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Journal

Angewandte Chemie International Edition, 55(38)

ISSN

1433-7851

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Publication Date

2016-09-12

DOI

10.1002/anie.201605757

Peer reviewed

A Synthetic Supramolecular Receptor for the Hydrosulfide Anion

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Abstract: Hydrogen sulfide (H_2S) has emerged as a crucial biomolecule in physiology and cellular signaling. Key challenges associated with developing new chemical tools for understanding the biological roles of H_2S include developing platforms that enable reversible binding of this important biomolecule. The first synthetic small molecule receptor for the hydrosulfide anion, HS^- , using only reversible, hydrogen-bonding interactions in a series of bis(ethynylaniline) derivatives, is reported. Binding constants of up to $90300 \pm 8700 M^{-1}$ were obtained in MeCN. The fundamental science of reversible sulfide binding, in this case featuring a key $CH\cdots S$ hydrogen bond, will expand the possibility for discovery of sulfide protein targets and molecular recognition agents.

Supramolecular hosts have been developed to selectively bind a variety of anionic species in solution, ranging from inorganic phosphates and phosphorylated biomolecules to halides and other anions of environmental or biological relevance.^[1] These synthetic supramolecular receptors use reversible, mostly non-covalent interactions to select anions based on factors such as their basicity, shape/charge, softness/hardness, position on the Hofmeister series, and hydrophobic/solvophobic effects. Notably lacking in the anion binding literature are efforts to target hydrosulfide (HS^-), the smallest monoanionic sulfur species, which has recently gained interest as an important biomolecule. Herein, we report the first examples of synthetic receptors that reversibly bind HS^- using solely hydrogen-bonding interactions. Importantly, a critical $CH\cdots S$ hydrogen bond is key to the strong binding of hydrosulfide, lending support to the hypothesis that appropriately polarized C–H hydrogen-bond donors^[1f,2] can target softer anions.^[1e,3]

Hydrogen sulfide (H_2S) plays diverse roles in the global sulfur cycle and has recently been implicated as an important biologically relevant signaling molecule.^[4] In the last decade

H_2S (and its more prevalent conjugate-base form at physiological pH, HS^-) has emerged as the third endogenously produced gasotransmitter, along with CO and NO. H_2S is now implicated in diverse (patho)physiological functions in the cardiovascular, immune, gastrointestinal, as well as other systems, making its absence in the supramolecular chemistry of anions even more surprising.^[5] In parallel to the biological advances in H_2S research, chemical tools for detecting and imaging H_2S are rapidly emerging and form a cornerstone of the investigative approaches used to study this critical biomolecule.^[6] Despite this importance, current detection methods are plagued by irreversibility, which presents a significant problem in developing chemical tools that provide real-time information on biological processes, suggesting that a supramolecular (that is, reversible) approach to HS^- binding would be an important contribution.

The pK_a of H_2S (7.0) ensures that both the neutral (H_2S) and monoanionic (HS^-) forms are present under physiological conditions, which complicates biological H_2S investigations and leads to significant unresolved questions on the specific chemistry and recognition events associated with the individual protonation states. Recently, HS^- was determined to be a viable substrate for Cl^-/HCO_3^- anion-exchange proteins,^[7] and a bacterial ion channel for HS^- transport was identified (Figure 1 a,b).^[8] Importantly, the recognition events involved in the sulfide transport of these systems rely on non-covalent, reversible interactions with HS^- rather than metal coordination or interaction with the sulfane sulfur pool. Taken together, these examples suggest that HS^- , which has until now been almost entirely overlooked, needs to be included in the complex landscape of biologically relevant anions, such as Cl^- , HCO_3^- , I^- , and NO_2^- . Despite the emerging importance of sulfide, HS^- has only appeared in anion screening sporadically, and we are unaware of any synthetic receptors able to bind H_2S or HS^- reversibly through well-defined non-covalent interactions.^[1b,9] Systems that could bind H_2S or HS^- selectively through reversible interactions would not only provide significant insights into potential HS^- -binding environments in biological contexts but also provide new strategies for developing reversible and real-time H_2S detection methods.

