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Anion Separation with Metal–Organic Frameworks

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The application of metal–organic frameworks (MOFs) to anion separations with a special emphasis on anion selectivity is reviewed. The coordination frameworks are classified on the basis of the main interactions to the included anion, from weak and non-specific van der Waals forces to more specific interactions such as coordination to Lewis acid metal centers or hydrogen bonding. The importance of anion solvation phenomena to the observed anion selectivities is highlighted, and strategies for reversing the Hofmeister bias that favors large, less hydrophilic anions, and for obtaining peak selectivities based on shape recognition are delineated. Functionalization of the anion-binding sites in MOFs with strong and directional hydrogen-bonding groups that are complementary to the included anion, combined with organizational rigidity of the coordination framework, appears to be the most promising approach for achieving non-Hofmeister selectivity.

1. Introduction

Metal–organic frameworks (MOFs), also called coordination polymers, or coordination networks, have developed into one of the most prolific areas of research in materials chemistry.[1] The extraordinary popularity of MOFs could be explained by the ease of their synthesis based on the self-assembly of metal cations with organic linkers possessing divergent coordinating groups. Another appealing feature characteristic to this class of materials is their crystallinity, which allows for their precise structural characterization by diffraction methods, thus facilitating their rational design and the formulation of structure/property relationships. Furthermore, the ability to readily modify the linkers by employing the power of organic synthesis is another great advantage over purely inorganic materials. While the initial focus in this area was the synthesis and structural characterization, an increasing number of MOFs is now being explored for many potentially useful properties, which may very soon lead to commercial applications.[2] One of the early recognized functionalities in MOFs was their anion-exchange ability, particularly for cationic frameworks made from neutral organic linkers, which intrinsically include charge-balancing anions. Since the first reported example

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of anion exchange in an MOF,[3] further examples of coordination frameworks with anion-exchange properties have been studied, revealing that the environment around the bound anions can vary considerably. It occurred to us to ask whether it was possible to identify systematic structural features that could in turn be related to selectivity in anion exchange. As selectivity is essential to any chemical separation process, a detailed understanding of the factors governing anion selectivity in MOFs is of paramount importance if this class of materials is to be successfully utilized in anion-separation applications. The primary scope of this review article is therefore to provide a concise summary of the progress in this area, including recent contributions from our own research, with a special emphasis on factors relating to anion selectivity. Toward this end, we found it helpful to draw comparisons to selectivity principles applicable to anion separation in molecular separation systems, where the basis for selectivity is better understood and somewhat simpler. Accordingly, in the following section on fundamentals of anion selectivity and separation, a general strategy is proposed for obtaining selectivity by design to overcome the dominant solvation-based Hofmeister bias that otherwise favors hydrophobic, charge-diffuse anions. Specific examples of anion exchange and separations with MOFs are then presented, which are organized around the main interactions between the anions and the coordination frameworks. Finally, the current status of the field is summarized at the end of the paper, emphasizing its outstanding challenges and suggesting future research directions.

2. Fundamentals of Anion Separations

Selectivity Patterns in Separations

Selectivity may be classified as monotonic, step, peak, or some combination thereof in the separation of a related group of species. Within the unified theory of separations,[4] a separation is effected by a driving force acting unequally on species having different properties. Monotonic selectivity, which has been referred to as bias,[5] simply follows a steadily increasing or decreasing trend according to some varying property within the family of interest. Step or threshold phenomena occur when a limit or discontinuity is reached. Peak selectivity follows from recognition due to complementary bonding interactions. Each of these selectivity types has its uses, and one is better than another only in the context of the economics of the intended use. Hence, inferior selectivity is often tolerated in practice except under demanding circumstances where, for example, one is faced with high concentrations of competing species, high purity requirements, or very expensive footprint costs. Given that separation problems from such arenas as pharmaceuticals, metal recycling, electronics materials, environmental cleanup, nuclear-waste treatment, or nuclear reprocessing are increasingly demanding, the need for new separation systems exhibiting peak selectivity is growing.

Toward understanding principles of anion selectivity in MOFs, we focus in this section on origins of selectivity in molecular systems. This approach presupposes that bonding interactions underlie selectivity generally, and thus, the interactions found in molecular systems should be discernible in MOFs, subject to additional lattice considerations present in the solid state. Although the growing literature on anion recognition[6] has emphasized complexation in homogeneous media, it is of greatest interest in separations to examine partitioning processes, wherein interactions in the receiving phase are played-off against the strong energy requirement of the initial step of anion dehydration. By extension, an MOF would be the receiving phase of interest in the latter part of this review. The present section will begin with the examination of solvation-based selectivity, in which the receiving phase is a fluid environment that may freely reoptimize interactions about any given extracted anion. The discussion will then turn to the effects of single-point interactions in the receiving phase and finally to the effects of multi-point interactions presented by structured host environments. In a broad sense, interactions in the receiving phase may be controlled in their degree of electrostatic or covalent character and associated degree of structural constraint. The net effect is to control the steepness and sign of monotonic selectivity or, more interestingly, to effect sharp departures giving rise to step or peak selectivity.

Hofmeister Effects on Selectivity

Almost 12 decades ago, Franz Hofmeister noted a particular ordering of anions in the ability of salts of a common cation to precipitate egg-white globulin.[7,8] The original ordering from this work was:

Sulfate > Phosphate* > Acetate > Citrate > Tartrate > Hydrogen carbonate > Chromate ≈ Chloride > Nitrate > Chlorate

(*tabulated by Hofmeister as phosphate but considered by him to be the monohydrogen phosphate dianion)

Hofmeister's key conclusion was that the effectiveness of the salts in precipitating the egg-white globulin increases with "their water attracting capacity." Because ion hydration is so strong and dominates in many chemical phenomena, it is not surprising that the "Hofmeister order" or variations of it have been broadly observed.[9–11] Indeed, a recent conference has been devoted to Hofmeister effects.[12] These phenomena have been divided into those that deal with bulk hydration or activity coefficients (Hofmeister's water-attracting capacity) and those involved with specific ion adsorption or surface effects (binding, partitioning, electrical double-layer, Donnan, etc.).[10] Because Hofmeister effects generally operate in complex systems, where the net observable properties arise from a combination of effects, there are often exceptions to the original order, as even noted immediately by Hofmeister himself.[13] Not surprisingly, the literature gives many variants of the Hofmeister order that include other anions, reversals of positions of certain anions in the order, and even complete reversal of the entire order. However, references to the "Hofmeister order" most often mirror the order of decreasing anion hydration energy or charge density.

Remarkably, the original observations of Hofmeister provide a useful starting point in interpreting the properties of MOFs that ultimately give rise to anion selectivity in crystallization. Given that the Hofmeister order is rather ubiquitous as a selectivity pattern in separations,[5] our premise is that controlling the binding environment of the anion within the MOF leads ultimately to controlled selectivity, especially selectivity that violates the Hofmeister order. We shall approach this question further below. At the outset, however, we recognize the importance of salting-out on solubility, expecting that the first role of Hofmeister effects on MOF solubility is to determine the solution-phase activity coefficients of dissolved MOF precursor components. By changing the anion in the solution phase, one in essence performs the classical Hofmeister experiment. The Hofmeister order would thus be expected on this basis. However, to the extent that one can control the aqueous-phase composition, one has some control over the salting effect in a given experiment. For example, one may employ low salt concentrations, where specific ion effects are minor. We will not concern ourselves further with this aspect of anion selectivity.

Solvation-Based Selectivity: Normal and Anti-Hofmeister Bias

Hofmeister effects have long been known in ion-partitioning processes, although not named as such until recently. The order of anion exchange in liquid/liquid systems typically obtained is:[5]

$PO_4^{3-} < CO_3^{2-} < SO_4^{2-} << Cl^- < Br^- < NO_3^- < SCN^- < I^- < ClO_4^-$

This order is preserved over many systems in which the receiving phase does not possess strong hydrogen-bond (H-bond) donors or other specific anion-binding sites, and for practical purposes, it is the Hofmeister order to which we will refer for anion partitioning. Its similarity with Hofmeister's original order[7] is evident. Many more anions can be added to this list according to criteria discussed below and in more detail elsewhere,[5] but such fine-tuning invariably produces exceptions from system to system. It may be noted that the order above is preserved in certain related anion-partitioning systems, such as anion-exchange resins[14] and liquid-membrane potentiometric sensors.[15] The literature on anion sensing by membrane electrodes is particularly abundant, explicitly recognizing the Hofmeister order as the order of potentiometric selectivity typically observed if no recognition agents are added.

In general, the Hofmeister order in liquid/liquid systems can be understood in straightforward manner as the dehydration of the anion and resolvation in the receiving phase.[5] In terms of standard Gibbs energies, we have $\Delta G_p° = \Delta G_S° - \Delta G_h°$, where subscripts p, S, and h refer to partitioning, solvation, and hydration, respectively. Table 1 gives a listing of selected $\Delta G_h°$ values and other data for a few anions of interest here,[16] presented in order of decreasing $\Delta G_h°$ and extractability.

Table 1. Ionic radii ($r_–$) and standard Gibbs energies of hydration ($\Delta G_h°$) and transfer ($\Delta G_{tr}°$) for representative anions.[a]

Anion	$r_–$ [nm]	$\Delta G_h°$ [kJ/mol]	$\Delta G_{tr}°$ 1,2-DCE [kJ/mol]	$\Delta G_{tr}°$ TFE [kJ/mol]	$\Delta G_{tr}°$ MeOH [kJ/mol]	$\Delta G_{tr}°$ $PhNO_2$ [kJ/mol]	$\Delta G_{tr}°$ FA [kJ/mol]
Ph_4B^-	0.421	42	–33		–24	–36	–24
Pic^-	0.329	–197	4		–6	–3	–7
ClO_4^-	0.225	–214	17	–3	6	10	–12
TcO_4^-	0.250	–251	15		6	5	–2
$CF_3SO_3^-$	0.230		20				
I^-	0.220	–275	25	–2	7	18	7
SCN^-	0.209	–280	19		6	16	7
ClO_3^-	0.208	–287	37			26	
N_3^-	0.180	–287			9		11
CN^-	0.187	–305	41		9	38	13
NO_3^-	0.200	–306	32		13	24	
Br^-	0.196	–321	38	–3	11	29	11
NO_2^-	0.187	–339					
Cl^-	0.181	–347	52	–6	13	35	14
HCO_3^-	0.207	–368					
OAc^-	0.194	–373	58		16		20
OH^-	0.152	–439					
F^-	0.126	–472	65		16	70	25
HPO_4^{2-}	0.200						
CrO_4^{2-}	0.229	–958					
SO_4^{2-}	0.218	–1090			31		
CO_3^{2-}	0.189	–1315					
PO_4^{3-}	0.230	–2773					

[a] Values of $\Delta G_{tr}°$ are given in kJ/mol relative to the tetraphenylarsonium tetraphenylborate extrathermodynamic assumption at 25 °C. Abbreviations: 1,2-DCE: 1,2-dichloroethane; $PhNO_2$: nitrobenzene; CH_3CN: acetonitrile; FA: formamide; MeOH: methanol; TFE: 2,2,2-trifluoroethanol. Data taken from compilations[16–18] and published results.[19]

It may be seen at once that the $\Delta G_h°$ values approximately follow Hofmeister's original order, the greater hydration corresponding to the greater protein precipitation ability. Further, the $\Delta G_h°$ values decrease with increasing charge density, as the $\Delta G_h°$ values are nearly proportional to $-Z^2/r_–$ (where Z is the charge and $r_–$ is the thermochemical radius). Further, except for tetraphenylborate, $\Delta G_h°$ values are negative and large. In the present context of anion extraction, anion hydration thus resists extraction, and for anions smaller than perchlorate, the Gibbs energy of hydration is typically not fully recovered in transfer to other solvents (positive $\Delta G_{tr}°$, where transfer refers to pure solvents, as opposed to mutually saturated in the case of partitioning). Thus, transfer for these ions is not favorable and requires an additional driving force to occur (e.g., cation co-extraction, binding, or ion-pairing). However, the values of $\Delta G_{tr}°$ approximately follow the same order as the values of $\Delta G_h°$, implying that hydration and solvation roughly follow the same order. The obtained Hofmeister behavior in partitioning thus corresponds to extraction strength increasing in order of decreasing anion hydration Gibbs energy. We have referred to such behavior as "Hofmeister bias"[20] or *normal Hofmeister* selectivity. As shown below, it is in principle (if not in the exceptional actual example) possible to reverse Hofmeister bias in anion extraction if the solvent is capable of exceeding the solvation of the ion in water. In this case, we may expect *anti-Hofmeister* behavior. By contrast, an ordering in which certain anions are displaced from Hofmeister bias or its reverse would be referred to as *non-Hofmeister* behavior.

