.[27–31] Whiting, Sheppard, and coworkers proposed that (under rigorously anhydrous conditions) the active species in boronic acid-mediated amidation catalysis is a "B-X-B" motif, which forms an interaction with carboxylates (Figure 1b).[32] Despite these precedents highlighting the potential application of such ditopic acids, *gem*-diboronic acids have not been explored for anion recognition. In this work, we investigate the scope, strength, and suitability of *gem*-diboronic acids for use in anion receptor chemistry in aqueous-containing media.

We prepared two receptors, 1 and 2, which contain either one or two *gem*-boronic acid motifs, respectively (Figure 2). The tetratopic receptor (2) was designed as a selective dicarboxylate receptor by considering three distinct criteria: 1) two sets of *gem*-diboronic acids to bind to each end of a dibasic substrate, 2) a spacer to provide >5.9 Å separation between each site, and 3) a mixture of rigid (benzene) and nonrigid (methylene) spacers to provide a balance of preorganization with appropriate flexibility to maximize binding affinity. Each receptor was accessible in two steps, via an intermediate pinacol-protected boronate. These boronates were accessed either by catecholborane-promoted double hydroboration of an alkyne, or by alkylation of a benzylic halide with lithiated bis[(pinacolato)boryl]methane (SI).

Single crystals of receptor 2 were obtained by vapor diffusion of dichloromethane into 5% aqueous DMSO (Figure 3).[33] Analysis of the X-ray structure revealed that all boron atoms maintained trigonal planar geometry (sum of angles around boron atoms: 359.8° and 359.9°). The receptor co-crystallized in an extended hydrogen-bonded network with adjacent receptor molecules, interacting through the B─OH groups. Interacting DMSO molecules also formed hydrogen-bonding interactions with the B─OH groups, and did not interact directly with the boron centers. In DMSO solution (0.5–5% H_2O), the ^{11}B NMR spectrum exhibited a resonance at 19.7 ppm, and the ^{1}H NMR spectrum indicated the presence of coordinated water molecules at 6.5 ppm (SI). By comparison, a control compound 3, which is analogous to receptor 2 but features two single boronic acids, was highly aggregated in solution, and formed a complex oligomeric mixture (SI). These data suggest that the *gem*-diboronic acid motif is less susceptible to the formation of anhydrides and boroximes than simple boronic acids, and more likely to interact with water through hydrogen bonding interactions than by addition to the empty boron p-orbital. This decreased tendency to aggregate and react provides a distinct advantage for *gem*-diboronic acids over simple boronic acids in the development of anion receptors.

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Table 1: Binding affinities of receptor 1 with a range of anions in 5% aqueous DMSO-d_6. Affinities were determined by ^{1}H or ^{31}P NMR. Data were fitted to a binding model using either the Bindfit web application[37] or HypNMR software. Values are the average of at least two replicates. The ΔG values were determined through gas phase calculations using the mimized energies of the receptor–substrate complex and subtracting the energies of the substrate and receptor independently.

Anion	Affinity ($\log K_{1:1}$)	Calc. ΔG (kcal mol^{-1}) (wb97xd/def2TZVP)	Predicted Binding Mode
SO_4^{2-} [a]	3.51 ± 0.01	−56.1	2× B—O
$H_2PO_4^-$	2.45 ± 0.19	−20.1	1× B—O, 2× H-bond
AcO^-	1.41 ± 0.26	−19.2	1× B—O
NO_2^- [a]	– [b]	−17.0/−18.4	1× B—O/1× B—O, 1× H-bond
NO_3^- [a]	– [b]	−8.1	1× B—O
Cl^- [a]	– [b]	−30.2	2× H-bond

[a] Binding affinity determined by displacement of acetate (4 equiv) from the receptor. [b] Anion did not displace acetate.

We assessed the anion binding capability of one-armed receptor 1 via NMR spectroscopy. Initial attempts to determine binding affinities by interrogating the resonances associated with the receptor hydrogens were unreliable due to peak broadening upon the addition of anions. ^{11}B NMR titrations of the receptor and anion were also uninformative, and did not conclusively indicate the binding mode of the anions (SI). Consequently, we evaluated binding affinities by analysis of changes in the spectra of the anion upon successive additions of the *gem*-diboronic acid receptor. Where the anion of interest was not NMR active, we performed a competition experiment with acetate. NMR titrations were carried out with 2 mM concentration of anion, and in 5% H_2O/DMSO-d_6: a highly competitive medium for a charge-neutral binding motif.

Receptor 1 displayed binding to sulfate, dihydrogen phosphate, and acetate in aqueous DMSO (Table 1), with the order of affinity $SO_4^{2-} > H_2PO_4^- > AcO^-$. This trend is distinct from the selectivity profiles of simple dual hydrogen bonding motifs such as ureas and squaramides, which typically display higher affinities toward acetate than dihydrogen phosphate.[34] The affinity of receptor 1 toward sulfate is also higher than that of other simple anion recognition motifs.[35] Other anions (nitrite, nitrate, and chloride) did not interact with sufficient strength to allow determination of binding affinity.[36] High-resolution mass spectrometry confirmed that the addition of tetrabutylammonium acetate to a solution of receptor 1 in acetonitrile led to the formation of the [M + acetate]$^-$ adduct (SI).