To approach this challenge, we reasoned that synthetic anion receptors could provide a viable platform to develop reversible HS^- -binding systems. To optimize selective binding for hydrosulfide, we initially assumed that the ideal receptor should feature hydrogen-bond donors to target the anionic portion of hydrosulfide and a hydrogen-bond acceptor (or suitable pocket of electron density) to accommodate the slightly acidic hydrogen atom. Aligned with these requirements, sulfide has a similar ionic radius to Cl^- ($S^{2-} = 1.84 \text{ \AA}$, $Cl^- = 1.81 \text{ \AA}$), and biological examples reveal that HS^- can

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Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201605757>.

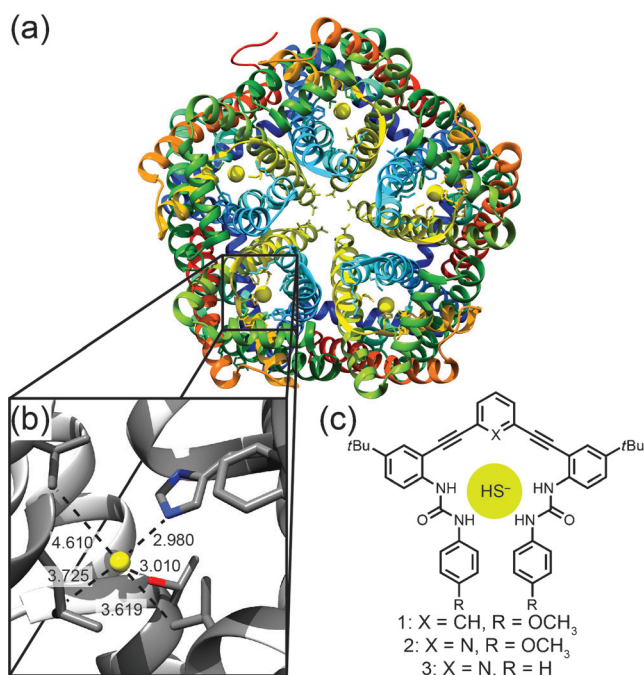


Figure 1. a) Protein structure of the bacterial hydrosulfide ion channel (HSC, PDB:3TDX) showing five individual channels with the bound anion represented as a yellow sphere. b) Enlargement of the binding pocket showing short contacts to His (2.980 Å), Thr (3.010 Å), Leu (3.725 Å), and Val (3.619 and 4.610 Å). Non-interacting helices are excluded for clarity. c) Synthetic receptors 1–3.

play similar roles as Cl^- .^[10] This similarity has not yet been exploited in the synthetic supramolecular community to target HS^- , perhaps because of a prevailing assumption that Cl^- and HS^- should have quite different binding properties based on their different protonation states, nucleophilicities, hardness/softness, shape, $\text{p}K_b$ (−8 vs. 7, respectively), and resulting hydrogen-bond-accepting ability.

In this light, we reinvestigated the bis(ethynylaniline) anion-binding receptors we have developed for Cl^- as a viable platform for non-covalent HS^- binding.^[11] These modular scaffolds bind anions through tunable urea N–H hydrogen bonds, and the central core can be easily modified to incorporate an additional hydrogen-bond-donating arene (**1**) or a hydrogen-bond-accepting pyridine group (**2,3**).^[3] The semi-preorganized binding pocket significantly reduces the entropic penalty for anion encapsulation, while maintaining the flexibility to accommodate different anions. The ability to tune the urea hydrogen-bond donors as well as the central core binding motif has resulted in a family of receptors that can selectively target a diverse range of analytes.^[5a,12] Additionally, recent work has suggested that C–H hydrogen-bond donors polarized by inductive electron-withdrawing groups (for example, the electronegative sp-hybridized alkyne carbon atoms in **1**) should exhibit selectivity for softer anions.^[3] Although the place of HS^- on the Hofmeister series and hard/soft acid/base (HSAB) theory tables is not clear, intuition suggests that hydrosulfide should be a softer anion than chloride. Motivated by these challenges, we report here the first examples of synthetic receptors that reversibly

bind HS^- using solely supramolecular interactions (Figure 1c).