To illustrate the major factors underlying anion selectivity in anion transfer, Figure 1 shows several plots of $\Delta G_{tr}°$ for a series of anions vs. $1/r_-$ for a range of solvents. Over a fairly substantial range of anion radii (0.133 nm for F^- to 0.421 nm for Ph_4B^-), it may be seen that, within some degree of scatter, extractability approximately increases with increasing anion radius for a given solvent. The scatter may be attributed in part to the nonspherical geometries for the eight nonhalide anions and overall varied nature of their properties (e.g., polarizability). As the anion radius increases, cavity formation begins to play a dominant role, because of the high cohesive energy density of water compared with organic solvents.[21] Cavity formation is an energetic cost or repulsive effect that has been related to the enthalpy of vaporization as the measure of difficulty in breaking solvent intermolecular interactions. In an extraction system with water as the starting phase, the effect is to repel the species into the receiving phase according to the molar volume of the species. Hence, as anion radii become larger than approximately perchlorate (r_- = 0.240 nm), the transfer apparently becomes favorable owing to the increasing dominance of the cavity-formation term of the ion-transfer process. In general, the plots are not linear, as they bend over to varying degrees, though they are often treated as linear, when the hydrophobic (significant cavity-formation term) anions like picrate and Ph_4B^- are omitted. It may be noted that acetonitrile, nitrobenzene, and 1,2-dichloroethylene have closely overlapping plots. In fact, one may find that analogous plots for other chemically diverse polar solvents fall about this band, provided that they do not have a strong H-bond donor ability ($\alpha < 0.5$, where α is the Kamlet–Taft solvatochromic H-bond parameter[22]). One may see that the exceptions are small-molecule solvents that are strong H-bond donors (formamide: $\alpha = 0.71$; methanol: $\alpha = 0.93$; 2,2,2-trifluoroethanol: $\alpha = 1.51$). In other words, these are solvents that can efficiently replace the H-bonds lost in the dehydration part of the transfer process. The H-bond donor ability clearly plays a dominant role. In fact, in a statistical analysis of ion transfer Gibbs energies, it was noted that the solvent H-bond donor ability is the major solvent property governing the magnitude of $\Delta G_{tr}°$.[23] Remarkably, the loss of bias with increasing α reaches such a degree with 2,2,2-trifluoroethanol that the trend apparently reverses, fluoride ion being transferred slightly more favorably than the other halides. Thus, where anion hydration for anions smaller than perchlorate is generally not fully recovered on resolvation, in the case of the very strong H-bond donor solvents like 2,2,2-trifluoroethanol, the resolvation slightly overcompensates the loss of hydration. An example of this principle at work in favoring fluoride over the larger halides using a phenol as solvent has been reported.[24]

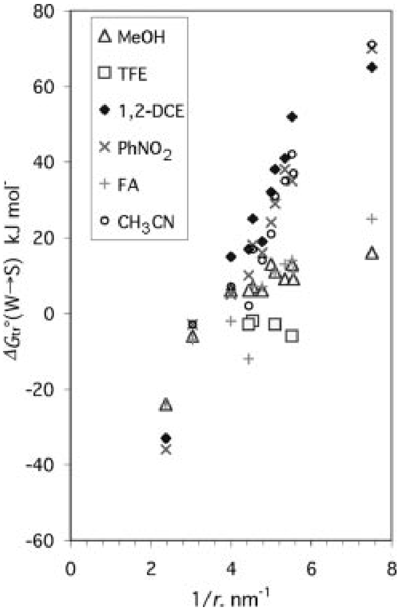

Figure 1. Standard Gibbs energies of transfer for univalent anions from water to organic solvents as a function of reciprocal anion thermochemical radius. Values of $\Delta G_{tr}°$ are given in kJ/mol relative to the tetraphenylarsonium tetraphenylborate extrathermodynamic assumption at 25 °C. Abbreviations: 1,2-DCE: 1,2-dichloroethane; $PhNO_2$: nitrobenzene; CH_3CN: acetonitrile; FA: formamide; MeOH: methanol; TFE: 2,2,2-trifluoroethanol. Data taken from compilations.[16–18]

To summarize monotonic anion selectivity, the process of anion transfer is strongly biased toward larger, charge-diffuse anions. This Hofmeister bias may be manipulated by varying the H-bond donor ability of the solvent and to a lesser extent by varying the size of the H-bond donor molecules, that is, the presumed number of H-bonds that the solvent can provide to a given anion based on packing considerations. The smaller the anion, the larger the effect. The trend can be reversed in principle by employing small, very strong H-bond donors as solvent molecules. For anions larger than perchlorate, cavity formation (lipophilicity) becomes dominant, and anion selectivity in this class becomes insensitive to H-bond donor ability. We will henceforth in this review interest ourselves in anions smaller than perchlorate as a class and refer to them without further distinction.

Overcoming the Hofmeister Bias

A Qualitative Model

Now that the Hofmeister bias has been seen to arise in solvation phenomena, we can begin to devise strategies to overcome it toward obtaining selectivity patterns of our own design. To organize our thinking in this regard, we have devized a qualitative model based on established foundational concepts in supramolecular chemistry[25] and bonding in coordination chemistry.[26] The model is shown in Figure 2. The diagram shows regions corresponding to normal-Hofmeister, anti-Hofmeister, and non-Hofmeister selectivity.

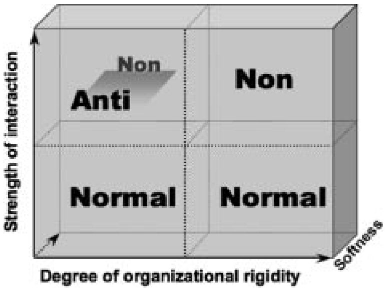

Figure 2. Selectivity in anion separation. The descriptors in the boxes refer to whether normal-Hofmeister, anti-Hofmeister, or non-Hofmeister selectivity is obtained.

It was seen above that the steepness and sign of the Hofmeister bias was controlled mainly by the strength of a primarily electrostatic interaction, H-bonding. Accordingly, as the *number* and *strength* of these individual interactions[25d] between solvent molecules and a given anion increase, normal Hofmeister bias decreases and then, in principle, reverses. Focusing for the moment only on H-bonding interactions, it is clear that the *total* strength of the interaction of the anion with its environment increases with increasing *complementarity*[25a,25c] between the arrangement of H-bonds donated by surrounding molecules and the receptor sites of the anion. However, solvent molecules are at best weakly constrained in their ability to assemble about the anion. Within their own steric constraints and thermal motion, they are free to maximize the net interaction with the anion and with themselves to come to a minimum Gibbs energy condition. If the anion is replaced with another anion, the solvent molecules will be able to move about to accommodate the new anion, again maximizing the total interaction. Thus, we have captured the concept of total interaction strength in the vertical axis in Figure 2, where H-bonding and other interactions can be manipulated subject to our own design. If the interactions are electrostatic and unconstrained, as in fluid systems, the effect is to produce either normal- or anti-Hofmeister selectivity.

To obtain non-Hofmeister selectivity, it is logical either to employ non-electrostatic interactions or to constrain the spatial arrangement of interacting groups or atoms about the anion. In any case, no strategy can succeed in this regard using only weak interactions, because of the steepness of the Z^2/r_- dependence. Thus, the lower regions of Figure 2 are the domain of normal Hofmeister selectivity. Most strategies for anion binding today employ H-bonding or other electrostatic interactions as the basis for recognition, and normal Hofmeister bias still tends to be commonly observed, leading us to conclude that systems so far investigated for separations often lack sufficiently strong and structurally constrained H-bond donor groups. The *affinity/selectivity* principle recently put forth[27] leads to the expectation that the greatest selectivity will occur with stronger interactions, which will magnify differences in the ability of a given host to accommodate anions of different size or structure. With a sufficiently strong total interaction with a given anion, implying strong individual interactions and with high overall complementarity, it is expected that peak selectivity for that anion will arise when the structure of the host environment is unable to rearrange to accommodate other anions. For molecular hosts, the familiar term *preorganization*[25b] embodies this concept, but this term loses meaning for self-assembled hosts that form in situ in the presence of the guests. Instead, we chose the term *organizational rigidity* for the horizontal axis in Figure 2, to capture both the concept of rigidity, meaning that the crystal lattice is unable to expand or contract, and structural uniqueness, meaning there is only one favorable way to assemble the subunits of the host framework.

The third axis in Figure 2 allows the introduction of a degree of softness or covalency into the interaction of donor groups with the anion. Given that the Hofmeister bias rests on the strength of electrostatic interactions, primarily H-bonding, then soft Lewis acid/base interactions[26] should lead to peak selectivity for soft or polarizable anions. This should be true even if the soft Lewis acid sites are not constrained in space.

In section 3 of this article, we try to make some comparisons of the above-presented model with literature observations as a way to test our thinking and to look for ways to escape the Hofmeister bias in anion separations. We believe the model is useful in describing three orthogonal concepts, that of total binding strength (embodying the concept of complementarity), organizational rigidity, and softness. However, the model is meant only to be a qualitative guide, with no fixed divisions between resultant selectivity patterns. Moreover, there are obvious limits to be encountered. For example, H-bond donor groups should not be so strong that proton-transfer processes occur, leading to considerations beyond this discussion. In addition, one does not desire to employ covalent interactions to the degree that the guest anion is chemically transformed or that the binding becomes irreversible. Host/guest chemistry and separation chemistry share the general approach of using reversible, non-covalent interactions.

Single-Point Interactions

Toward ultimate shape selectivity that violates the Hofmeister bias in a separation, one must assemble groups in space that interact with an anion along defined vectors. Solid-state host assemblies like MOFs are well suited for this task, though most of the insight obtained thus far on anion recognition has emerged from studies of molecular systems in solution. From the literature on anion coordination chemistry, one can make use of H-bonding, coulombic, Lewis acid/base, van der Waals, hydrophobic, and other interactions.[28,29] Let us first examine selectivity inherent in certain single-point interactions that must ultimately be assembled in the complete host/guest supramolecular structure.