To provide clarity into the binding mode of the *gem*-diboronic acid motif with anions, we calculated the gas phase structures and affinities of receptor 1 with a range of anions (Table 1 and Figures S1–S7). These calculations show that *gem*-diboronic acids can likely interact with anions through a combination of hydrogen bonding interactions and by addition to the empty boron p-orbital. The calculated free energies of interaction largely follow the same trend as the experimentally determined binding affinities, and correctly predict the affinity trend: $SO_4^{2-} > H_2PO_4^- > AcO^-$. Sulfate, which displays the largest affinity and $|\Delta G|$, is calculated to form two B—O interactions with the *gem*-diboronic acid motif forming a 6-membered heterocycle (Figure S3). Calculated structures of anions with lower affinities indicated only a single B—O interaction, and/or hydrogen bonding interactions with B—OH groups (Figures S5–S8). There was disparity between the experimental and calculated values for chloride. However, chloride is predicted to interact with the receptor via hydrogen bonding interactions only (Figure S8), because *gem*-ditopic boranes are geometrically mismatched to interact with multiple lone pairs on a single atom (e.g., chloride), whereas substrates with lone pairs on different atoms (e.g., sulfate, phosphate, and acetate) are geometrically matched to the *gem*-diboronic acid motif, forming 5- or 6-membered heterocycles.[26] It is likely that, in an aqueous environment, interactions between chloride and the receptor are outcompeted by the solvent. These data suggest that interaction of the anion directly at boron can be more significant than hydrogen bonding contributions.

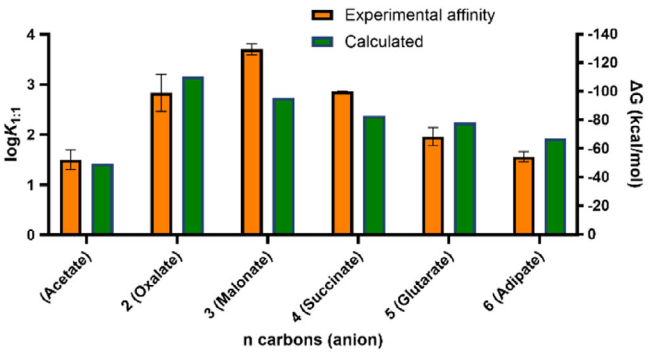


Figure 4. Experimental and calculated binding affinities of receptor 2 with a range of carboxylate anions in 5% aqueous DMSO-d_6. Affinities were determined by ^{1}H NMR titration. Data were fitted to a binding model using either the Bindfit web application[36] or HypNMR software. Values are the average of at least two replicates. The ΔG values were determined through gas phase calculations (Wb97xd/def2SVP) using the minimized energies of the receptor–substrate complex and subtracting the energies of the substrate and receptor independently.

Receptor 2 was used to assess the directionality of the anion-*gem*-diboronic acid interaction, and the suitability of this motif for recognition of more complex anions. Although this receptor possesses two *gem*-diboronic acid motifs, titration data indicated formation of a 1:1 receptor:acetate complex only. This finding was supported by calculated interaction energies, which indicated that a second binding event is endergonic for AcO^-, SO_4^{2-}, and $H_2PO_4^-$. The affinities of receptor 2 for acetate were not significantly higher than those obtained for receptor 1 (Figure 4 and Tables S1 and S2), while the affinity for dihydrogen phosphate was

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approximately doubled (as may be expected for a receptor with an additional binding site).[38] Next, we performed ^{1}H NMR titrations with a range of dicarboxylates, which differed in their length and flexibility, to determine the ideal length of the guest anion. The C6 dicarboxylate adipate bound to receptor 2 with a 1:1 affinity, comparable to that of acetate. However, as the distance between the carboxylate groups was reduced, the binding affinities sharply increased until a maximum was reached at malonate (C3). Malonate was found to bind with an affinity nearly an order of magnitude greater than the C2 and C4 dicarboxylates oxalate and succinate, and two orders of magnitude greater than acetate, suggesting the length of this guest is well matched to the binding site of receptor 2.

The flexibility of the guest anion was also found to be important to effect binding. Fumarate, a C4 dicarboxylate with a length comparable to the extended conformation of succinate, bound to receptor 2 with an affinity that matches that of acetate. These data suggest that the carboxylate-*gem*-diboronic acid interaction is highly directional, and strong binding only occurs when receptor and anion are well-matched. Once again, calculated interaction energies in the gas phase largely matched experimentally determined affinities (Figure 4). Oxalate was calculated to display the highest affinity; however, it did not displace malonate from receptor 2 and the measured binding affinity, determined from the displacement of succinate, was lower than that of malonate. This disparity is potentially due to differences in hydration of the two anions, which are not accounted for in the calculations.