To investigate whether HS^- is a suitable guest for hosts **1–3**, we titrated a 0.5–1.0 mM solution of each host in 10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$ with $\text{NBu}_4\text{SH}^{[13]}$ and monitored the titrations by ^1H NMR spectroscopy (Supporting Information, Figure S1). In each case, we observed that the urea NH resonances shifted significantly downfield upon HS^- addition, consistent with anion binding (Figure 2). For example, upon

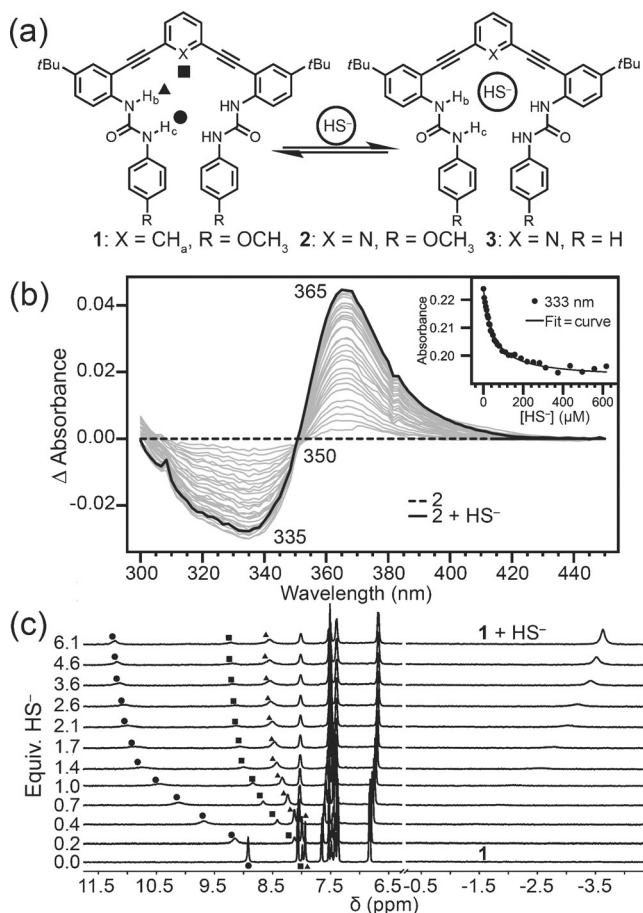


Figure 2. a) Representation of the HS^- host–guest equilibrium. b) Representative UV/Vis difference titration of $10\ \mu\text{M}$ **2** with NBu_4SH in CH_3CN . Inset: Fit of the titration data to a 1:1 binding isotherm. c) ^1H NMR spectra of a titration of $0.988\ \text{mM}$ **1** with NBu_4SH in 10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$.

addition of HS^- to a solution of **1**, the aryl CH_a shifted from 7.99 to 9.24 ppm, and the NH_b and NH_c urea protons shifted downfield from 7.94 and 8.92 to 8.63 and 11.18 ppm, respectively. Demonstrating the preference of each receptor **1–3** for HS^- over H_2S , the addition of H_2S gas to any of the receptors failed to change the UV/Vis or NMR spectra of the hosts. We also confirmed that the observed changes in the NMR spectra upon HS^- addition were not due to the deprotonation of the urea NH groups. Addition of the strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) produced significantly different UV/Vis and NMR spectra than those observed upon HS^- addition (Supporting Information,

Figure S14). On the basis of the high nucleophilicity of HS^- , we also confirmed that the anion did not irreversibly modify the alkyne moieties of the host scaffolds by monitoring the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** before and after the addition of 10 equivalents of HS^- (Supporting Information, Figure S13). Additionally, titration data of the host with HS^- could be fitted to simple 1:1 binding isotherm models. Taken together, these results support the hypothesis that HS^- binds within the host pocket and does not covalently modify the host scaffold.