Coulombic interactions are anti-Hofmeister and will therefore influence bias. Whereas solvation involves the idealized lone ion surrounded by solvent molecules, real separation systems involve interactions with counterions. These can be incorporated into receptor design itself[25a,28,29] but otherwise must still be allowed for as one of the governing factors in the resultant selectivity obtained. Viewing extraction as a step-wise process, the first step can be taken as ion partitioning followed by other interactions, which include ion-pairing or coordination. Ion-pairing usually favors small anions for a given cation, and this interaction opposes Hofmeister bias.[5] However, for univalent ions, ion-pairing is generally a weaker influence on selectivity as compared with solvation, and thus, Hofmeister bias persists, albeit attenuated. A prime example is the use of lipophilic quaternary ammonium salts as liquid/liquid anion exchangers, and the selectivity is also seen in strong-base anion-exchange resins.[5,14] It has been seen that the size of the cation determines the steepness of the bias, smaller quaternary ammonium cations possessing smaller alkyl chains, giving larger attenuation of Hofmeister bias.

More generally, coordination of anions with Lewis acid sites allows wide latitude in obtaining desired selectivity, leading to potential departures from Hofmeister bias selectivity. Such interactions may be treated as coordination or ion-pairing phenomena as appropriate, but in general the effect on selectivity derives from the bonding interaction with the Lewis acid site. Accordingly, the hard/soft acid/base concept[26] lends itself well in manipulating selectivity. Because the origin of Hofmeister behavior is so strongly influenced by the H-bonding ability of the solvating environment and because H-bonding is largely electrostatic, it may be expected that, constraining steric or multi-point (chelating) effects being absent, hard Lewis acid sites may tend to give rise to normal- or anti-Hofmeister bias. The hard/hard interaction itself tends to be anti-Hofmeister, the question being whether this effect is sufficiently strong to overcome the Hofmeister bias of the ion-partitioning step. If the charge on the hard Lewis acid site is not high, the strength of the coordination interaction is usually insufficient to reverse the Hofmeister bias of ion partitioning but only to attenuate it. This is typically the case with extraction of alkali and alkaline earth cations by crown ethers, which has been long known to follow the normal Hofmeister bias.[5,19,20,30] Accordingly, salts with charge-diffuse anions are easier to extract, implying that such anions (like perchlorate) would exchange for more hydrophilic ones (like nitrate or chloride) associated with the organic-phase crown ether complex of the extracted metal cation. This bias has been used to advantage to extract sodium pertechnetate from nuclear waste (high in nitrate), for example.[31,32] It should be pointed out that the actual coordination of the anion to Lewis acid centers in solution in most cases is not confirmed, and it is possible that the anion interacts through a mediating water molecule or outer-sphere ion-pairing.

As the charge of the Lewis acid site increases, it is indeed found that the Hofmeister bias can be disturbed or reversed in accordance with a strong hard/hard interaction, though steric influences are typically present. Thus, an enhanced fluoride selectivity is often observed, and the selectivity may overall be non- vs. anti-Hofmeister. Examples are known in which sorbent materials containing higher-charged metals like Fe^{III} and Zr^{IV} prefer small, hydrophilic anions.[33,34] In liquid/liquid extraction and transport, a (salen)Mn^{III}-type complex and a neutral tetraaza-macrocyclic Ni^{II} complex were observed to have enhanced fluoride selectivity.[35] In transport using these respective carriers, the following orders were found: $F^- > Br^- > Cl^- > NO_3^-$ and $Cl^- > F^- > NO_3^- > Br^-$, while in extraction, the Mn^{III} complex gave the order $Br^- > NO_3^- > F^-$ and the Ni^{II} complex detectably extracted only F^-. Neutral tris(β-diketonato) complexes of lanthanides transport Cl^- faster than Br^-, I^-, and even ClO_4^-.[36]

The use of Lewis acid sites for selective anion binding has been under investigation for development of potentiometric anion sensors, providing insight into anion-binding selectivity in ion partitioning. Typical membrane electrodes employ a polymer membrane, such as poly(vinyl chloride), containing a plasticizer, solvating additives, quaternary ammonium anion exchanger, and possibly an ion receptor. Without an anion receptor, the normal Hofmeister order of electrode selectivity is obtained in accordance with a governing solvation principle.[15,37] Added Lewis acid anion receptors yield selectivity patterns violating the normal Hofmeister order. Metalloporphyrins[38] and phthalocyanates[39] yield varied responses depending on the bound metal ion. With hard metal ions like Zr^{IV},[38b] Lu^{III},[38c] and Al^{III},[39] it is typical for the F^- response to be enhanced relative to the other anions, which still tend to follow the Hofmeister order. Fluoride and thiocyanate are even selected in preference to perchlorate using (octaethylporphyrin)Zr^{IV}.[38b] With (octaethylporphyrin)In^{III}, a striking rejection of nitrate and perchlorate in favor of thiocyanate and iodide was obtained in electrodes designed for salicylate response.[38a] Other types of Lewis acid receptors have also yielded non-Hofmeister selectivity in membrane electrodes. Thiocyanate selectivity has been obtained using a (Schiff base)Cd complex[40] and triphenyltin chloride.[41] Iodide selectivity was achieved with a lipophilic Hg^{II} complex.[42] A remarkable non-Hofmeister selectivity was obtained with certain organodifluorotin(IV) compounds, giving the order: $F^- > CH_3COO^- > Cl^- > I^- \approx Br^- > ClO_4^- > NO_2^- > NO_3^- > SCN^-$.[43]

Multipoint Recognition

Researchers have taken an active interest in finding synthetic molecular receptors that violate Hofmeister behavior in separations by use of constrained multipoint binding interactions. Despite the considerable challenge posed by the steep bias in ion partitioning (Z^2/r_- dependence),[44] the progress made so far indicates that a combination of sufficiently strong and structurally constrained binding sites on the host can succeed in this regard. Starting with less effective systems, the bidentate H-bond donors that have been examined appear to be too weak with respect to H-bond strength or rigidity to effect significant departures from Hofmeister bias. In that the anions are still largely open to the influence of solvation, overall complementarity is low, and the affinity/selectivity principle[27] would imply only perturbation or attenuation of Hofmeister bias. These near-normal Hofmeister systems thus lie in the lower left box in the selectivity model shown in Figure 2. Examples in liquid/liquid extraction include diphenylurea[45] and *m*-diphenyldisulfonamides,[20,46] though peak selectivity for iodide has been claimed for monothiouronium receptors.[47] Receptors offering four or more H-bonds on flexible arms show greater signs of disrupting the expected Hofmeister order. However, typically the charge-diffuse anions like ClO_4^-, I^-, and SCN^- are still favored, and non-Hofmeister behavior tends to take the form of enhancements for certain anions or switched preferences within the series. Even with a rigid steroidal platform supporting two or three arms, "cholapod" receptors with varied H-bond donor functionalities (imide, amide, carbamate, urea, thiourea, and sulfonamide) still basically follow near-normal Hofmeister behavior in liquid/liquid extraction.[27,48] Tris- and tetrakis(amide) receptors employing polyaza-macrocycle platforms exhibited normal Hofmeister bias in transport.[34] Evaluated in ion-selective electrodes, this group also includes iodide-selective bis(thiouronium) receptors,[47] tripodal tris(ureas) with enhanced sulfate sensitivity,[49] and bis(thiourea) receptors employing a rigid steroidal platform also with enhanced sulfate sensitivity.[50]

The greatest degree of success in achieving non-Hofmeister behavior (upper right box in Figure 2) has involved macrocyclic geometries in which H-bond donor functionalities are constrained as part of the ring structure and also systems employing Lewis acid binding sites. An elegant demonstration of the macrocyclic effect on extraction selectivity was obtained by cyclization of two urea arms on a steroid platform, whereupon the nearly normal Hofmeister behavior of the uncyclized analog was transformed in the most striking case to the non-Hofmeister ordering: $Br^- > I^- \approx Cl^- > NO_3^- > PF_6^- > CH_3COO^- \approx EtSO_3^-$.[51] The selectivity order depended upon the link used in the cyclization. Fluorinated calixpyrroles featuring strong H-bond donation and the constraints of macrocyclic geometry exhibit non-Hofmeister behavior in liquid/liquid extraction.[52] Orders observed for the octafluorocalix[4]pyrrole and the decafluorocalix[5]pyrrole differed as follows: $ClO_4^- > I^- \approx Br^- \approx Cl^- > NO_3^- > F^-$ and $ClO_4^- > I^- \approx NO_3^- > F^- > Br^- > Cl^-$, respectively. Interestingly, the selectivity order for calix[4]pyrrole is anti-Hofmeister: $HPO_4^{2-} \approx F^- \approx OH^- > Cl^- > Br^-$.[53]

Receptors containing metal cations as well as H-bond donor groups offer the potential for anion/metal interaction and greater encapsulation of the anion, and the metal complexation can also serve to organize the anion-binding groups. Only a limited number of systems have been studied in extractive separations; (salophene)uranyl receptors bearing two sulfonamide sidearms were shown to be selective carriers for $H_2PO_4^-$ vs. Cl^-, the latter being the anion preferred by solvation effects alone.[54] A salicylaldoxime complex of Ni^{II} exhibits the normal Hofmeister Cl^-/SO_4^{2-} selectivity in transport experiments in which protonation of amine-containing sidearms provides both cationic and H-bond donor sites.[55] The metal ion serves only to organize the sidearms rather than serve as an anion-coordination site. Normal Hofmeister selectivity ($I^- > Br^- > Cl^-$) was also observed in transport of alkali metal salts by macrobicyclic receptors in which the two N atoms of the crown ether diaza-18-crown-6 are bridged by isophthalamide-type bridges capable of donating two H-bonds.[56] In this case, mild cation/anion interaction and structural constraints suffice only to attenuate the normal Hofmeister order. Selective transport of Cl^- over other halide ions was observed with transition-metal-containing resorcinarenes bearing bis(pyridylmethyl)amine sidearms for metal-ion binding.[57]

3. Anion Separation with Metal–Organic Frameworks

Conceptually, we pose the question as to whether a strategy can be devized for obtaining separation selectivity by design in MOFs by taking some lessons learned from the study of molecular systems as discussed above and as illustrated in Figure 2. Quite simply, we are led to expect that normal Hofmeister selectivity will arise from H-bonding or other interactions involving the anion in the receiving-phase (MOF) environment that are weaker than those in water. Stronger H-bonding or other interactions that could compensate for anion dehydration would lead to anti- or non-Hofmeister behavior depending on the softness of the host binding sites and the degree of organizational rigidity of the MOF. In particular, MOFs offer the potential to achieve the extreme organizational rigidity that has been so elusive in molecular hosts. Provided that the included anions interact sufficiently strongly with surrounding groups within the MOF, which requires a high degree of complementarity between the binding sites of the guest anion and the host MOF, it should therefore be possible to approach perfect peak selectivity with total exclusion of all but the target anion. This ideal condition leads to non-Hofmeister selectivity in the upper right quadrant of Figure 2. If there are multiple ways to assemble the MOF to accommodate different anions or if the unit-cell parameters are adjustable, then the resulting lower degree of organizational rigidity would lead leftward in the diagram in Figure 2 toward anti- or non-Hofmeister behavior depending on the softness of the individual binding interactions. Regarding the lower right quadrant of the diagram, a question remains as to whether a rigid MOF with little or no ability to donate H-bonds would exhibit step or threshold selectivity. This may be true, as we suspect it is for molecular systems, but among the anions below the size threshold that could fit inside the MOF cavities, the larger, poorly hydrated anions would still be preferred, which is in effect Hofmeister behavior. The size cut-off effect may also apply to less rigid frameworks, as the crystal lattice can only expand to the point that the intermolecular interactions that insure the crystal cohesion become too weak relative to the solvation of the MOF components, which would lead to crystal dissolution. Alternatively, if anion binding represents a significant portion of the total lattice energy, the MOF crystal may only form with those anions whose interaction energies exceed a certain threshold, which would also lead to step selectivity.

