Sulfate separation by selective crystallization of a urea-functionalized metal–organic framework†

Radu Custelcean,* Vincent Sellin and Bruce A. Moyer

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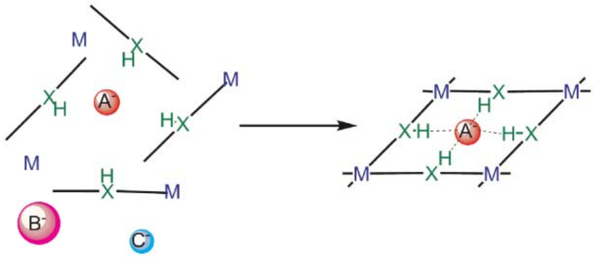
Encapsulation of SO_4^{2-} into a Ni coordination framework functionalized with urea anion-binding groups allows selective separation of this strongly hydrophilic anion from a highly competitive aqueous environment.

Anion complexation by synthetic receptors is an important and current area of inquiry, with an increasing number of anion-selective hosts being reported every year.[1] Nearly all of these studies are concerned with binding or sensing phenomena in homogeneous solutions, whereas coupling anion binding with transport is necessary to effect anion separation, as required for such applications as environmental remediation or nuclear waste cleanup.[2] However, transport imposes its own intrinsic selectivity that the receptor must overcome, as transferring an anion from water into an organic phase is strongly biased by the anion's hydration energy, favoring larger, less hydrophilic anions.[3] Due to its large standard Gibbs energy of hydration (-1080 kJ mol^{-1}), sulfate separation from aqueous solutions presents a particular challenge. Nature responds to this challenge by encapsulating the sulfate with an array of seven hydrogen bonds, as found in the sulfate-binding protein.[4] While a few synthetic receptors have been shown to effectively encapsulate sulfate with various hydrogen-bonding groups,[5] their potential for sulfate separation remains to be explored.

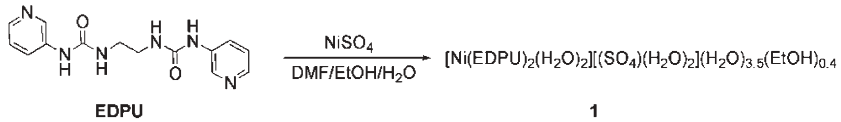
We have recently articulated an alternative approach to anion separation that involves competitive crystallization of metal–organic frameworks (MOFs)[6] functionalized with hydrogen-bonding groups for specific anion complexation.[7] Unlike the traditional anion-exchange approach, which employs the MOF as a solid-phase ion exchanger,[8] this strategy involves the MOF crystallization process as a tool for anion separation. Specifically, the MOF is competitively crystallized from an anionic mixture, a process that may result in the selective inclusion of certain anions (or group of anions) depending on their size, shape, symmetry, and specific interactions with the coordination network (Scheme 1). The MOF may thus be essentially considered an 'infinite' anion-binding host, self-assembled *in situ* through metal–ligand coordination. As MOFs can be designed into many different architectures, they may be utilized as versatile platforms for arranging the anion-binding groups, thereby providing multiple possibilities for controlling the anion selectivity. Urea is a particularly attractive hydrogen-bonding group that is highly complementary to oxoanions,[9] and was recently employed for the functionalization of metal–organic discrete receptors[10] and MOFs.[5a,11] To date, however, selective separation of oxoanions using simple mono-urea linkers remained elusive, as less discriminatory anion–metal coordinative interactions competed with the hydrogen bonding by the urea groups.[7a] We therefore anticipated that the employment of more elaborate linkers, with multiple chelating urea groups, would result in a more selective binding and separation. Herein we describe a functional MOF assembled from a bis-urea ligand, which selectively includes sulfate through multiple hydrogen bonds from the urea groups, thus allowing SO_4^{2-} separation from aqueous solutions containing F^-, Cl^-, Br^-, I^-, NO_3^- and ClO_4^-, as competing anions.



Scheme 1 Selective anion encapsulation by competitive crystallization of MOFs.

Reaction of ethylenedi(*m*-pyridylurea) (EDPU) in DMF–EtOH with an aqueous solution of $NiSO_4$ afforded a blue solid with the composition $[Ni(EDPU)_2(H_2O)_2][(SO_4)(H_2O)_2](H_2O)_{3.5}(EtOH)_{0.4}$ (**1**), as indicated by single-crystal X-ray diffraction‡ and elemental analysis. The FTIR spectrum of **1** displays characteristic peaks for the urea groups at 3299 cm^{-1} (NH) and 1675 cm^{-1} (CO), and for the sulfate anion at 1108 cm^{-1}.

Crystal structure determination of **1** revealed a layered network with rhomboid-grid architecture, with Ni^{2+} cations lying on inversion centers and coordinated octahedrally by four equatorial pyridine groups and two axial water molecules (Fig. 1). There are two independent Ni^{2+} and EDPU linkers in the unit cell.



