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Sulfate Recognition by Persistent Crystalline Capsules with Rigidified Hydrogen-Bonding Cavities**

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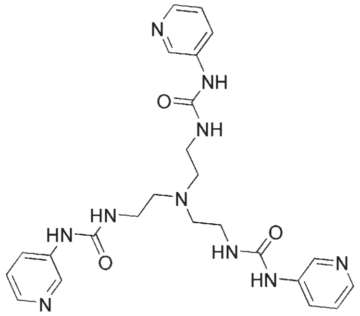
Selectivity is a fundamental property of pervasive importance in chemistry and biology as reflected in phenomena as diverse as membrane transport, catalysis, sensing, adsorption, complexation, and crystallization. Although the key principles of complementarity and preorganization governing the binding interactions underlying such phenomena were delineated long ago,[1] truly profound designed selectivity has proven elusive, in part because synthetic molecular architectures are neither maximally complementary for binding target species nor sufficiently rigid. Even if a host molecule possesses a high degree of complementarity for a guest species, with almost no exceptions it can distort its structure or even rearrange its conformation altogether to accommodate competing guests. One approach taken to overcome this challenge has been to devise three-dimensional rigid molecules that bind species within complementary cavities. Although rare examples have been reported to demonstrate the principle,[1b] such cases are not generally of practical utility, because of synthetic inaccessibility and often poor kinetics. Alternatively, more readily synthesized flexible architectures are generally employed,[2] but then the challenge becomes one of locking their structures in place. This locking has been somewhat easier to accomplish in self-assembled capsules,[3,4] though other challenges emerge, such as finding means to internally functionalize the cavities of the capsules.[5] Taking a cue from natural binding agents[6] that derive their rigidity from a network of molecular interactions, especially hydrogen bonding, we present herein an example of a crystalline capsule that recognizes sulfate by a highly complementary array of rigidified hydrogen bonds. We have been employing crystalline host environments functionalized with anion-coordinating groups as a means to obtain maximal three-dimensional complementarity and rigidity.[7] In the present study, we focused on the problem of sulfate recognition and separation,[8,9] motivated in part by its high relevance to environmental remediation and nuclear-waste cleanup[10] but also by the challenge of overcoming the Hofmeister bias that disfavors transfer of densely charged, highly hydrated anions.[7d] The crystalline capsules described herein display hydrogen-bonding cavities that are highly complementary to tetrahedral divalent oxoanions, and remarkably persistent in the presence of other oxoanions of various shapes and basicities, despite being made from rather simple and flexible building blocks. This system thus presents a rare opportunity to examine anion selectivity under the ideal condition of a constant hydrogen-bonding host environment, and, at the same time offering a potentially practical solution for sulfate separation from highly competitive aqueous salt solutions.

The tripodal tris-urea ligand **L1** was selected for this study based on analogous urea derivatives of tris(2-aminoethyl)amine that exhibited recognition of sulfate in solution and the crystalline state.[9a,11] Notably, the *m*-CN-Ph substituted tris-urea ligand encapsulated sulfate in a 2:1 complex when incorporated into a silver coordination polymer, with the resulting formation of 12 hydrogen bonds representing the highest coordination number reported for SO_4^{2-} ions in a synthetic receptor.[9a] However, selective and efficient separation of sulfate from aqueous solutions with this or other analogous crystalline frameworks proved elusive so far owing to the low stability and relatively high solubility of the frameworks in water. We reasoned that functionalization of this tripodal scaffold with stronger coordinating groups, such as pyridines, would facilitate the incorporation of this anion receptor into more robust crystalline frameworks with superior sulfate-separation abilities.



L1

Crystallization of **L1** with various MSO_4 salts (M = Zn, Cd, Co, Mg) from 1:1 H_2O/MeOH solutions afforded single crystals with the composition $MSO_4(\mathbf{L1})_2(H_2O)_6$, (**1**) as determined by X-ray diffraction and elemental analysis. Crystal-structure determination showed that, regardless of M, all the solids are isostructural with the same space group