An important issue with direct implications on how one can best approach the anion separation with MOFs is the anion-exchange mechanism in this class of materials. Figure 3 depicts the two mechanisms generally expected for anion exchange in MOFs. The early studies almost universally assumed a solid-state exchange mechanism, similar to those found in ion-exchange resins or zeolites, which occurs by diffusion of the ions in and out of the crystals with preservation of the structural integrity of the coordination network. This assumption was generally based on the observation that MOFs have very low solubility in most solvents, and, in some cases, on the structural similarities between the initial and final frameworks. However, a recent study by the groups of Champness and Schröder challenged this commonly accepted view, and demonstrated without equivoque that, at least in certain one-dimensional coordination polymers, the apparent anion exchange from water is solvent-mediated, involving dissolution and recrystallization of the MOF crystals.[58,59] This process is driven by the difference in solubility between the initial and final MOF phases, and does not require substantial water solubilities. In fact, anion exchange by dissolution/recrystallization has long been known in simple inorganic salts. For example, silver chloride, which for all practical purposes is considered water-insoluble, exchanges 90% of Cl^- by I^- within minutes, a process that is driven by the even smaller solubility of AgI in water. This process was exploited for the recovery of radioactive iodide from fission products.[60]

Although the dissolution/recrystallization appears the most likely mechanism for anion exchange from water, we cannot completely rule out the possibility that the anion exchange may occur by a solid-state exchange mechanism in some cases, or a combination of the two mechanisms. Such a scenario, however, requires that the anion diffusion through the coordination network be fast enough to compete with the dissolution/recrystallization process. To the best of our knowledge, no solid-state anion-exchange mechanism has been unequivocally demonstrated for any MOF to date.[61]

We have recently articulated an alternative approach to anion separation that involves competitive crystallization of the coordination networks.[62] This strategy differs from the traditional anion-exchange approach with the MOFs treated as separation agents, in that the crystallization process involved in the MOF synthesis is in itself exploited as a separation tool. More specifically, the MOF is competitively crystallized from a mixture of anions, which may result in the selective inclusion of certain anions depending on their size, shape, or specific interactions with the network. Such an approach avoids the common problem of slow ion-exchange kinetics in the solid state and broadens the applicability of MOFs to one of the commercially most important and economical separation technology, namely crystallization.

Whether the anion separation is realized by ion exchange, similarly to zeolites or ion-exchange resins, or by competitive crystallization, anion selectivity in MOFs is ultimately determined by the intermolecular interactions between the anion and the crystalline MOF matrix. It is therefore instructive to classify the MOFs that have relevance to anion exchange or separation based on the nature and

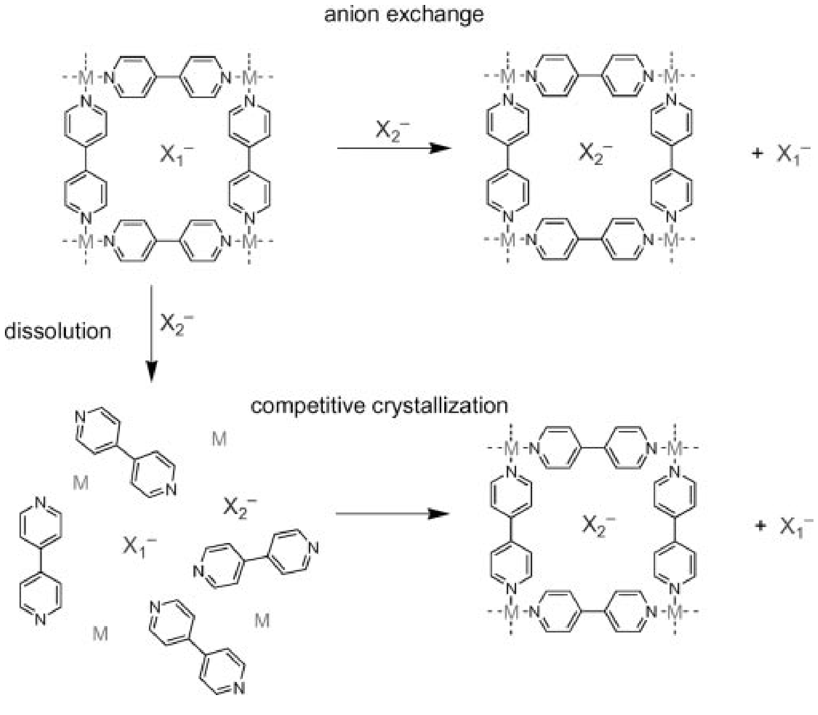

Figure 3. Generic representation of the two main mechanisms expected for anion exchange in MOFs.

strength of anion/framework interactions, and try to correlate these with the observed anion selectivities. Figure 4 illustrates the main types of interactions involving anions inside MOF crystals. The most common situation (case a) involves van der Waals interactions between the anion and the coordination network, with long-range coulombic interactions with the cationic framework additionally present. These interactions are typically too weak to overcome the solvation bias and thus lead to normal Hofmeister selectivity. A step (threshold) selectivity based on the anion size may nevertheless be expected, as too-large anions may not fit inside the MOF lattice and could therefore be excluded. The next case involves direct anion coordination to the metal centers in the network (case b). These Lewis acid/base interactions may partly compensate for the anion dehydration and thus attenuate the Hofmeister bias, or, if they are sufficiently strong, they may even reverse it (anti-Hofmeister selectivity). However, unless the MOF is organizationally rigid or unless the metal coordination sites are soft, peak selectivity (non-Hofmeister) is unlikely to be observed. Cases c and d involve specific hydrogen bonding or combinations of hydrogen bonding and metal coordination between the anion and the framework. These interactions may be very specific, and, as a function of their number and strength, may overcome the solvation bias resulting in

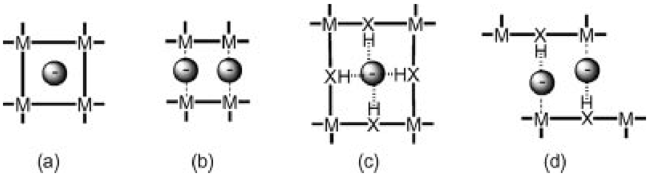

Figure 4. Typical intermolecular interactions involving anions inside MOFs. (a) van der Waals and coulombic; (b) metal coordination; (c) hydrogen bonding; (d) hydrogen bonding and metal coordination.

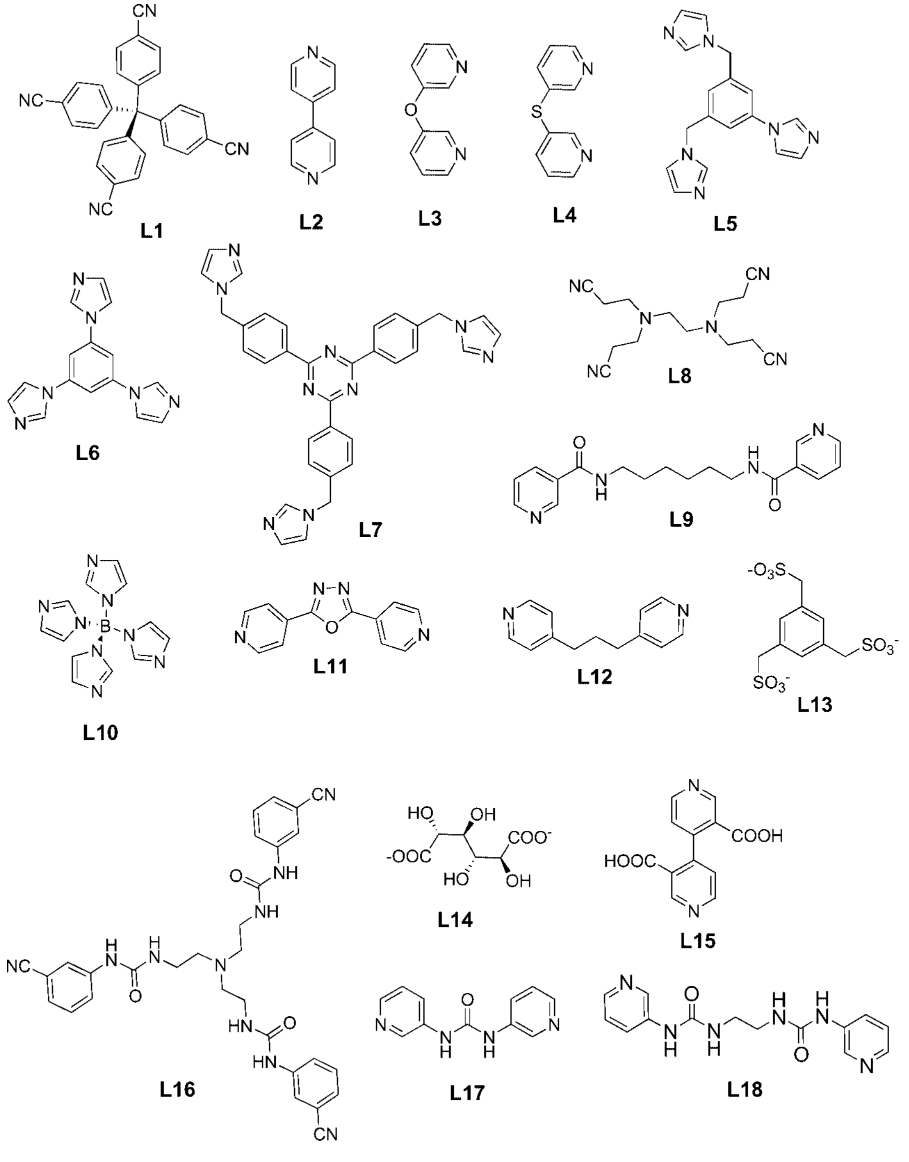

Figure 5. MOF linkers employed for anion exchange or separation.

either anti-Hofmeister or non-Hofmeister selectivities, depending on the rigidity of the framework.

In the following pages, specific examples of each class of anion interactions will be presented in the order of increasing binding strength, starting with nonspecific van der Waals interactions and moving towards more selective metal coordination and hydrogen-bonding interactions. Figure 5 lists the organic linkers involved in the MOFs discussed in this review.

Anion Inclusion by van der Waals and Coulombic Interactions

As most coordination solids reported in the literature are built from relatively large and nonpolar organic linkers (Figure 5), the resulting anion-binding sites are fairly hydrophobic, an environment not very different from those found in nonpolar organic solvents or ion-exchange resins. Anion inclusion selectivity in these solids is thus typically dominated by solvation effects, which results in Hofmeister bias, favoring larger, less hydrophilic anions such as ClO_4^- or PF_6^-.