EDPU **1**

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6119, USA. E-mail: custelceanr@ornl.gov; Fax: 865-574-4939; Tel: 865-574-5018

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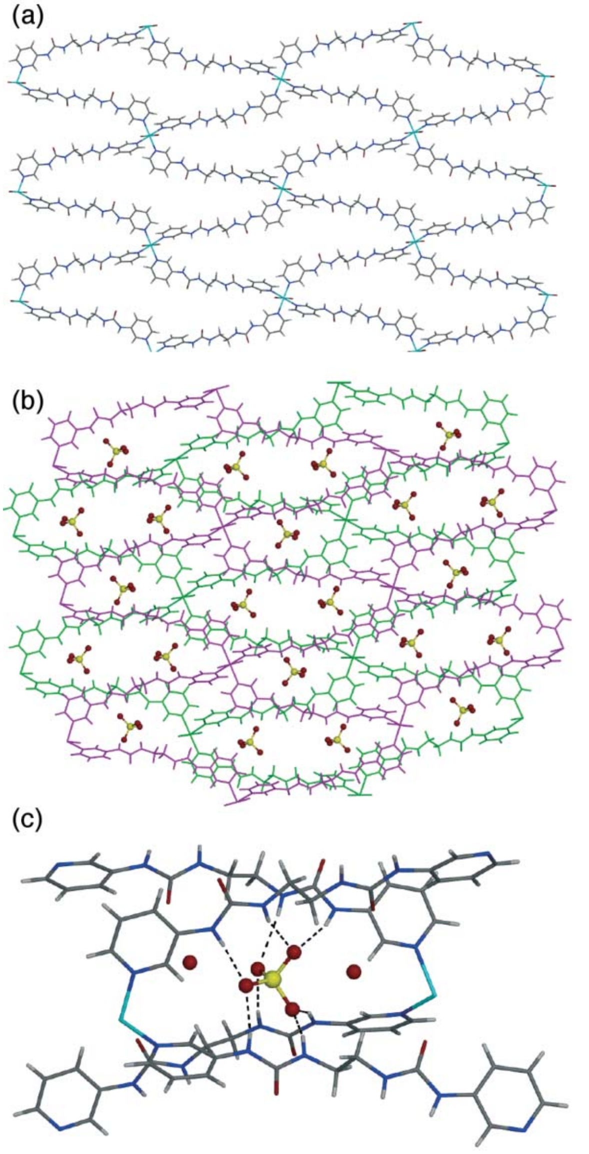

Fig. 1 Crystal structure of **1**. (a) Nickel coordination layer displaying the rhomboid-grid architecture. (b) Stacking of adjacent layers depicted as green and magenta stick models, with the sulfate anions shown as ball-and-stick models. (c) Intercalation of sulfate *via* eight hydrogen bonds from four urea groups.

The EDPU linker is fully extended with the ethylene assuming an *anti* conformation, which results in an average linker length, measured as the distance between the pyridine N atoms, of 15 Å, and a rhomboid size, measured between the Ni nodes, of 33.7 and 13.9 Å, respectively. Adjacent coordination layers in the crystal are stacked along the [−1 0 2] direction and are offset by 0.5(a + b). Sulfate anions are intercalated between layers and are chelated by four urea groups from four different EDPU linkers, two from each layer, in a total of 8 hydrogen bonds. Table 1 (ESI†) lists the geometric parameters for the observed hydrogen bonds between the sulfate and the urea groups in the framework. Two water molecules are also included and form two additional hydrogen bonds with the sulfate, with observed O···O distances of 2.78 and 2.87 Å, respectively. The two water molecules further hydrogen-bond to a urea CO group in one layer and a coordinating water molecule from an adjacent layer, thus increasing the cohesion among layers.[12]

When aqueous solutions of other Ni(II) salts (*e.g.*, chloride, nitrate, or perchlorate) were mixed with DMF–EtOH solutions of EDPU, under the same conditions as in the synthesis of **1**, no MOF crystals were formed even after one month. It thus appears that the strong hydrogen bonds between sulfate and the urea groups are critical for the stability of **1**. As a result, other anions that are weaker hydrogen-bond acceptors cannot provide sufficient cohesion between layers, and remain dissolved in solution. Furthermore, crystallization of **1** was virtually unperturbed by the presence of equivalent amounts of F^-, Cl^-, Br^-, I^-, NO_3^- or ClO_4^- (added as single sodium salts), as indicated by powder X-ray diffraction.[13] These observations suggested the possibility for sulfate separation by selective crystallization of **1**. To test this idea, a competition experiment was set up, in which a 3 : 1 EtOH–DMF solution containing two equivalents of EDPU was mixed into an aqueous solution containing 1 equivalent of $NiSO_4$, and 2 equivalents of each NaF, NaCl, NaBr, NaI, $NaNO_3$ and $NaClO_4$. The resulting precipitate was filtered and analyzed by FT-IR, powder X-ray diffraction (Fig. 2), and elemental analysis, which supported the selective formation of **1**.

