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# Benzene-based tripodal isothiouronium compounds as sulfate ion receptors

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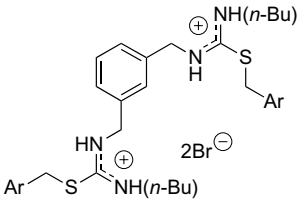
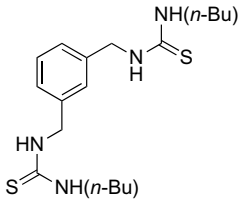
**Abstract**—Novel benzene-based tripodal isothiouronium receptors are synthesized for the selective recognition of tetrahedral oxoanions. The binding study by isothermal titration calorimetry indicates that the cationic receptors bind sulfate ions preferably in a tripodal mode, while they show a mixed binding mode toward phosphate ion. The tripodal isothiouronium receptors show large $\Delta G^0$ values toward sulfate ions in methanol, which are entropy driven. The results demonstrate that a subtle structural constraint can lead to different binding modes toward structurally similar anions.


In nature, phosphate and sulfate binding proteins recognize the anions through multiple hydrogen bonds.[1] Mimicking the nature, artificial receptors utilize hydrogen bonding as the main binding force for the recognition of these oxoanions. As the hydrogen bonding donors, functional groups such as amide, sulfonamide, urea, and thiourea have been widely used.[2] Artificial receptors with these neutral ligands, particularly tripodal receptors, have attracted much attention for the efficient recognition of such tetrahedral oxoanions.[3] Also, receptors with cationic ligands such as guanidinium and isothiouronium have been studied for enhanced binding affinity toward these anionic guests.[4] Considering that phosphate and sulfate anions are tetrahedral, cationic tripodal receptors, given a 1:1 binding mode, are more appealing than the corresponding dipodal receptors. Surprisingly, cationic tripodal receptors for tetrahedral oxoanions have received little attention.[5] Anslyn and co-workers have shown that benzene-based tripodal receptors with guanidinium ligands efficiently recognize anions such as citrate and inositol phosphate.[6] Because the benzene-based tripodal system provides a preorganized ligand structure, it would be interesting to develop related cationic receptors toward the tetrahedral oxoanions.[7] Herein, we wish to report benzene-based tripodal isothiouronium compounds as selective sulfate ion receptors.

We have chosen isothiouronium groups as hydrogen donor ligands because both tripodal and luminescent analogs[8] can be readily synthesized from the corresponding thiourea compounds. The benzene-based tris(isothiouronium) receptors, BTT **1a** and **1b**,[9] were synthesized from the corresponding thiourea, which was in turn prepared from mesitylene (Scheme 1). As a reference compound, we prepared a bis(isothiouronium) analogue, BBT **2**, similarly starting from 1,3-bis(bromomethyl)mesitylene (Scheme 2).[10] Hong and co-workers showed that a related, but less preorganized, dipodal isothiouronium receptor **3**,[4c] which was synthesized from the corresponding thiourea receptor **4**,[11] strongly bound dihydrogen phosphate.




**3**, Ar = *p*-$NO_2$-Ph




**4**

*Keywords*: Anion recognition; Tripodal receptors; Thiouronium compounds; Sulfate recognition; Preorganization.

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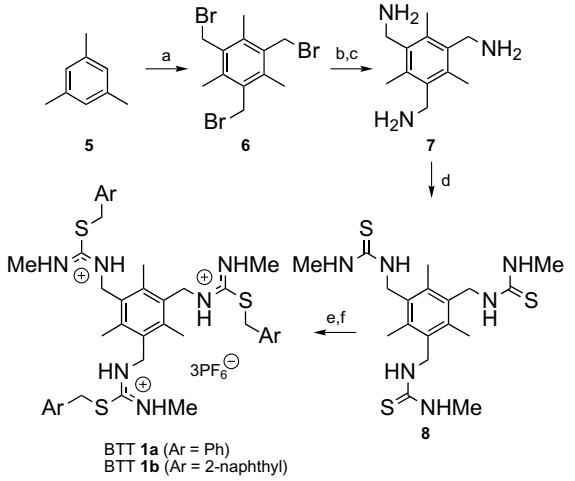
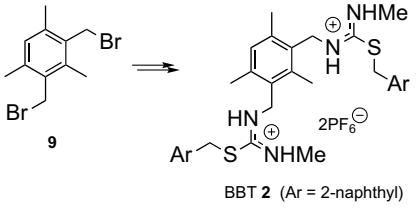