One of the first deliberately designed coordination networks, reported by Robson et al. in 1990,[3] was built from linker **L1** and Cu^I cations, which resulted in a 3D coordination framework with a diamondoid topology containing large pores filled with disordered solvent and BF_4^- counteranions. The BF_4^- anions could be easily exchanged with PF_6^-, but the reversibility and selectivity of the exchange was not reported. Five years later, Yaghi et al. reported another 3D coordination framework of Cu^I with **L2**, which included hydrated NO_3^- as counteranion. The disordered nitrate anions were loosely bound inside the channels, and could be easily exchanged in aqueous media by either hydrophobic BF_4^-, or hydrophilic SO_4^{2-}. The anion-exchange selectivity was, however, not addressed in this study.[63] When $NiClO_4$ was used with the same linker, a different coordination framework was obtained, which displayed a 1D railroad topology that included large channels filled with additional linker molecules, water solvent, and perchlorate anions. The anions were once again disordered, indicating weak interaction with the channel walls. Removal of the water solvent from the channels further increased the mobility of the perchlorate anions, which could be easily exchanged with PF_6^-.[64]

An interesting series of coordination polymers was reported by Jung et al., who used linker **L3** with various silver salts AgX (X = NO_3^-, BF_4^-, ClO_4^-, and PF_6^-) to assemble 1D helical coordination frameworks that included the anions inside the cationic cylindrical channels created inside the helices (Figure 6).[65] The coordination helices showed remarkable flexibility, adjusting their helical pitch to the size of the anion, from 7.4 to 9.6 Å. The anions could be readily exchanged with each other, which can be explained by their nonspecific interactions with the hydrophobic channels, and the high flexibility of the helices. However, no anion-selectivity information was provided. When the analogous linker **L4** was used instead, similar coordination polymers with helical topology were obtained, which also displayed anion exchange abilities, with the large ClO_4^- and PF_6^- being preferred over the smaller NO_3^- or BF_4^- anions (Hofmeister selectivity).[66]

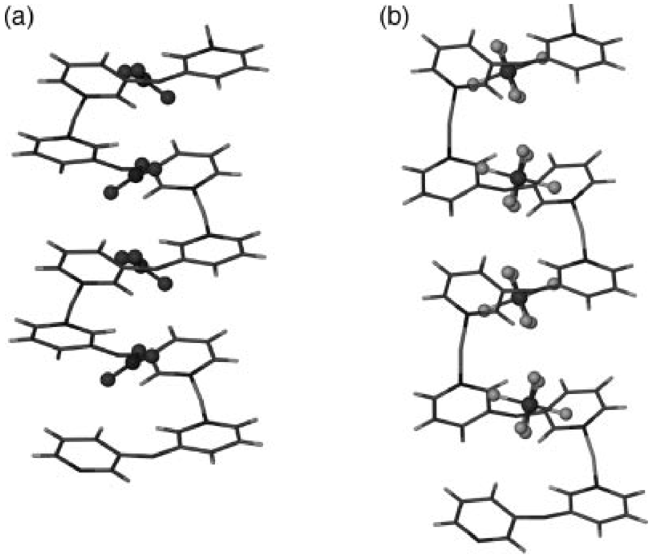

Figure 6. Crystal structures of [Ag(**L3**)]X showing helical coordination polymers (stick) with anions (ball-and-stick) included in the cylindrical channels inside helices: (a) X = NO_3^-; (b) X = PF_6^-.

A number of MOFs intercalating anions between hydrophobic 2D coordination layers have been reported. For example, Suh et al. described a series of Ag coordination polymers containing linker **L8**, and NO_3^-, ClO_4^-, and $CF_3SO_3^-$ anions, and reported their anion exchange properties.[67] The structures containing perchlorate or triflate displayed 2D coordination networks with the anions intercalated between the hydrophobic layers, while the structure containing the nitrate displayed 1D coordination chains, with the NO_3^- coordinating the silver cations (Figure 7). Pairwise anion exchange experiments showed Hofmeister selectivity with ClO_4^- being the most favored anion. Nitrate, on the other hand was favored over $CF_3SO_3^-$, which is a perturbation from the Hofmeister series, a fact that may be attributed to NO_3^- coordination to the Lewis acid Ag^+.

Sun et al. reported a series of layered cationic frameworks with anion exchange properties, containing linkers **L5**–**L7** coordinating various transition metals.[68] Figure 8 illustrates a typical example involving linker **L5** and $Cd(NO_3)_2$, with the nitrate anions and solvent water molecules occupying the space between the cationic Cd(**L5**)$_2$ layers.[68b] The nitrate anions could be completely exchanged by ClO_4^- with the formation of an isostructural coordination network, as found by powder X-ray diffraction and FTIR. The anion exchange was not completely reversible, as only about 50% of ClO_4^- could be exchanged with NO_3^-, indicating Hofmeister selectivity. The NO_2^- anion, on the other hand, could be reversibly exchanged with NO_3^-, apparently due to the more similar free energies of hydration of these two anions compared with the less hydrophilic ClO_4^-.

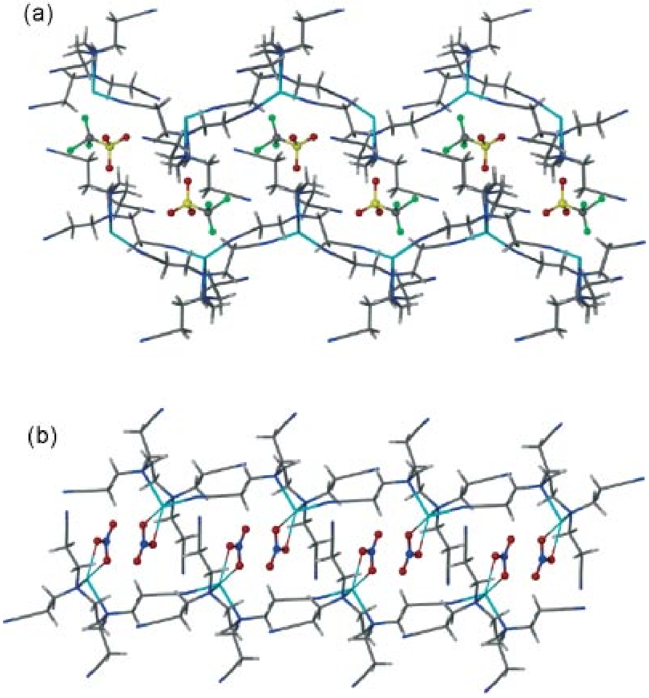

Figure 7. X-ray crystal structures of [Ag(**L8**)]X [X = $CF_3SO_3^-$ (a), NO_3^- (b)], showing the intercalation of the anions between hydrophobic layers (a) or chains (b). Coordination frameworks and anions are shown as stick and ball-and-stick models, respectively.

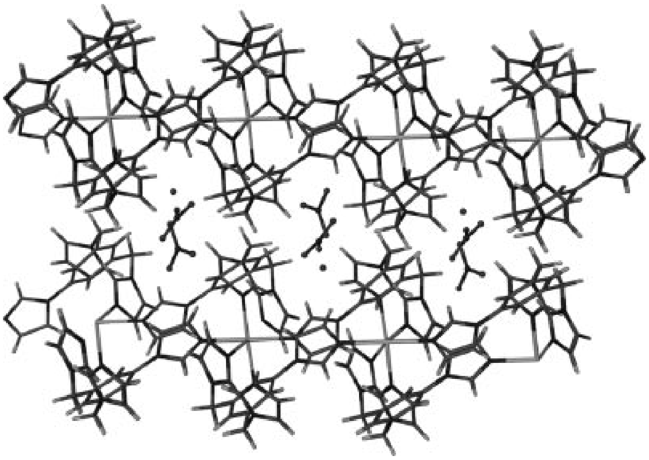

Figure 8. Crystal structure of $[Cd(\mathbf{L5})_2](NO_3)_2(H_2O)$ with the nitrate and water intercalated between coordination layers. Coordination framework and anions are shown as stick and ball-and-stick models, respectively.

An interesting case of anion selectivity was found by Kitagawa et al. in a coordination polymer obtained from **L2** and Cu^{2+} in the presence of an equimolar mixture of PF_6^- and ClO_4^- anions, which resulted in a 2D layered structure containing two types of channels, with the two anions included separately in each channel.[69] It is remarkable that despite the absence of any specific interactions between the anions and the coordination framework, the two anions were individually recognized by the two slightly different channels, which resulted in the separation of PF_6^- and ClO_4^-, albeit only on a molecular scale (Figure 9).

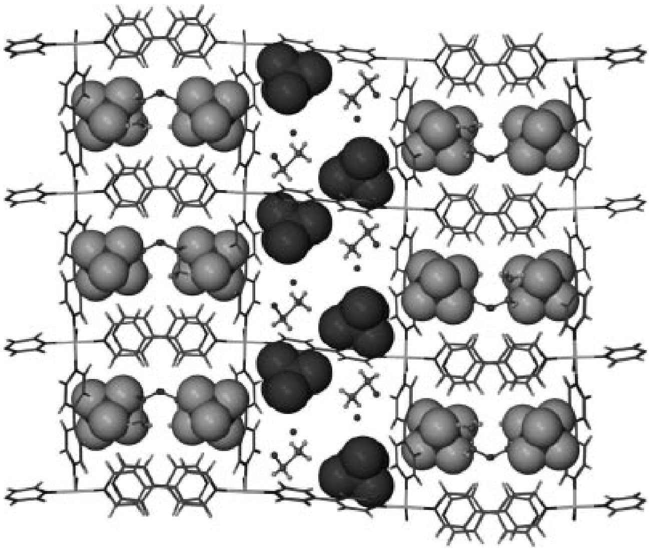

Figure 9. Crystal structure of $[Cu_2(\mathbf{L2})_5(H_2O)_4](ClO_4)_2(PF_6)_2(H_2O)_2$-$(EtOH)_4$ showing the segregation of ClO_4^- and PF_6^- in alternating channels. Coordination framework, anions, and solvent are depicted as stick, space-filling, and ball-and-stick models, respectively.

Anion Inclusion by Metal Coordination

Because most metal cations in MOFs have significant Lewis acidity, it is not uncommon for the metal nodes to serve as binding sites for the anions. Considering that these interactions may be relatively strong and directional, it can be anticipated that the presence of anion–metal coordination bonds could reverse the Hofmeister bias otherwise expected for anion exchange in hydrophobic MOFs. It should be kept in mind, however, that anion–metal coordination interactions do not operate alone in the crystal, and the ubiquitous van der Waals forces may remain in many cases the overall dominant interactions between the anion and the coordination framework, thus leading to Hofmeister selectivity. The same result should be expected if the anion is exposed to a significant degree to the water solvent present in the channels (poor complementarity).

An early example of exchange of an anion associated with a metal center in an MOF was reported by Yaghi et al.[70] Nitrate anions in $[Ag(\mathbf{L2})](NO_3)$ interact weakly with the silver nodes in this 3D coordination network, and can be exchanged reversibly by PF_6^-, MoO_4^-, BF_4^-, or SO_4^{2-}. However, since the structures of the resulting exchanged solids have not been elucidated, and competition experiments have not been reported, it is difficult to evaluate the anion selectivity of these MOFs.

An extensive anion exchange study in a series of coordination polymers with the general formula [Ag(**L9**)]X (X = ClO_4^-, NO_3^-, $CF_3SO_3^-$) was reported by Yip et al.[71] The linker connects the silver nodes into 1D coordination

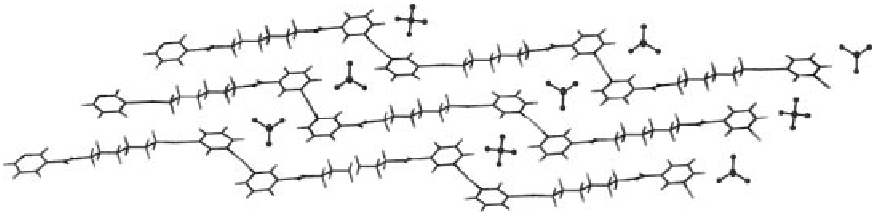

Figure 10. Crystal structure of [Ag(**L9**)](ClO$_4$) showing perchlorate anions intercalated between coordination layers and positioned within close proximity to the silver nodes. ClO$_4^-$ anions are disordered, and only one orientation is depicted for clarity. Coordination framework and anions are shown as stick and ball-and-stick models, respectively.

chains, which are further associated into layers by NH···O hydrogen bonds among the amide groups. The anions are weakly coordinated to the Ag cations and are located between the layers, with the perchlorate and nitrate anions displaying significant disorder (Figure 10). Despite the anions being coordinated to the Ag Lewis acid centers, these interactions were apparently not strong enough to completely overcome the anion solvation bias in this series of coordination polymers, as pairwise anion exchange experiments indicated the following selectivity: $ClO_4^- > NO_3^- > CF_3SO_3^-$. While the preference for perchlorate indicates Hofmeister behavior, the selectivity of NO_3^- over $CF_3SO_3^-$ represents a perturbation from the Hofmeister series, which may be the result of the stronger nitrate coordination to the Ag nodes.