To determine whether receptors **1–3** exhibited selectivity for HS^- over similar anions, we performed comparison titrations with NBu_4Cl under identical conditions. We initially expected that pyridine-based hosts **2** and **3** would exhibit higher binding affinities for HS^- because of the hydrogen-bond-accepting pyridine core; however, titration data established hosts **2** and **3** had significantly lower binding constants for both anions than did phenyl-core host **1**. This difference suggests that the extra C–H hydrogen bond donated from the phenyl core is a key component in establishing the binding magnitude and selectivity. This result was contrary to our initial hypothesis that HS^- should also act as a weak hydrogen-bond donor to an acceptor on the host receptor (for example, the pyridine nitrogen of **2** and **3**).^[14] Despite the lower binding affinities, the pyridine-based hosts **2** and **3** exhibited 6-fold higher selectivity for HS^- over Cl^- , whereas host **1** exhibited a 2.8-fold improvement in selectivity. The higher selectivity could be due to the putative $\text{N}\cdots\text{HS}^-$ hydrogen bond from the pyridine lone pair acting as a hydrogen-bond acceptor, which provides an additional stabilizing interaction for HS^- and a destabilizing interaction for Cl^- . The phenyl core of host **1** donates a hydrogen bond to both anionic guests, resulting in a decreased selectivity for hydro-sulfide, even if this C–H hydrogen bond is an important component to the higher overall binding energy.

To further investigate the difference in anion selectivity, binding constants were also measured by UV/Vis spectroscopy in CH_3CN (Table 1). We expected that removal of the DMSO co-solvent would increase the observed binding affinities since acetonitrile is a slightly less competitive solvent (especially as a hydrogen-bond acceptor). Addition of NBu_4SH to 10 μM solutions of **1**, **2**, or **3** resulted in attenuation of the 330 nm absorbance with a concomitant increase at 360 nm, proceeding through a well-anchored isosbestic point near 350 nm. As expected, removal of DMSO produced significantly higher binding affinities, with binding constants of 90 300 M^{-1} for host **1** and circa 25 000 M^{-1} for hosts **2** and **3**. For **1**, the selectivity for HS^- over Cl^- remained

similar to that of the 10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$ system, whereas in the case of the pyridine core, a significant increase in selectivity is observed (ca. 18.5:1, $\text{HS}^-:\text{Cl}^-$). The difference between the binding energy of HS^- with **1** and **2** is the same in both solvents ($\Delta\Delta G = 0.90 \text{ kcal mol}^{-1}$), whereas the Cl^- binding energy exhibits a larger solvent dependence ($\Delta\Delta G = 1.24$ ($\text{DMSO}/\text{CH}_3\text{CN}$) vs. 1.83 (CH_3CN) kcal mol^{-1}). For HS^- , the $\Delta\Delta G$ is the difference between two stabilizing hydrogen-bond motifs, which suggests that a C–H \cdots S hydrogen bond is up to an estimated 0.90 kcal mol^{-1} stronger than an S–H \cdots N hydrogen bond. The $\Delta\Delta G$ of Cl^- binding is larger because this represents the difference between a small repulsive $\text{N}\cdots\text{Cl}$ contact and an attractive C–H \cdots Cl hydrogen bond.

To further establish the reversibility of HS^- binding (Figure 3a), we treated a solution of **1** in 10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$ (Figure 3b) with two equivalents of NBu_4SH to form