**Scheme 1.** Syntheses of BTTs **1**. Reagents and conditions: (a) $(CH_2O)_n$, 30 wt % HBr/AcOH, 95 °C, 12 h; (b) $NaN_3$, acetone, reflux, 3 h, 90% for two steps; (c) $LiAlH_4$, THF, reflux, 12 h, 81%; (d) MeNCS, $CH_2Cl_2$, rt 3 h; (e) $ArCH_2Br$, MeOH, reflux, 24 h, 91–100% for two steps; (f) $NH_4PF_6$, MeOH, rt 24 h, 50–60%.




**Scheme 2.**

The $^1$H NMR spectrum of tris(thiourea) **8** exhibited a $C_3$-symmetric structure in $CD_3OD$ at ambient temperature; however, those of BTTs **1** indicated slow equilibration of conformers, probably due to steric bulkiness of the isothiouronium moiety. For example, BTT **1a** existed as two conformers in a ratio of ~5:3, presumably so-called *ababab*- and *aaabbb*-type conformers.[12] These conformer peaks merged into a $C_3$-symmetric structure upon raising the temperature over 60 °C.

The formation of host–guest complex was supported by $^1$H NMR analysis. For example, upon addition of $SO_4^{2-}$ in $CD_3OD$, those broad and split peaks of BTT **1b** due to the conformational equilibrium merged into sharp peaks, and also chemical shift changes occurred for certain protons [–$SCH_2$–: $\delta$ 4.58 and 4.43 (m) → 4.63 (s); –$CH_2NH$–: 4.94 and 4.90 (s) → 4.88 (s) ppm for $SO_4^{2-}$].

The binding characteristics of BTTs **1** and BBT **2** toward sulfate and phosphate anions were evaluated by isothermal titration calorimetry (ITC).[13] This ITC analysis directly gives the standard enthalpy change $\Delta H^0$, and estimation of $\Delta G^0$ and the host–guest stoichiometry $n$ by titration curve fitting. Thus, $\Delta S^0$ can also be calculated from the Gibbs–Helmholtz equation. The ITC measurements were carried out at 303 K in MeOH.[14] Tetramethylammonium salts of sulfate and phosphate ions were used.

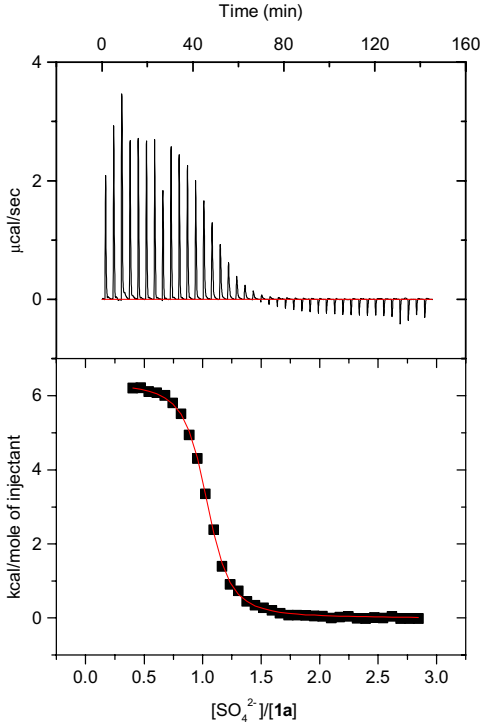



**Figure 1.** ITC titration data of BTT **1a** with $SO_4^{2-}$ in MeOH at 303 K.

Figure 1 shows typical calorimetric data (raw and integration data) obtained in the titration of $SO_4^{2-}$.[15] After subtraction of heat of dilution from the raw data and nonlinear curve fitting under 'one set of sites model'[16] gave those thermodynamic parameters for the binding process.