Crystallization of **L2** and Cu^{2+} from an equimolar mixture of NO_3^- and PF_6^- resulted in the inclusion of both anions in a 1:3 ratio. The 2D square grids of the resulting coordination network are further linked in the third dimension by alternating NO_3^- and PF_6^-, with two additional PF_6^- anions being included inside the hydrophobic channels of the crystal (Figure 11). Attempts to co-include other anions such as BF_4^- or SO_4^{2-} failed, and only PF_6^- was included in the presence of these two anions. Thus, the more hydrophobic PF_6^- seems to be preferred by this coordination network, although the inclusion of NO_3^- but not of BF_4^- or SO_4^{2-} indicates peak selectivity.[69]

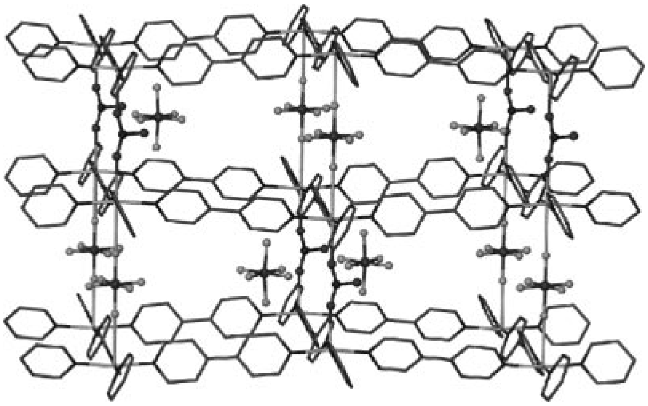

Figure 11. Crystal structure of [Cu$_2$(PF$_6$)(NO$_3$)(**L2**)$_4$](PF$_6$)$_2$(H$_2$O)$_2$ showing 2D Cu^{II} coordination grids connected by bridging NO_3^- and PF_6^- anions, and the inclusion of additional PF_6^- anions inside the channels. Included water solvent is not shown. Anions are depicted as ball-and-stick models and the framework as a stick model.

The anion selectivity in MOFs containing metal-binding sites can also be controlled by the match between the hardness or softness of the anion (Lewis base) and metal center (Lewis acid). For example, the 2D coordination network made from **L10** and soft Pb^{2+} Lewis acid metal centers can easily exchange nitrate with the softer iodide. The nitrate anions do not coordinate the metal nodes and occupy the interlayer space together with solvating water molecules. Upon exposure to an aqueous solution containing 1 molequiv. of KI, the nitrate could be completely exchanged with iodide, with the latter coordinating the Pb^{2+} Lewis acid centers (Figure 12).[72]

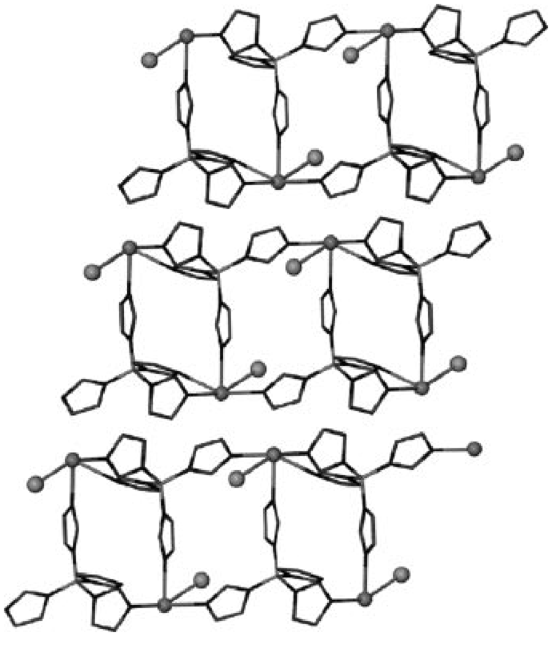

Figure 12. Crystal structure of [Pb(**L10**)]I showing a layered framework with the iodide anions coordinating the lead metal centers. The I$^-$ and Pb^{2+} are depicted as balls and **L10** is shown as a stick model.

A clear example of anti-Hofmeister selectivity was observed in the anion exchange in a series of MOFs built from **L11** and Cu^{2+}.[73] When PF_6^- and ClO_4^- were used as anions, two isostructural coordination networks with interpenetrated 3D diamondoid topologies were obtained, with the non-coordinating hexafluorophosphate or perchlorate anions and water solvent molecules occupying the pores. These anions could be irreversibly exchanged with the more hydrophilic N_3^- or SO_4^{2-} anions, with complete reorganization of the coordination networks. Figure 13 depicts the crystal structure of the sulfate-exchanged framework, which consists of layers of Cu^{2+} coordinated by μ_3-bridging sulfate anions, with the organic linkers connecting the inorganic layers. Apparently, the strong and specific coordinating bonds to the copper centers resulted in the sulfate anions being preferred against the weaker Lewis bases PF_6^- or ClO_4^-. However, since the two structures have completely different architectures (and therefore different stabilities), it is not clear to what extent the preference for sulfate can be attributed to its stronger Lewis basicity or to the inherent difference in stability between the two coordination networks.

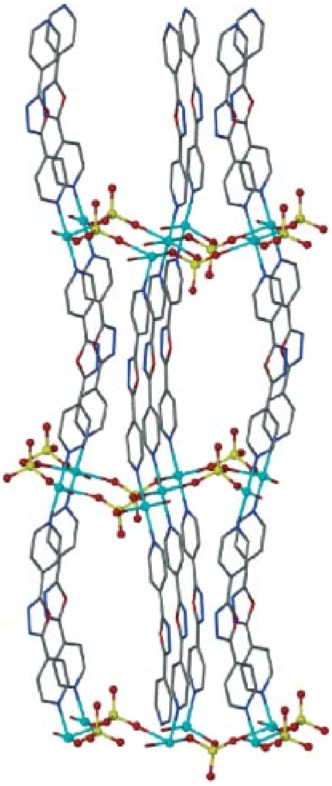

Figure 13. Structure of [Cu(**L11**)(H_2O)(SO_4)](H_2O)$_2$ showing Cu^{II}–SO_4 coordination layers connected by **L11** linkers into a 3D framework. The sulfate anions and the copper centers are depicted as ball-and-stick models and the linker is shown as a stick model. Water molecules included in the channels are not shown.

That the framework stability can decisively influence the anion exchange selectivity in MOFs was clearly demonstrated in the coordination networks [Ag(**L12**)(X)] (X = ClO_4^-, PF_6^-).[74] The two solids have similar coordination structures consisting of 1D coordination chains, with the anions weakly coordinating the silver centers. The two structures differ though in the number and strength of the inter-chain Ag–Ag interactions. The perchlorate anion was irreversibly exchanged with hexafluorophosphate, a process that was driven by the argentophilic interactions that were stronger and more numerous in the PF_6^- structure. This example is a clear illustration of how other types of intermolecular forces in MOF crystals can override the anion-framework interactions, and thus control the anion selectivity.

Anion Inclusion by Hydrogen Bonding

Among the intermolecular interactions involving anions, hydrogen bonding appears to have the greatest potential for inducing non-Hofmeister selectivity. In this regard, the ready availability of chelating hydrogen-bonding groups that can establish multiple contacts with the targeting anions, and the possibility of appending multiple such groups to organic linkers by using the power of organic synthesis, offer great prospects for the design of MOFs with shape recognition and non-Hofmeister selectivities. One of the remaining challenges associated with the utilization of hydrogen-bonding groups, though, is their tendency to self-associate, which diminishes or completely eliminates their ability to bind anions. The elaboration of functional MOFs for anion recognition and separation needs therefore to incorporate effective molecular- and crystal-design strategies that prevent such self-neutralizing "reactions" among the hydrogen-bonding groups from occurring.

The most common situation of anion hydrogen bonding in MOFs involves coordinating water as a proton donor. An example of coordination network in this category that was explored as an anion exchanger is [Ba_2(**L13**)(H_2O)$_5$]Cl, reported by Shimizu et al.[75] This structure can be described as consisting of cationic barium sulfonate layers pillared by the mesitylene linkers into a 3D coordination network containing channels occupied by chloride anions (Figure 14). The Ba^{2+} centers are further coordinated by water molecules, which act as hydrogen-bond donors to Cl^-. Most chloride anions (75–85%) could be exchanged by fluoride when the crystals were suspended in MeCN containing 1 equiv. of F^-. However, since the anion exchange was effected from a relatively nonpolar solvent, the inclusion of the more hydrophilic fluoride inside the polar channels of this coordination framework is not surprising, and may be considered normal Hofmeister behavior.

The microporous coordination polymer made from the hydrophilic linker **L14** and Tb^{3+} was recently reported to selectively sense anions (Figure 15).[76] Despite its neutral charge, this coordination network can absorb different anions (as sodium salts) into its hydrophilic channels functionalized with free –OH groups. The anion inclusion was detected by the luminescence enhancement caused by the interactions of the anions with the network, presumably through hydrogen bonding. The response to various anions was found to follow the order: $CO_3^{2-} > CN^- > I^- > Br^- > Cl^- >> F^- \approx SO_4^{2-} \approx PO_4^{3-}$. One may easily notice that except for carbonate and cyanide the other anions conform to the Hofmeister behavior, indicating that the presence of the –OH hydrogen-bonding groups is not sufficient to reverse the solvation bias in this MOF. The strikingly different selectivity for carbonate and cyanide, which are both relatively strong bases, suggests to us a different mechanism

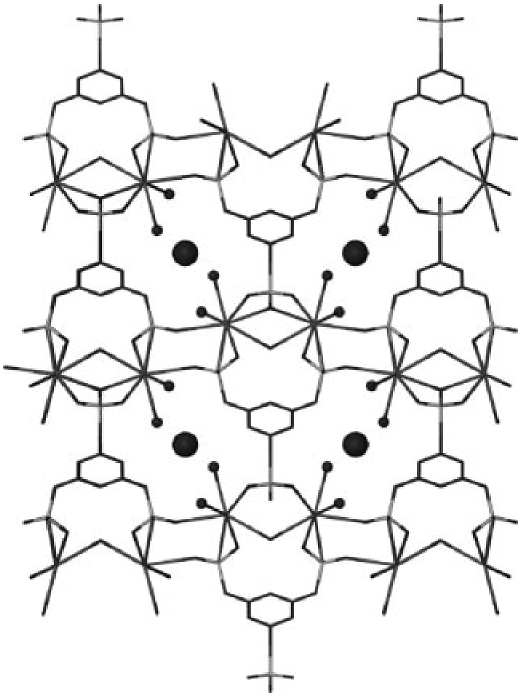

Figure 14. Structure of the [Ba_2(**L13**)$(H_2O)_5$]Cl coordination network showing chloride anions (large balls) included in polar channels decorated with water molecules (small balls) acting as hydrogen-bond donors. The water protons could not be located from the X-ray structure.

for their binding, possibly involving deprotonation of the OH groups. Unfortunately, no structural information about the binding of the anions (and the sodium countercation) inside the channels of this material is available, which makes the interpretation of the observed selectivity difficult.