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($P2_1/n$) and very similar unit cell and geometrical parameters (Supporting Information). The following study was therefore solely focused on the Mg^{2+} system (**1a**), which appeared most practical for sulfate separation. The structure of **1a**[12] consists of centrosymmetric SO_4^{2-}(**L1**)$_2$ anionic units with the sulfate encapsulated by 12 hydrogen bonds from six urea groups (Figure 1 a), which may be considered the optimal coordination number for sulfate.[9a] The SO_4^{2-} ion coordination geometry deviates however from the ideal C_3 symmetry predicted by molecular modeling (one chelating urea for each of the six O-S-O edges),[13] with the most notable difference that one of the urea groups binds an O vertex rather than an O-S-O edge of the sulfate. This situation is most likely the result of the centrosymmetric geometry imposed by the crystal symmetry, which also causes the sulfate to be rotationally disordered over two positions to compensate for its lack of an inversion center. The SO_4^{2-}(**L1**)$_2$ complex is incorporated in a hydrogen-bonded capsule by 12 additional hydrogen bonds from six water molecules, each bridging, through its two protons, a pyridine N and a urea C=O acceptor (Figure 1 b). The resulting quasioctahedral arrangement of the water molecules around the hydrogen-bonded capsules matches the coordinating geometry of the metal cations, present as $Mg^{2+}(H_2O)_6$ hydrates, which leads to the formation of a three-dimensional framework with distorted NaCl topology (Figure 1 c,d). This structure thus represents a rare example of a hydrogen-bonded network with octahedral connectivity.[14] We note that the sulfate encapsulation is dependent on the formation of this crystalline framework, as only a 1:1 SO_4^{2-}/**L1** complex could be detected in solution (CH_3OD/D_2O, 1:1) by an NMR Job's plot analysis (Supporting Information), in agreement with other solution binding studies of similar receptors.[11] This result reinforces the strength and uniqueness of the crystallization approach to anion recognition and separation, which allows exclusive binding modes that are otherwise difficult to achieve in solution.

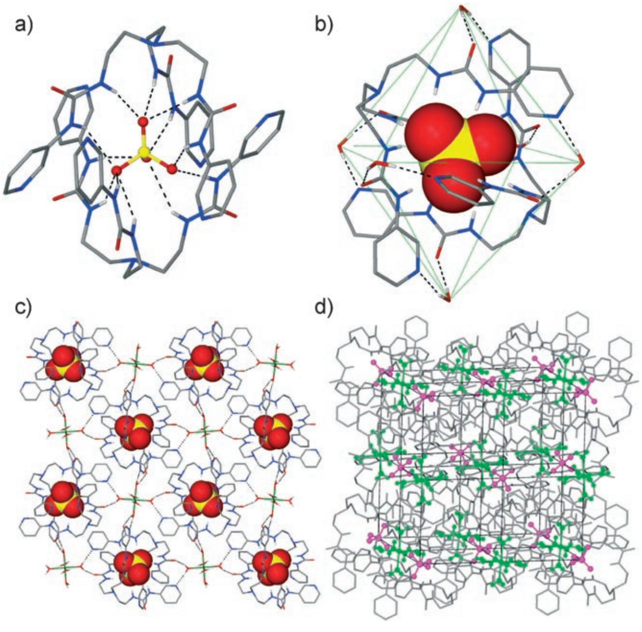

Figure 1. Crystal structure of **1a**. a) Sulfate encapsulation by 12 hydrogen bonds (dashed lines) from six urea groups; yellow S, red O, blue N. b) Hydrogen-bonded capsule assembled from two **L1** (stick model), one SO_4^{2-} ion (space filling model), and six bridging water molecules (stick model). c) A slice of the hydrogen-bonded framework obtained by self-assembly of the anionic capsules with Mg^{2+} ions (green). d) 3D representation of the octahedral framework with NaCl topology; magenta SO_4^{2-}, green $Mg^{2+}(H_2O)_6$, gray **L1**.

Attempts to crystallize similar frameworks under the same conditions from monocations such as Na^+ or K^+ in the presence of different monoanions of various shapes and basicities, such as ClO_4^-, NO_3^-, HCO_3^-, HSO_4^-, and $H_2PO_4^-$, resulted in no crystals. Likewise, monoanionic MgX_2 salts, where $X = F^-$, Cl^-, Br^-, I^-, ClO_4^-, and NO_3^-, failed to produce any crystals in the presence of **L1** under similar conditions. It thus appears that the presence of a dication/dianion pair, which provides a stronger electrostatic stabilization, is critical for the formation of **1** from water. This feature allowed us to separate sulfate from excess nitrate by selective crystallization of **1a**. Indeed, competitive crystallization experiments indicated that **1a** could be isolated in high yield (88%) from a 100-fold excess of $NaNO_3$,[15] as determined by FTIR and elemental analysis (Supporting Information). This promising result is particularly relevant to the problem of nuclear-waste cleanup, where it is desirable that sulfate be removed from nitrate-rich nuclear wastes prior to their vitrification, owing to the low solubility in the glass and the corrosive nature of SO_4^{2-}.[10] It is also a striking demonstration of the power of crystallization techniques to effect essentially infinite selectivity for the crystal-forming species among competing species.