For both gas phase calculations and calculations including implicit solvent correction, receptor 2 exhibited 2-point binding between the diboronic acid motifs and substrates with only one B—O interaction for each *gem*-diboronic acid site (Figures S13–S18). We hypothesized that hydrogen bonding between substrate and boronic acids in the gas phase structures could alter the number of observed B—O interactions. Given that substrate–boronic acid H-bonding is likely diminished under experimental conditions with H-bonding solvent, we tested this hypothesis using a modified receptor, 2^{Me} (where $B(OH)_2$ was replaced with $B(OMe)_2$), which maintains similar steric, electronic, and acidity profiles to 2 but diminishes H-bonding capabilities (Figure 5). In each case for modeled (C2–C6 substrates), we observed a distinct trend: 2^{Me} consistently exhibited higher degrees of B—O bonding than 2, with 4-point binding observed for glutarate, succinate, and oxalate (Figures S26–S30).[39] The higher B—O bonding in 2^{Me} enables computational comparison to two methylated ditopic analogues, 1^{Me} and 3^{Me}. The 1^{Me} analogue is a derivative of 1, containing *gem*-ditopic boranes, while 3^{Me} contains a single borane on either side of the rigid benzene linker. The computational models uncover a thermodynamic trend for each of the dicarboxylate substrates where $1^{Me} < 3^{Me} < 2^{Me}$ for substrate binding (Figure 5). These data indicate that exploitation of two key design principles, *gem*-ditopic boranes and boranes positioned so that they are capable of binding each end of a dicarboxylate substrate, ultimately results in a thermodynamic additive effect for the tetratopic receptor.

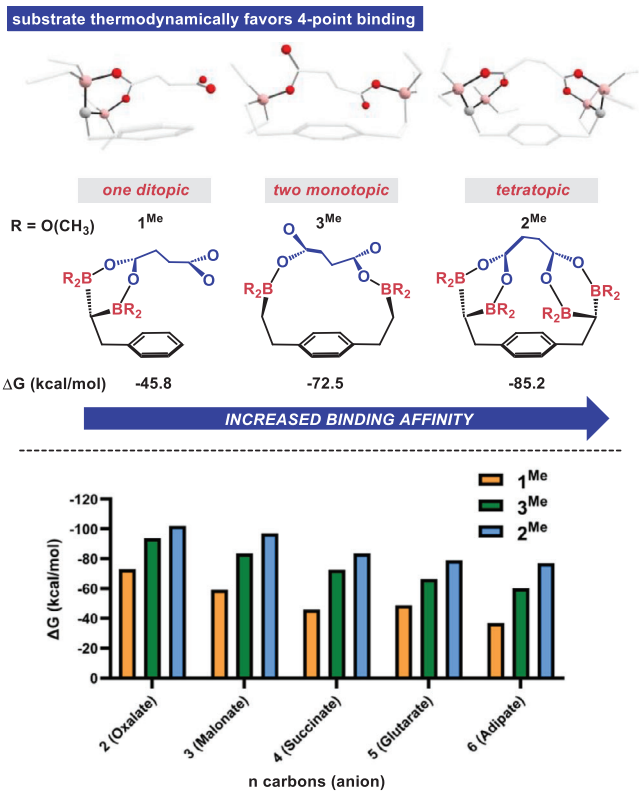


Figure 5. Calculated structures and binding modes of 1^{Me}, 2^{Me}, and 3^{Me} with succinate (top) and thermodynamic evaluation of substrate binding for range of carboxylate anions (bottom).

The affinities of receptor 2 with glutarate may be compared with similar receptors reported by Hamilton[40,41] and by Gunnlaugsson,[42] which contain two amide, urea, thiourea, or guanidinium groups linked by an aromatic group. Hamilton's amide receptor did not interact at a measurable level with glutarate in 100% DMSO,[40] and the urea and thiourea receptors displayed comparable affinities in 100% DMSO[41,42] to those obtained for receptor 2 in the presence of 5% water, indicating that the *gem*-diboronic acid motif binds carboxylates with higher affinity than (thio)ureas in competitive media.[43] It appears that the *gem*-diboronic acid–glutarate interaction is not as strong as the guanidinium–glutarate interaction, which benefits from an electrostatic interaction as well as hydrogen bonds.[41] Of particular note, the *gem*-diboronic acid motif outperforms other neutral anion recognition motifs such as amides, ureas, and thioureas, displaying stronger binding affinities for carboxylate anions, and a highly directional interaction. Despite its simplicity, receptor 2 also represents one of the most selective examples of malonate recognition reported to date.[44]

Gem-diboronic acids form high-affinity, directional interactions with a range of oxoanions, including carboxylates, sulfate, and dihydrogen phosphate. A single *gem*-diboronic acid motif is sufficient to bind to these anions, even in highly competitive aqueous-containing media. This motif also offers a selectivity profile that is distinct from those of other common anion recognition motifs, such as (thio)ureas and squaramides. *Gem*-diboronic acids therefore represent a

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new motif for selective anion recognition in aqueous media. Finally, we showcased their utility using 2, which represents one of the most selective receptors (1 order of magnitude) for malonate reported to date.

Supporting Information

The authors have cited additional references within the Supporting Information.[45–53]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Anion receptor · Anion recognition · Boronic acid

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