The $\Delta H^0$ and $-T\Delta S^0$ data in Table 1 indicate that the complex formation is driven mainly by favorable entropy changes. Schmidtchen and co-workers already pointed out that the binding of sulfate anion by guanidinium receptors in methanol is entropy driven.[4e,f] The positive $\Delta H^0$ value in Table 1 reflects an endothermic reorganization of the highly solvated host and guest species in the protic solvent. The net increase of solvent molecules liberated from these highly solvated species before and after complex formation contributes to the entropy increase, which outweighs the unfavorable enthalpy change. The inflection point in the calorimetric isotherm occurs near the molar ratio of 1.0, which corresponds to the host–guest stoichiometry $n = 1$. Thus, the cationic tripodal receptors **1a** and **1b** interact with $SO_4^{2-}$ in a 1:1 binding mode, as we intended in their

**Table 1.** Thermodynamic data for the host–guest complexation determined by isothermal titration calorimetry

| Entry | Guest[a] | Host | $n$[b] | $\Delta G^{0c}$ | $\Delta H^{0c}$ | $-T\Delta S^{0c}$ |
|---|---|---|---|---|---|---|
| 1 | $SO_4^{2-}$ | **1a** | 1.01 | −8.3 | +6.4 | −14.7 |
| 2 | $SO_4^{2-}$ | **1b** | 0.84 | −8.4 | +7.2 | −15.6 |
| 3 | $SO_4^{2-}$ | **2** | 0.6 | −6.0 | +8.8 | −14.8 |

[a] $Me_4N^+$ salts.
[b] Host–guest stoichiometry.
[c] Unit: kcal mol$^{-1}$.

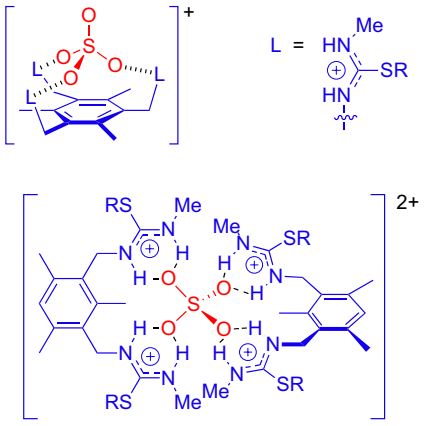



**Figure 2.** Supposed binding modes for the 1:1 and 2:1 complexes of BTTs **1** and BBT **2** toward $SO_4^{2-}$.

design. In contrast, in the case of BBT **2** a smaller $\Delta G^0$ value was obtained and the $n$ value was fluctuated near 0.6. These results suggest that a 2H:1G complex may form in the case of BBT **2** (Fig. 2).

Similar ITC experiments toward $PO_4^{3-}$ gave different results from those of $SO_4^{2-}$. ITC titrations with BTT **1a** toward the $PO_4^{3-}$ ion[17] suggest that a complex binding process is involved, in contrast to the case of $SO_4^{2-}$. The calorimetric raw data in Figure 3 suggests that the binding process involves at least two equilibria since more than single inflection points seem to exist.