To assess the sulfate selectivity against more competitive anions of similar charge, we investigated the ability of SO_3^{2-}, CO_3^{2-}, and SeO_4^{2-} to form similar hydrogen-bonded frameworks in the presence of Mg^{2+} and **L1**. While the first two anions have different shapes than SO_4^{2-} (trigonal-pyramidal and trigonal-planar, respectively), SeO_4^{2-} has similar tetrahedral shape but is slightly larger than sulfate ($r_{X-O} = 1.49$ and 1.65 Å for X = S and Se, respectively).[16] This series is thus ideal for probing the shape and size selectivity of **1a** (taking into account the differences in anion basicity and hydration). All three anions were found to form hydrogen-bonded frameworks that are isostructural to **1a**, with the same general formula of $MgX(\mathbf{L1})_2(H_2O)_6$ ($X = SO_3^{2-}$ (**1b**), CO_3^{2-} (**1c**), SeO_4^{2-} (**1d**)), same space group, and slightly different unit-cell parameters.[17] To assess the sulfate selectivity against these anions, we performed pairwise competitive crystallization experiments with 1:1 molar mixtures of $MgSO_4$ and Na_2X salts ($X = SO_3^{2-}$, CO_3^{2-}, SeO_4^{2-}) in the presence of two equivalents of **L1**, and analyzed the anionic compositions of the precipitated solids by FTIR spectroscopy and elemental analysis (Supporting Information). Qualitative analysis of the infrared spectra (Figure 2) clearly indicates that sulfate is selectively separated in each case. Table 1 summarizes the selectivities observed as determined quantitatively by elemental analysis.

As can be seen from Table 1, the competition experiments established the following anion selectivity order: SO_4^{2-} >

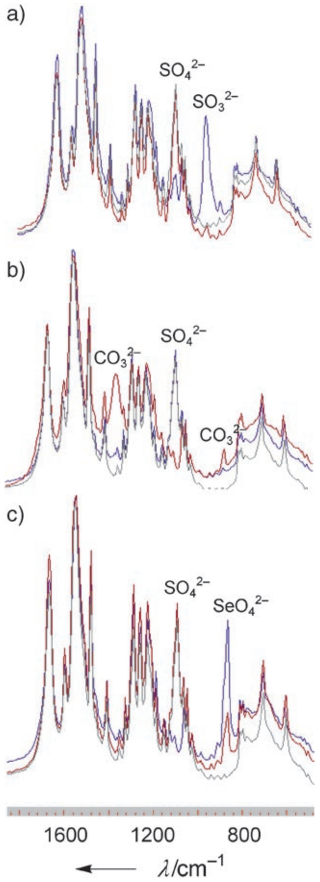

Figure 2. FTIR analysis of the competitive crystallization experiments. a) SO_4^{2-}/SO_3^{2-} competition: **1a** is shown in green, **1b** in blue, and the solid crystallized from $MgSO_4/Na_2SO_3$ in red. b) SO_4^{2-}/CO_3^{2-} competition: **1a** is shown in green, **1c** in red, and the solid crystallized from $MgSO_4/Na_2CO_3$ in blue. c) SO_4^{2-}/SeO_4^{2-} competition: **1a** is shown in green, **1d** in blue, and the solid crystallized from $MgSO_4/Na_2SeO_4$ in red.

Table 1: Sulfate selectivity against SO_3^{2-}, CO_3^{2-}, and SeO_4^{2-} ions.