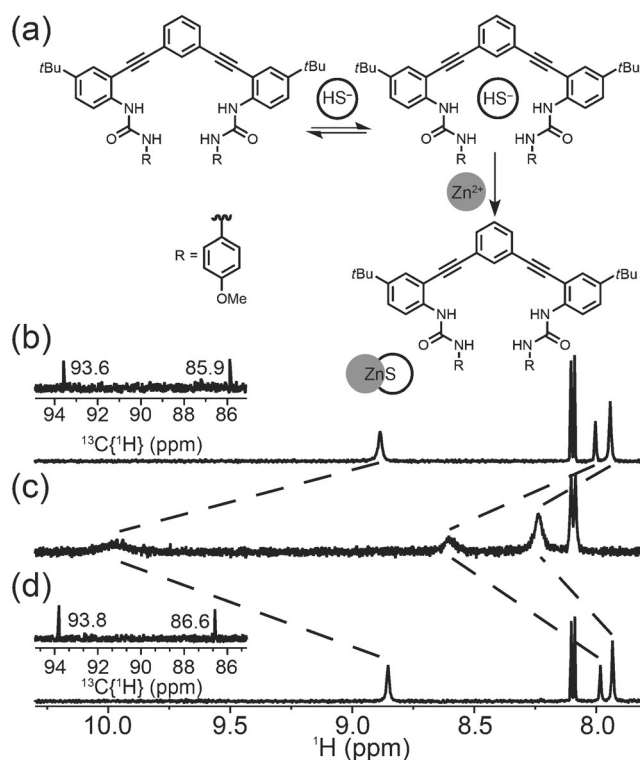


Figure 3. a) Reversibility reaction scheme. b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a 1.0 mM solution of **1** in 10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$. Inset: $^{13}\text{C}\{^1\text{H}\}$ resonances corresponding to the alkyne region of **1**. c) Treatment with 2 equiv of NBu_4SH . d) Addition of 4 equiv of $\text{Zn}(\text{OAc})_2$. Inset: $^{13}\text{C}\{^1\text{H}\}$ resonances corresponding to the alkyne region of **1**.

Table 1: HS^- and Cl^- binding parameters in hosts **1–3**.

Host	Solvent	HS^-		Cl^-	
		$\log(K_a)$	ΔG [kcal mol^{-1}]	$\log(K_a)$	ΔG [kcal mol^{-1}]
1	10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$	$3.70 \pm 0.07^{[a]}$	−5.05	$3.25 \pm 0.03^{[a]}$	−4.43
	CH_3CN	$4.96 \pm 0.04^{[b]}$	−6.76	$4.53 \pm 0.07^{[b]}$	−6.18
2	10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$	$3.04 \pm 0.06^{[a]}$	−4.15	$2.34 \pm 0.07^{[a]}$	−3.19
	CH_3CN	$4.30 \pm 0.07^{[b]}$	−5.86	$3.19 \pm 0.07^{[b]}$	−4.35
3	10% $[\text{D}_6]\text{DMSO}/\text{CD}_3\text{CN}$	$3.12 \pm 0.07^{[a]}$	−4.25	$2.34 \pm 0.02^{[a]}$	−3.19
	CH_3CN	$4.45 \pm 0.07^{[b]}$	−6.07	$3.08 \pm 0.06^{[b]}$	−4.20

[a] Obtained by fitting NMR spectroscopic data. [b] Obtained by fitting UV/Vis spectroscopic data.

the HS^- -bound adduct (Figure 3c), after which four equivalents of $\text{Zn}(\text{OAc})_2$ were added. Addition of $\text{Zn}(\text{OAc})_2$ rapidly resulted in precipitation of ZnS and regenerated the NMR spectrum corresponding to free **1** (Figure 3d). Further addition of five equivalents of NBu_4SH regenerated the HS^- host–guest complex, confirming reversible

binding. Importantly, the $^{13}\text{C}\{^1\text{H}\}$ resonances of the alkyne carbons did not shift significantly (Figures 3b,d), confirming that there was no covalent modification of the receptor scaffold.