Since $PO_4^{3-}$ has multiple binding sites, we carried out 'inverse titration' using BTT **1a**. Thus, a $PO_4^{3-}$ solution in a calorimetric cell was titrated with BTT **1a**. Non-linear curve fitting under 'one set of sites model' provided $\Delta G^0 = -7.6$ and $n$ value of 0.6.[18] Of notable is that under the inverse addition mode larger heat evolution results upon titrant injection (Fig. 4). From the inflection point, which is near $n = 0.5$, a new 1H:2G binding mode may be suggested in this case. Under the inverse titration condition, we can expect that a relatively excess amount of $PO_4^{3-}$ exists compared to BTT **1a** at the initial stage, and thus the 1H:2G complex may be formed

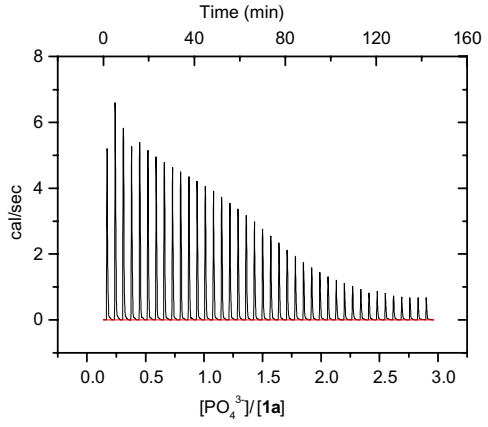



**Figure 3.** ITC titration data of BTT **1a** with $PO_4^{3-}$ in MeOH at 303 K.

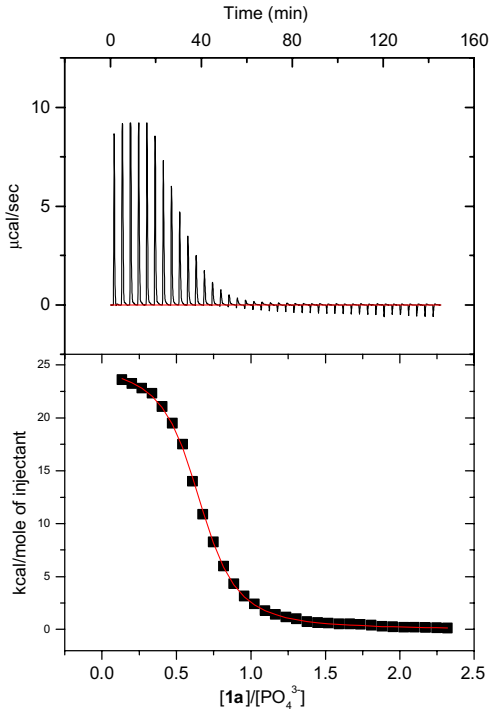



**Figure 4.** The inverse titration data of BTT **1a** with $PO_4^{3-}$ in MeOH at 303 K.

(Fig. 5). Then, further addition of BTT **1a**, after an equivalent point, may not involve a marked solvent reorganization through host–guest interactions, and thus results in a small or little change in the binding isotherm (Fig. 4). We carried out a similar inverse titration toward $SO_4^{2-}$ and observed nearly the same behavior (1H:2G complex formation). The different ITC

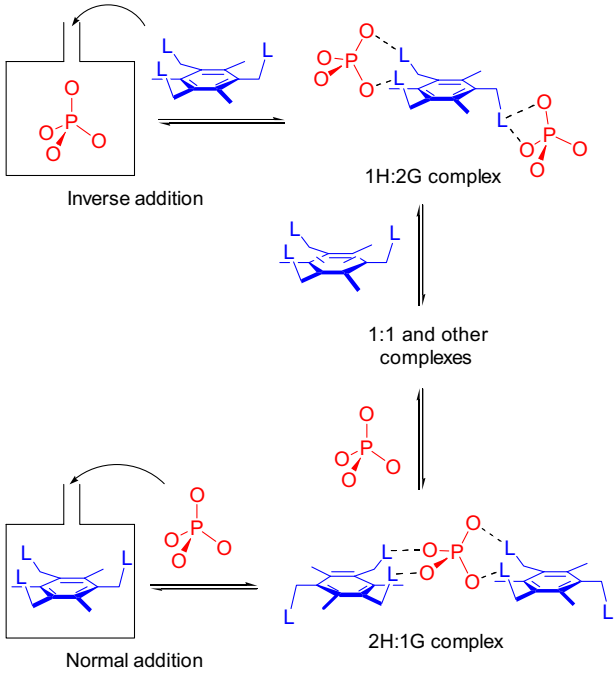
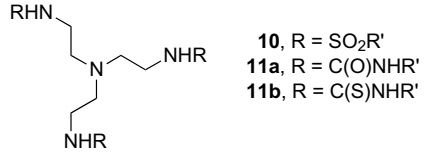