Anion (X)/crystal	Sep. factor (α)[a]	$\Delta(\Delta E_{lat})$[b]	PA[c]	$\Delta G^0{}_h$(X)[d]
SO_4^{2-}/**1a**	-	0	−1889	−1080
SO_3^{2-}/**1b**	372	75.3	−1971	−1295
CO_3^{2-}/**1c**	53	58.7	−2042	−1315
SeO_4^{2-}/**1d**	5	33.8	−1863	−900

[a] Separation factor: $\alpha(SO_4^{2-}/X) = [(\text{mol } SO_4^{2-})/(\text{mol X})]_{crystal}/[(\text{mol } SO_4^{2-})/(\text{mol X})]_{solution}$. [b] Calculated lattice energies (relative to **1a**), where $\Delta E(\mathbf{1x})_{lat} = E(\mathbf{1x})_{crystal} - E(X)_{gas} - 2E(\mathbf{L1})_{gas} - E[Mg(H_2O)_6{}^{2+}]_{gas}$ (**x** = **a**–**d**), calculated at the PBE level with planewave bases (see details in the Supporting Information). [c] Gas-phase proton affinities of anions calculated at the B3LYP/6-31+G** level (see details in the Supporting Information). [d] Experimental Gibbs energies of hydration.[18] All energies are in kJ mol^{-1}.

$SeO_4^{2-} > CO_3^{2-} > SO_3^{2-}$. This trend differs from the orders of hydrogen-bond acceptor abilities of the anions (estimated from the gas-phase proton affinities): $CO_3^{2-} > SO_3^{2-} > SO_4^{2-} > SeO_4^{2-}$, or of the Hofmeister series (based on ΔG_h): $SeO_4^{2-} > SO_4^{2-} > SO_3^{2-} > CO_3^{2-}$. Rather, the observed anion selectivity order agrees with the relative crystal stabilities of **1a** > **1d** > **1c** > **1b**, as found from lattice-energy calculations using the experimental crystal structures (Supporting Information). For comparison, the selectivity expected from crystallization of the corresponding Mg salts is: $MgCO_3 > MgSO_3 > MgSO_4$,[19] which follows the increasing anion radii order. The combined experimental and computational data thus indicate peak selectivity for sulfate against both stronger bases, such as carbonate and sulfite, and less hydrophilic, larger anions, such as selenate.

The remarkable selectivity for SO_4^{2-} ions appears to be determined both by the nearly ideal complementarity of the binding site for sulfate and the rigidity of its hydrogen-bonding environment. First, the complementarity provides for shape and size recognition through the urea functional groups in **1a**, which, as shown in Figure 3a, completely encapsulate the sulfate with an array of favorably positioned hydrogen bonds.[20] In direct contrast, the CO_3^{2-} and SO_3^{2-} ions, with their different shape, do not fit very well within these hydrogen-bonding cavities, as they require a different geometric arrangement of the urea groups for optimal binding.[13] In fact, these anions display repulsive interactions (shown in red in Figure 3a) between one NH proton and the positively charged C and S atoms, with contact distances of 2.66 and 2.75 Å that are significantly shorter than the corresponding sums of the van der Waals radii of 2.90 and 3.00 Å, respectively. Such contacts are absent in the case of the tetrahedral SO_4^{2-} and SeO_4^{2-} ions because of the effective shielding by the fourth O atom in these anions. Second, **L1** shows remarkable rigidity when constrained within these water-bridged crystalline frameworks (Figure 3b,c), despite its otherwise flexible structure. Such rigidity prevents the receptor from adjusting its geometry to optimize the binding of the competing anions, which contributes to the observed discrimination between sulfate and selenate despite their nearly identical shape and size. This system is thus reminiscent of protein receptors, which despite their inherent flexibility can achieve remarkable selectivities by forming well-defined and rigid binding sites, whose structural integrity is dependent on the presence of multiple noncovalent interactions and the inclusion of water. It is also important

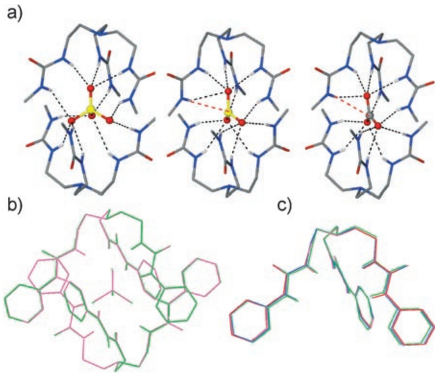

Figure 3. a) Anion binding sites in **1a** (left), **1b** (middle), and **1c** (right). Hydrogen bonds are shown as black dotted lines and repulsive interactions in **1b,c** as red dotted lines. b) Overlay of **1a** (magenta) and **1d** (green). $Mg(H_2O)_6$ cations were removed for clarity. c) Overlay of the **L1** structures in **1a**–**d**.

to note that the sulfate recognition in **1a** is distinct from anion templating[21] or induced-fit phenomena, since virtually identical structures are obtained with the other anions despite the wide variation in their size and shape. This *structural persistence* is apparently a result of the hydrogen-bonded water bridges that rigidify the framework in much the same way as found in calixarene capsules sustained by incorporated water molecules.[3c]