Single crystals of $[\mathbf{1}\cdot\text{HS}^-][\text{NBu}_4^+]$ were grown by layering *n*-hexane onto an equimolar solution of $\mathbf{1}$ and NBu_4SH in THF in a glovebox. $[\mathbf{1}\cdot\text{HS}^-][\text{NBu}_4^+]$ crystallizes in the space group *Pna*2₁ with one molecule of THF per unit cell. Consistent with the solution NMR data, the HS^- occupies the binding pocket created by an aryl proton and four urea protons with the NBu_4^+ cation sitting just above the sulfide-phenyl core plane (Supporting Information, Figure S15). The structure shows five hydrogen bonds from the host to the bound sulfide guest. The C–H \cdots S hydrogen bond (3.711 Å) is longer than those formed between the distal bis(urea) protons (3.277 and 3.281 Å) (Figure 4). The average of the five

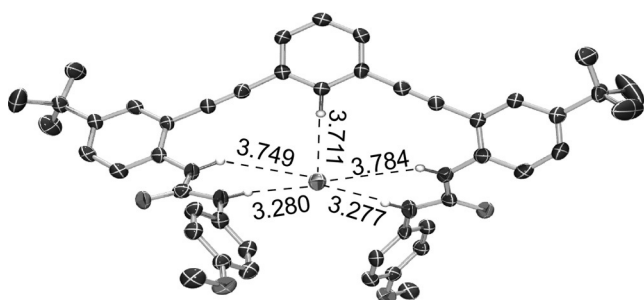


Figure 4. ORTEP representation showing selected hydrogen bond distances. Ellipsoids are set at 50% probability.^[16] Hydrogen atoms not interacting with the bound HS^- are removed for clarity.

hydrogen bond distances from the host to the guest is 3.56 Å, which falls within previously defined criteria for hydrogen bonds.^[2b,15] The host conformation in $[\mathbf{1}\cdot\text{HS}^-]$ is remarkably similar to the previously published chloride-bound structure, with an RMS distance between the two structures of only 0.184 Å (Supporting Information, Figure S16).^[14] These data demonstrate the similar recognition geometries required for Cl^- and HS^- binding, again highlighting the potential for HS^- to be a substrate for classical Cl^- binding domains in both native and synthetic systems.

In conclusion, we report a series of bis(ethynylaniline) derivatives capable of binding the hydrosulfide anion with association constants as high as $90300 \pm 8700 \text{ M}^{-1}$, representing the first reversible binding of the hydrosulfide anion by a synthetic receptor. ^1H NMR and UV/Vis spectroscopy indicate stronger binding of hydrosulfide by the phenyl core receptor $\mathbf{1}$; however, a greater selectivity for HS^- is observed in the pyridine cores ($\mathbf{2}$ and $\mathbf{3}$). The preference for the phenyl core highlights the unexpected conclusion that a C–H \cdots S contact is favored over an N \cdots H–S contact by up to $0.9 \text{ kcal mol}^{-1}$. This difference may be related to the mechanisms that underlie anion-binding selectivities beyond the usual factors of shape, size, and charge. Importantly, these results indicate that hydrogen bond polarizability and other aspects of HSAB theory are relevant to the characterization of anion-selective host–guest systems. Additionally, these

data suggest that C–H hydrogen-bond donors are important components of reversible hydrosulfide targeting. Taken in total, these experiments establish the reversible binding of HS^- to synthetic host molecules and highlight that HS^- is an important, and thus far overlooked, biologically important anion that can be targeted by synthetic molecular architectures. These studies also begin to establish the design rules for targeting the hydrosulfide anion using such synthetic receptors. Moreover, we anticipate that the basic science of non-covalent sulfide binding to synthetic targets will help to identify new target proteins for sulfide binding, while also informing new potential sulfide detection strategies that do not rely on the irreversible covalent modification of sensing platforms.

Acknowledgements

This work was supported by the NSF (CHE-1454747 to M.D.P.), Sloan Foundation, and NIH (R01-GM087398 to D.W.J./M.M.H.). NIH GM087398 funded early stage intellectual property that was licensed by SupraSensor Technologies/Enterprises, a company co-founded by D.W.J./M.M.H. The NMR facilities at the University of Oregon are supported by the NSF (CHE-1427987).

Keywords: anion binding · gasotransmitters · molecular recognition · sulfide · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11480–11484
Angew. Chem. **2016**, *128*, 11652–11656

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- [16] CCDC 1472308 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: June 14, 2016

Published online: August 11, 2016