**Figure 5.** Initial binding modes depending on the inverse and normal ITC additions in the case of $PO_4^{3-}$ (charge is omitted for clarity).

results depending on the addition modes seem to be not unusual in cases where both the host and guest have multiple binding sites.

To get additional information on the binding modes depending on the guests, we carried out electrospray ionization (ESI) mass analyses. We were able to confirm a 1:1 host–guest complex formation between BTT **1a** and $SO_4^{2-}$ readily. Also, in the case of $PO_4^{3-}$ we were able to observe a 1:1 host–guest complex albeit with low intensity. However, attempts to observe other binding modes such as 2H:1G or 1H:2G under various conditions were not successful. We also attempted to get binding information by NMR titration, but failed due to small binding-induced chemical shifts and peak overlapping.

The different binding behavior observed with BTTs **1** toward $SO_4^{2-}$ compared to $PO_4^{3-}$ may be related to the structure complementarity between the host and guest. The 'cavity' of our tripodal receptor system seems to fit $SO_4^{2-}$ but does not match $PO_4^{3-}$, probably owing to larger size of the latter ion.[19] Such subtle structural selectivity may arise from a relatively rigid/preorganized structure of the benzene-based tripodal system. In addition to this structural effect, different solvation energy between the two anions should be also an important factor. An opposite guest selectivity was observed in the cases of tripodal sulfonamide- and urea-type receptors (**10**, **11**) based on a flexible tris(2-aminoethyl)amine backbone, which was studied in an aprotic solvent.[3d,e]




**10**, R = $SO_2R'$
**11a**, R = C(O)NHR'
**11b**, R = C(S)NHR'

Recently, Hoffmann and co-workers reported a related example in which the guest selectivity was changed through conformational preorganization of a flexible host.[20] The structural factor seems to be very subtle: our dipodal receptor BBT **2** shows a significant affinity toward $SO_4^{2-}$ but not toward $PO_4^{3-}$, which makes it difficult to be determined by ITC. An opposite trend was observed by bis(isothiouronium) receptor **3** that is structurally very similar to BBT **2**.[4c] In our case, the presence of a methyl group between the two isothiouronium ligands in BBT **2** seems to cause a subtle change in the bonding distance and angle in such a way to accommodate $SO_4^{2-}$ better than $PO_4^{3-}$.

The tripodal isothiouronium receptors **1a** show a similar level of affinity toward the sulfate ion as that of a bis(guanidinium) receptor of Schmidtchen and co-workers,[4e] from which we may expect a higher affinity from a tripodal receptor based on the guanidinium ligands.

In summary, novel isothiouronium-based tripodal cationic receptors are synthesized for the selective recognition of tetrahedral oxoanions. Binding studies by isothermal titration calorimetry in methanol indicate that the cationic receptors bind sulfate ions preferably in tripodal modes, while they bind phosphate ions in complex modes. The different binding modes seem to be originated from subtle structural complementarity due to the ligand preorganization, in addition to the different solvation energy in methanol. Studies toward preorganized tripodal receptors with different ligands including luminescence properties are under investigation.