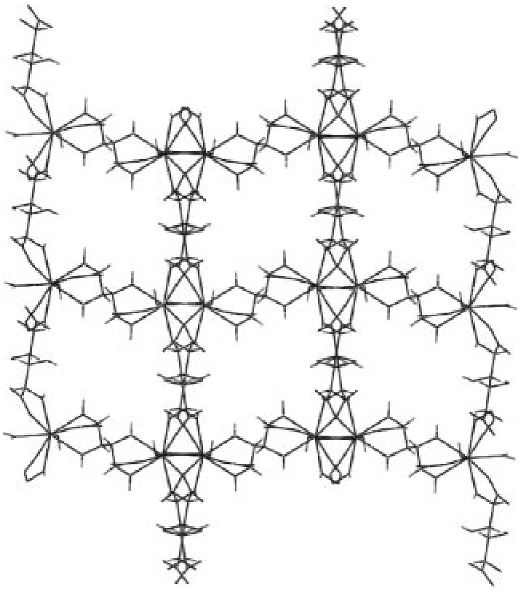

Figure 15. Crystal structure of [Tb(**L14**)$_{1.5}$$(H_2O)_2$]$(H_2O)_5$, with the water included in the channels removed.

Work in our group has involved the design and synthesis of coordination frameworks functionalized with hydrogen-bonding groups for anion recognition and separation. Along this line, we synthesized a cationic square-grid coordination network assembled from Cu^{2+} and linker **L15**, which contained 1D channels functionalized with free –COOH binding groups (Figure 16).[77] The availability of free carboxylic groups in a coordination network is remarkable, as these groups typically become involved in the network assembly through coordination to the metal centers or hydrogen bonding. The key factors for the formation of this functional MOF appear to be the low pH (1.6) involved in its synthesis, which kept the carboxylic groups protonated and thus unavailable for metal coordination, and the aqueous solvent, which prevented the –COOH groups from self-associating by hydrogen bonding. The carboxylic groups remained thus available to bind anionic guests included in the channels of this MOF. Competitive crystallization experiments found that this coordination network preferentially includes halides against NO_3^-, SO_4^{2-}, or ClO_4^- oxo anions, with a slight preference for chloride. Single-crystal X-ray structural analysis showed the inclusion of $Cl(H_2O)_4^-$ clusters hydrogen-bonded by the carboxylic groups inside the 1D channels. The clusters assume a square-pyramidal geometry, which is the most stable structure of $Cl(H_2O)_4^-$, as predicted by theoretical calculations. The observed peak selectivity for halides can be rationalized by the good complementarity (size, symmetry, and hydrogen-bond functionality) between the channels of the MOF host and the $Cl(H_2O)_4^-$ guest. The larger oxo anions, by comparison, would have to lose most of their solvating water to fit inside the channels, which would be energetically unfavorable. On the other hand, Br^- and F^- are known to form water clusters that are similar in size and shape with the $Cl(H_2O)_4^-$, which may account for the reduced selectivity observed within the halide series. This system provides an example of non-Hofmeister anion selectivity in an MOF (upper-right quadrant in Figure 2), that results from the combination of high complementarity (insured by functionalization with H-bonding groups) with structural rigidity. Furthermore, this example inspires an alternative approach to anion separation with MOFs, where the coordination framework host can be designed to selectively include anion/water clusters of different sizes and geometries, which may result in selectivities that are different from those normally associated with "naked" anions.

Looking to improve anion recognition and selectivity in MOFs, we turned our attention to urea proton donors. Urea is a particularly effective anion-binding group, as it is capable of chelating the targeted anion with its two preorganized NH protons, which may result in enhanced binding strength and recognition abilities.[78] We and others have demonstrated that ureas can be easily incorporated as functional units into coordination frameworks, wherein they can specifically chelate various oxo anions.[79] Although ureas are prone to self-association into hydrogen-bonded tapes, we found that substitution with the electron-withdrawing pyridine groups, such as in linkers **L17** and **L18**, greatly

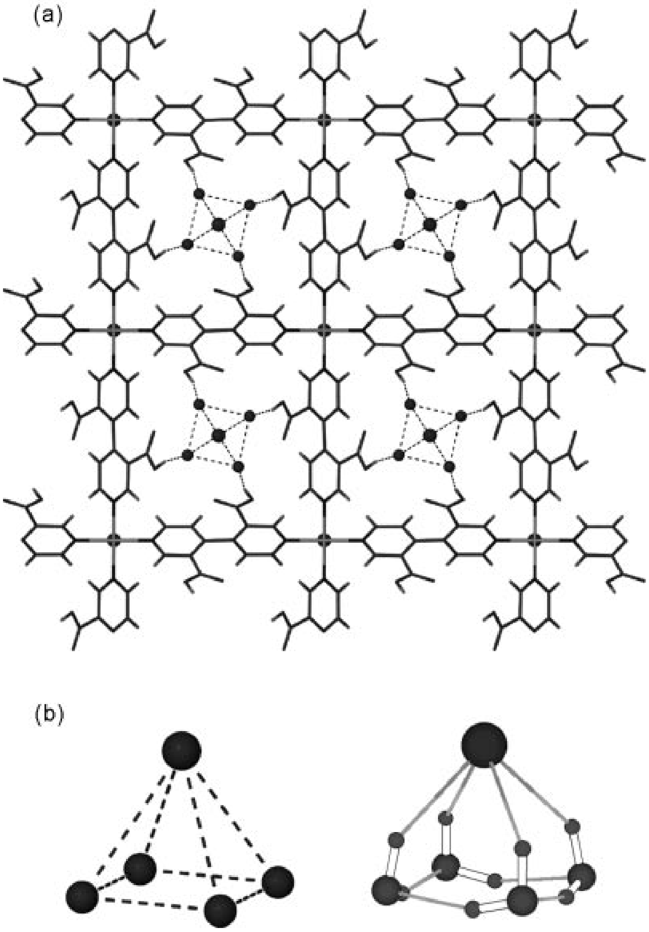

Figure 16. Structure of [CuCl(**L15**)$_2$]Cl(H$_2$O)$_4$. (a) Square-grid coordination network (stick) functionalized with –COOH groups that bind Cl(H$_2$O)$_4^-$ clusters (balls) included in the channels. (b) Structure of Cl(H$_2$O)$_4^-$ as found in the crystal (left) and as calculated in the gas-phase (right).

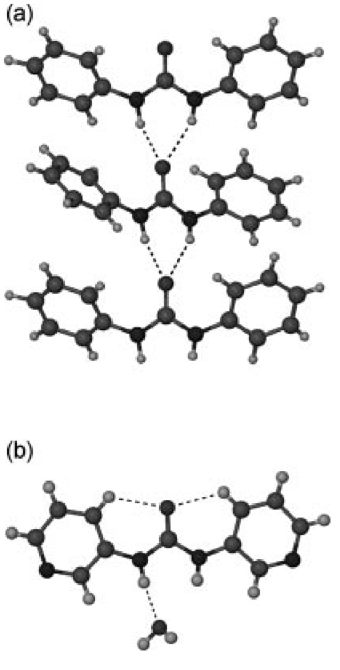

Figure 17. (a) Typical self-association of ureas in hydrogen-bonded tapes, as found in the crystals of diphenylurea. (b) Intramolecular CH···O hydrogen bonds in the crystals of bis(*m*-pyridyl)urea hydrate showing intramolecular CH···O interactions and intermolecular hydrogen bonding to the included water.

diminishes this tendency as a result of stronger intramolecular CH···O hydrogen bonds, which decreases the ability of the C=O group to engage in intermolecular hydrogen bonds (Figure 17).[79a,80]

The urea-functionalized linker **L17** forms 1D coordination polymers with ZnCl$_2$, ZnBr$_2$, ZnI$_2$, and ZnSO$_4$ from water/ethanol mixtures, with the coordination chains further linked by urea···anion hydrogen bonds and anion–Zn coordination bonds (Figure 18).[62] In direct contrast, Zn(NO$_3$)$_2$ and Zn(ClO$_4$)$_2$ do not form coordination networks under the same conditions, which prompted us to investigate the possibility of anion separation by selective crystallization of Zn(**L17**) coordination networks. Addition of an ethanolic solution of **L17** to an aqueous solution containing 1 equiv. of Zn(NO$_3$)$_2$ and 1 equiv. of each NaCl, NaBr, NaI, NaClO$_4$, and Na$_2$SO$_4$ resulted in selective crystallization of the halides as a solid solution with the composition Zn(**L17**)(Cl)$_x$(Br)$_y$(I)$_z$ ($x + y + z = 2$), and total exclusion of the oxo anions, as demonstrated by FTIR spectroscopy and X-ray diffraction. Although sulfate can form a coordination polymer under these conditions, this anion proved uncompetitive against the halides, as the formation of the [Zn(**L17**)(SO$_4$)(H$_2$O)$_3$](EtOH) phase that would otherwise be observed is apparently inhibited by the presence of the competing anions. Furthermore, the size and charge mismatch of SO$_4^{2-}$ apparently prohibits its inclusion in the Zn(**L17**) halide phase. The composition of the precipitated solid from the competitive crystallization experiment was found to be time-dependent (Figure 19). Thus, after 30 min, the kinetically controlled crystalline product consisted of mainly the Zn(**L17**)Cl$_2$ phase, with a small amount of the Zn(**L17**)Br$_2$ phase also present. Elemental analysis indicated that chloride was the major halide found in this solid, followed by bromide and iodide, which corresponds to an anti-Hofmeister selectivity. The preference for the smaller, more densely charged Cl$^-$ against the more hydrophobic Br$^-$ and I$^-$ in the Zn(**L17**)Cl$_2$ phase can be rationalized on the basis of the strong interactions of the halides with the Zn^{2+} Lewis acid centers and hydrogen bonding to the urea groups, which apparently provide a more stabilizing environment than that found in water. This solid, however, slowly redissolved, and, after 5 d, the thermodynamically more stable Zn(**L17**)Br$_2$ was the only phase observed. This phase also included chloride and iodide in a solid solution form, with the relative amounts of the halides still corresponding to an anti-Hofmeister selectivity. The relative halide content continued to change if the precipitated solid was left in the supernatant solution for up to 2 weeks, when the dominant halide in the solid became Br$^-$, followed by Cl$^-$ and I$^-$ (Figure 19). A crystal structure of the Zn(**L17**)Br$_2$ phase showed that it contained two different halide sites, with only one of them participating to hydrogen bonding with the urea groups (Figure 18), which