We have illustrated herein a striking example of anion recognition and separation based on crystallization of rigid hydrogen-bonded capsule frameworks made from a simple, flexible ligand functionalized with complementary urea groups, which allowed us to selectively separate the environmentally relevant sulfate from highly competitive mixtures of aqueous anions. The unusual persistence of a common framework structure in the presence of different anions of various sizes, shapes, and basicities provided a unique opportunity for assessing anion selectivities in hosts with a virtually constant hydrogen-bonding environment. While we specifically targeted sulfate separation in this particular study, this approach could be applicable to separation of other guest molecules or ions through appropriate crystal design.

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[12] Crystal data for **1a**: $C_{48}H_{72}MgN_{20}O_{16}S$, $M_r = 1241.64$, monoclinic, space group $P2_1/n$, $a = 12.4806(6)$, $b = 18.3478(10)$, $c = 13.0001(7)$ Å, $\beta = 91.4960(10)°$, $V = 2975.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.386\ \mathrm{g\,cm^{-3}}$, $T = 173$ K, $R_1 = 0.0487$, $wR_2 = 0.1112$.[17b]

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[15] The yield obtained in the competitive crystallization is greater than the 71 % yield observed in the synthesis of **1a** (Supporting Information), which is likely a result of salting-out by the $NaNO_3$. Preliminary experiments indicate that **L1** can be recovered by crystallization, after dissolution of **1a** into aqueous HCl, sulfate removal as $BaSO_4$, and pH adjustment to 6–7.

[16] Average values from Cambridge Structural Database (CSD 5.28, November 06).

[17] a) Crystal data for **1b**: $C_{48}H_{72}MgN_{20}O_{15}S$, $M_r = 1225.62$, monoclinic, space group $P2_1/n$, $a = 12.5076(7)$, $b = 18.2295(11)$, $c = 12.9307(8)$ Å, $\beta = 91.6430(10)°$, $V = 2947.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.381\ g\,cm^{-3}$, $T = 173$ K, $R_1 = 0.0620$, $wR_2 = 0.1498$; crystal data for **1c**: $C_{49}H_{72}MgN_{20}O_{15}$, $M_r = 1205.58$, monoclinic, space group $P2_1/n$, $a = 12.4253(6)$, $b = 18.2988(10)$, $c = 12.8511(7)$ Å, $\beta = 92.3620(10)°$, $V = 2919.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.371\ g\,cm^{-3}$, $T = 173$ K, $R_1 = 0.0578$, $wR_2 = 0.1321$; crystal data for **1d**: $C_{48}H_{72}MgN_{20}O_{16}Se$, $M_r = 1288.52$, monoclinic, space group $P2_1/n$, $a = 12.4822(6)$, $b = 18.3577(10)$, $c = 13.1051(7)$ Å, $\beta = 91.4760(10)°$, $V = 3002.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.425\ g\,cm^{-3}$, $T = 173$ K, $R_1 = 0.0362$, $wR_2 = 0.0897$. b) CCDC-662209 (**1a**), CCDC-662210 (**1b**), CCDC-662211 (**1c**), CCDC-662212 (**1d**) 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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[19] ΔG_{cryst} for the reaction $Mg^{2+}{}_{(aq)} + X^{2-}{}_{(aq)} \rightarrow MgX_{(cryst)}$ are -29.5, 17.5, and $28.7\ kJ\,mol^{-1}$ for $X = CO_3{}^{2-}$, $SO_3{}^{2-}$, and $SO_4{}^{2-}$, respectively (no data available for $MgSeO_4$); calculated from tabulated values in D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttal, *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplement No. 2.

[20] The sulfate disorder in **1a** suggests that entropy may play a role in the strong affinity for this anion (F. P. Schmidtchen, *Coord. Chem. Rev.* **2006**, *250*, 2918–2928). However, considering that the other anions are also rotationally disordered in **1b–d** (with the sulfite and carbonate displaying somewhat larger thermal ellipsoids than sulfate and selenate), it is unlikely that entropy is a determining factor in the observed sulfate selectivity.

[21] a) M. D. Lankshear, P. D. Beer, *Acc. Chem. Res.* **2007**, *40*, 657–668; b) N. Gimeno, R. Vilar, *Coord. Chem. Rev.* **2006**, *250*, 3161–3189.