A particularly important problem that is highly relevant to the U.S. Department of Energy (DOE) is sulfate separation from aqueous solutions containing excess nitrate, as found in radioactive waste tanks at many DOE sites.[2] In an effort to assess the selectivity and efficiency of sulfate separation from nitrate by

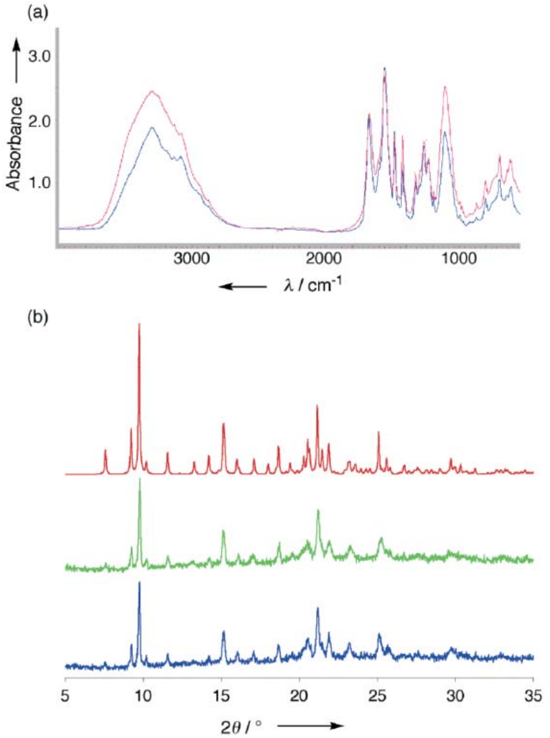

Fig. 2 Competitive crystallization of **1**. (a) FT-IR spectra of the crystals obtained from $NiSO_4$ alone (red) and $NiSO_4$ in the presence of the NaX (X = F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-) anionic mixture (blue). (b) Powder X-ray diffraction patterns. Red: simulated pattern from the single-crystal X-ray data of **1**. Green: experimental pattern from **1**. Blue: experimental pattern from the solid crystallized in the presence of the anionic mixture.

selective MOF crystallization we performed a preliminary competition experiment involving crystallization of **1** from a twenty-fold excess of nitrate (molar ratio) present as sodium salt. Once again, selective crystallization of sulfate was observed, as indicated by the powder X-ray pattern and FT-IR spectrum of the isolated solid, which were identical with those corresponding to reference compound **1**. However, only 27% of the sulfate was recovered from solution in this one-step crystallization, as the large excess of $NaNO_3$ increased the aqueous solubility of **1** significantly, suggesting the need for using an excess of the EDPU linker or multiple crystallization steps for quantitative sulfate removal. While sulfate recovery has not been optimized, it is already evident that the selective MOF crystallization is a viable approach for sulfate separation, as it allows effective removal of this or other highly hydrophilic anions from a competitive aqueous environment, a process that has proven so far extremely difficult with conventional organic receptors. As MOFs are versatile materials that can be designed into many different architectures, thereby allowing for positioning of functional groups for optimal binding of virtually any targeted anion, this strategy holds great promise for the field of anion separation.

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Notes and references

‡ *Crystal data* for **1**: $C_{30}H_{46}N_{12}NiO_{13}S$, M = 873.52, blue plate, 0.33 × 0.12 × 0.03 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 13.237(3), b = 13.908(3), c = 23.358(5) Å, β = 95.11(3)°, V = 4283.0(15) Å^3, Z = 4, D_c = 1.364 g cm^{-3}, T = 173(2) K, $2\theta_{max}$ = 56.7°, 54655 reflections collected, 10669 unique (R_{int} = 0.0546). Final GooF = 1.070, R_1 = 0.0825, wR_2 = 0.2213, R indices based on 7124 reflections with $I > 2\sigma(I)$, 544 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.572 mm^{-1}. CCDC 623115. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616761f

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12 Disordered ethanol and water molecules occupy the interlayer space and could not be accurately modeled from the X-ray data. Removal of these solvent molecules and subsequent analysis with SQUEEZE, part of the PLATON package (A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34), yielded 179 e$^-$/unit cell, which is in good agreement with the 182 e$^-$/unit cell corresponding to 3.5 H_2O and 0.4 EtOH equivalents found by elemental analysis.

13 Single crystals obtained in the presence of NaCl or $NaNO_3$ were also analyzed by X-ray diffraction and found to have a structure identical with **1**.