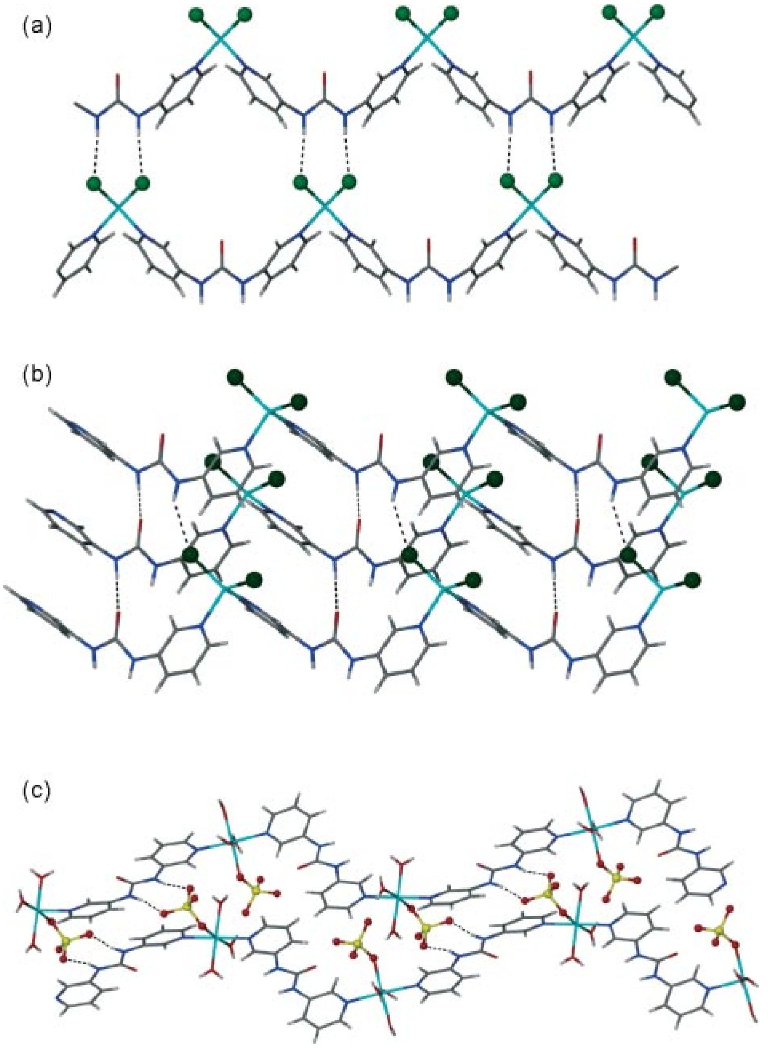

Figure 18. Crystal structures of the 1D Zn(**L17**) coordination polymers. (a) Structure of Zn(**L17**)Cl_2 showing the binding of the Cl^- to the Zn^{2+} centers and urea groups. (b) Structure of Zn(**L17**)Br_2 [isostructural with Zn(**L17**)I_2] showing two binding sites for the Br^-. (c) Structure of [Zn(**L17**)(SO_4)(H_2O)$_3$](EtOH) showing the sulfate anions coordinated to the Zn^{2+} and hydrogen-bonded to urea groups. Coordination chains are shown as stick models and anions are shown as ball-and-stick models.

explains the lower discrimination among halides found in the final solid. Nevertheless, the Zn(**L17**)Br_2 phase is thermodynamically more stable than the Zn(**L17**)Cl_2 one, apparently due to its more efficient crystal packing. This observation points to another important factor in anion selectivity in MOF crystallizations, which is the overall lattice stabilities of the competing coordination networks, which ultimately dictate their solubilities.

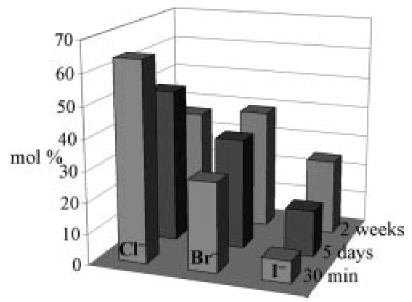

Figure 19. Halide compositions of the solids obtained from the competitive crystallizations of [Zn(**L17**)]X_2 coordination networks.

The concomitant inclusion of different halides in the same structural frameworks simplifies the interpretation of the observed selectivity by careful examination of the coordination environments around the included anions. This was conveniently done by structural analysis of single crystals grown from 1:1 mixtures of different zinc halide salt pairs. For example, crystallization of a 1:1 mixture of $ZnCl_2$ and $ZnBr_2$ with a stoichiometric amount of **L17** resulted in concomitant formation of both the Zn(**L17**)Br_2 (major) and Zn(**L17**)Cl_2 (minor) single-crystalline phases. X-ray diffraction analysis of the major phase showed segregation of the two halides between the two different halide sites. Thus, the site hydrogen-bonded to urea contained 66% Cl^-, while the non-hydrogen-bonded site contained only 40% Cl^- (with the Br^- occupying the remaining 34% and 60%, respectively, of the two sites), which corresponded to the $ZnCl_{1.06}Br_{0.94}$(**L17**) overall crystal composition. On the other hand, the two equivalent halide sites in the Zn(**L17**)-Cl_2 minor crystal phase are both hydrogen-bonded by NH protons from an urea group, which translated into a higher chloride content of 71% [corresponding to the $ZnCl_{1.42}Br_{0.58}$(**L17**) crystal composition]. Analogous crystallization of a 1:1 mixture of $ZnBr_2$ and ZnI_2 with a stoichiometric amount of **L17** resulted in exclusive formation of the $ZnBr_2$(**L17**) phase, which, however, contained both bromide and iodide in different proportions depending on the crystal site. Thus, the urea-hydrogen-bonded site contained 59% Br^-, whereas the non-hydrogen-bonded site contained only 33% Br^-, corresponding to a crystal composition of $ZnBr_{0.92}I_{1.08}$(**L17**). An even more dramatic segregation of halides was found in the mixed crystals obtained from a 1:1 mixture of $ZnCl_2$ and ZnI_2, which contained 85% Cl^- on the hydrogen-bonded site and only 26% Cl^- on the non-hydrogen-bonded site [corresponding to the $ZnCl_{1.11}I_{0.89}$(**L17**) crystal composition]. These mixed structures allowed us to formulate some simple structure/selectivity principles for halide inclusion in these coordination frameworks. Thus, in the Zn(**L17**)Cl_2 phase, with all halide sites equivalent and consisting of strong coordination to the Zn^{2+} centers and hydrogen bonding to urea, the more densely charged and stronger base Cl^- was preferred against the larger, less basic Br^-. In the Zn(**L17**)Br_2 phase, on the other hand, the more acidic site hydrogen-bonded to urea included significantly larger proportions of the more basic halide, whereas the larger, less basic halides preferred the non-hydrogen-bonded site, where van der Waals forces were dominant. All these observations strongly indicate an anti-Hofmeister selectivity within the halide series. However, it should also be noted here that the total exclusion of the oxo anions could be considered as a non-Hofmeister behavior, or peak selectivity for the halide group.

In order to achieve higher selectivity for oxo anions, we reasoned that the design of more elaborate linkers, containing multiple urea groups positioned optimally around the anion, should result in superior shape recognition and peak selectivity. Towards this end, we have been interested in the design of coordination polymers with exclusive sulfate selectivity. Molecular models suggested that sulfate ideally accommodates 6 urea groups, each binding to one of the 6 O–S–O edges of the tetrahedral SO_4^{2-} in a total of 12 hydrogen bonds (Figure 20a).[78a] Linker **L16**, built from TREN, seemed ideal for this purpose, as indicated by molecular modeling, which showed that sulfate can accommodate two such TREN-based linkers. Indeed, crystal-structure analysis showed that the coordination framework obtained from **L16** and Ag_2SO_4 encapsulates the sulfate (Figure 20), with 6 urea groups saturating the anion by 12 hydrogen bonds (three to each O atom).[81] For comparison, proteins are known to bind sulfate by only 7 hydrogen bonds, and the highest sulfate coordination number previously observed in a synthetic host was 8.[82] Other anions of various shapes and basicities, such as BF_4^-, NO_3^-, $MeSO_3^-$, or CH_3COO^- did not form a coordination polymer with **L16** under similar conditions due to their negligible interactions with this linker, as indicated by NMR spectroscopy. Instead, crystallization of the free linker through urea···urea hydrogen bonding was observed in the presence

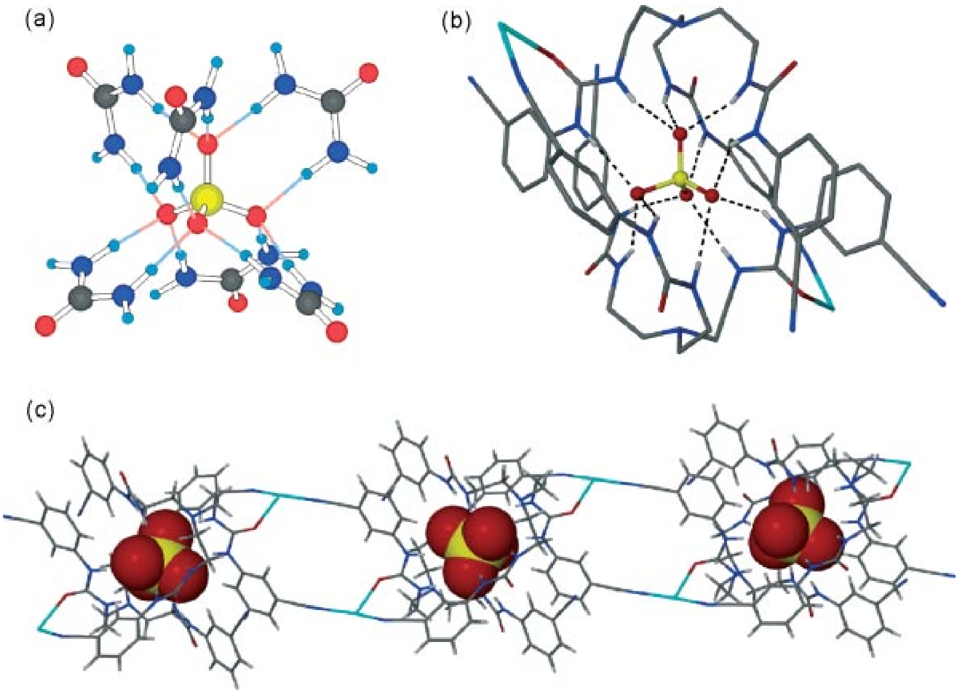

Figure 20. Encapsulation of SO_4^{2-} in an urea-functionalized coordination polymer. (a) Molecular model showing optimal sulfate binding by 12 hydrogen bonds from 6 urea groups. (b) Sulfate encapsulation in the coordination cage obtained from **L16** and Ag_2SO_4. (c) 1D chain obtained by linking the cages through CN···Ag coordination bonds. The coordination framework and the sulfate anions are shown as stick and space-filling models, respectively.

of these anions, which indicates threshold selectivity, with only the strongly interacting sulfate anion being able to compete against linker self-association.[83]

4. Conclusions and Future Prospects

With their great structural diversity and ease of synthesis, MOFs are versatile materials for anion separations. However, without proper crystal structure control, this architectural variety may appear in the same time daunting to someone who wants to design an anion receptor with predictable anion selectivity. Like with any other potential applications of MOFs, further progress in crystal engineering of these materials is needed before they can be predictably used for anion separations. Towards this end, it is important to find new MOFs that preserve a common structural framework in the presence of various anions, to allow for unambiguous interpretation of the observed anion selectivity based on the interactions of the anions with the coordination frameworks. MOF functionalization with strong and specific anion-binding groups such as Lewis acid metal centers or hydrogen-bonding groups for complementary anion coordination is typically needed for selectivities that depart from the solvation bias. Like with discrete anion receptors in solution, the best peak selectivity is observed in MOFs that combine structural constraints and rigidity with a sufficient number of strong binding groups that are optimally positioned around the anion for shape recognition. To date, however, there is a very limited number of coordination frameworks that satisfy these conditions, which can be explained by the fact that most of these solids have not been specifically designed for anion recognition and separation. As a result, the vast majority of MOFs studied to date show typical solvation-controlled Hofmeister selectivities. More systematic structure/properties studies need to be done to better understand the principles governing anion selectivities inside the MOF cavities, with the ultimate goal to obtain peak selectivities for targeted anions by deliberate design. Sorely needed at this time are more quantitative studies of anion exchange and separations, including competition experiments, anion-exchange isotherms, thermodynamic and kinetic measurements, and mechanistic investigations of anion transport. Computational studies could also offer valuable information about the energetics of anion binding inside the coordination frameworks, as well as the electronic and steric requirements for optimal anion selectivity. Such fundamental inquiries may eventually reward us with new materials with unprecedented efficiencies in real-world separations.

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