## Acknowledgements

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9. Selected spectroscopic data: **1a**: $^1$H NMR ($CD_3OD$, 300 MHz) $\delta$ 9.7–8.9 (br m, 6H, –NH), 7.6–7.4 (m, 15H), 4.7–4.5 (m, 12H, $–CH_2–$), 3.2 and 3.0 (br s, 9H, $–NCH_3$), 2.2 (br s, 9H); $^{13}$C NMR ($CD_3OD$, 75 MHz) $\delta$ 165.8 and 165.6, 139.1, 134.8, 130.3, 129.2, 128.9, 128.2, 44.4 and 44.0, 36.0, 31.8 and 31.4, 16.3. **1b**: $^1$H NMR ($CD_3OD$, 300 MHz) $\delta$ 9.7–8.9 (br m, 6H, –NH), 8.1–7.5 (m, 21H), 4.94 and 4.89 (s, 6H, $–CH_2N–$), 4.58 and 4.43 (m, 6H, $–SCH_2–$), 3.2 and 3.0 (br s, 9H, $–NCH_3$), 2.2–1.9 (m, 9H); $^{13}$C NMR ($CD_3OD$, 75 MHz) $\delta$ 165.8 and 165.5, 138.9, 132.8, 132.5, 130.1, 129.0, 128.7, 128.0, 127.7, 126.7, 126.6, 44.4 and 43.7, 36.3 and 35.8, 31.9 and 31.4, 15.9. **8**: $^1$H NMR ($CD_3OD$, 300 MHz) $\delta$ 7.36 and 7.24 (br s, 6H, –NH), 4.57 (d, $J = 2.4$ Hz, 6H), 2.96 (d, $J = 2.4$ Hz, 9H), 2.43 (s, 9H, $–ArCH_3$); $^{13}$C NMR ($CD_3OD$, 75 MHz) $\delta$ 183.0, 136.7, 132.8, 43.5, 30.7, 15.0.
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14. A typical ITC experimental. A solution of $(Me_4N^+)_2SO_4^{2-}$ in methanol (2.0 mM) was introduced by 45 μL injections, in total 200 μL, into a methanol solution of BTT **1a** (1.5 mL, 0.1 mM) in a calorimetry cell (Microcal Inc.). The solution was kept at an operating temperature of 303 K. Analysis and curve fitting using the software Origin™ afforded the thermodynamic data.
15. The raw data in terms of microcalories/second plotted against time cross over the zero level, owing to traces of water remaining in the guest salt. Attempts to remove water completely from the guest was not successful. All the sample preparations were carried out in a glove box under nitrogen.
16. The 'one set of sites' model applies for any number of sites $n$ if all sites have the same $K$ and $\Delta H$.
17. We prepared $(n\text{-}Bu_4N^+)_3PO_4^{3-}$ by treatment of equimolar amounts of $n$-$Bu_4NOH$ and $H_3PO_4$ in methanol. We found that attempted purification of the resulting salt by recrystallization in various solvents (MeOH–$Et_2O$, MeOH–EtOAc, MeOH–$CHCl_3$, MeOH–benzene, etc.) was not reproducible or did not provide the desired salt. The chemical entity of the salt was monitored by volumetric titration. We found that mixing of equimolar amounts of the reagents and subsequent evaporation of the solvent under vacuum, without recrystallization, gave the salt suitable for the ITC titrations.
18. Nonlinear curve fitting under conditions of two non-identical and independent binding sites or two identical and dependent sites model did not give better fit. Thus, the $\Delta G^0$ value can be used only as an estimation.
19. The distance between the two oxygens of $PhSO_3^-$ is 2.42 Å, while that of $PhP(OH)O_2^-$ is 2.55 Å, see: (a) Kelly, T. R.; Kim, M. H. *J. Am. Chem. Soc.* **1994**, *116*, 7072–7078; (b) The thermochemical radii of $SO_4^{2-}$ and $PO_4^{3-}$ are 2.14 and 2.27 Å, respectively, see: Solís-Correa, H. *J. Chem. Educ.* **1987**, *64*, 942–943.
20. (a) Hoffmann, R. W.; Hettche, F.; Harms, K. *Chem. Commun.* **2002**, 782–783; (b) Hettche, F.; Hoffman, R. W. *New J. Chem.* **2003**, *27*, 172–177.