A coordinatively saturated sulfate encapsulated in a metal–organic framework functionalized with urea hydrogen-bonding groups†

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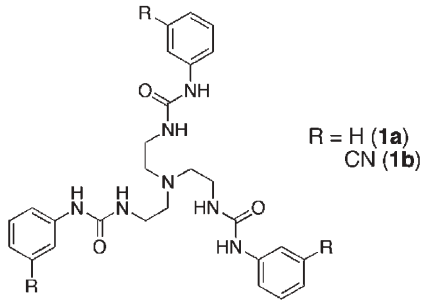
A functional coordination polymer decorated with urea hydrogen-bonding donor groups has been designed for optimal binding of sulfate; self-assembly of a tripodal tris-urea linker with Ag_2SO_4 resulted in the formation of a 1D metal–organic framework that encapsulates SO_4^{2-} anions *via* twelve complementary hydrogen bonds, which represents the highest coordination number observed for sulfate in a natural or synthetic host.

Anion binding by synthetic receptors is an important and contemporary aspect of supramolecular chemistry.[1] Sulfate complexation and extraction from water is particularly challenging due to the high charge density of this anion, which translates into a large free energy of hydration of −1080 kJ mol^{-1}.[2] While Nature's sulfate-binding proteins use solely hydrogen bonding for this task,[3] synthetic receptors have involved either hydrogen bonding alone (in neutral hosts), or a combination of hydrogen bonding and electrostatic interactions (in cationic hosts) for sulfate complexation.[4] Recently, Bowman-James has categorized the binding of anions based on their coordination numbers by analogy with the understanding of cation coordination originally developed by Werner.[5] The extension of the coordination-number concept is helpful in defining the notions of complementarity and the maximum coordination number (saturation) for a given anion, which can aid the design of optimal anion-binding host structures. For the specific case of sulfate, as a prime example of interest to us, the highest coordination number previously observed within a natural or synthetic host was eight.[3,4] However, electronic-structure calculations by Hay *et al.* led to the expectation that sulfate ideally accommodates 12 hydrogen bonds, one to each oxygen atom in each of the six O–S–O planes.[6] In the course of examining receptors complementary for oxoanions such as sulfate, we have started to explore metal–organic frameworks (MOFs)[7] as anion-binding hosts.[8] While the anion coordination is known to influence the self-assembly of MOFs,[9] we thought that a molecular-design approach could lead us to MOF linkers possessing appropriately positioned arrays of hydrogen-bond donor groups to achieve maximum complementarity between sulfate and the MOF hosts. Herein we report an MOF functionalized with urea binding sites[9] that indeed encapsulates and coordinatively saturates sulfate through the unprecedented formation of 12 hydrogen bonds.

We founded our design on the tris-urea structure **1a** built from the tris(2-aminoethyl)-amine linker, which has been recently found to act as a sulfate receptor.[10] Functionalization of **1a** with metal-coordinating –CN groups afforded the analogous sulfate receptor **1b** that can also act as an MOF linker.



While structural data for the anion binding by **1a** is missing, our molecular modeling (MMFF94)[11] confirmed that this C_3-symmetrical ligand has good shape complementarity for SO_4^{2-}, and can bind the anion in two distinct modes that involve all three urea groups in chelate hydrogen bonding (Fig. 1).

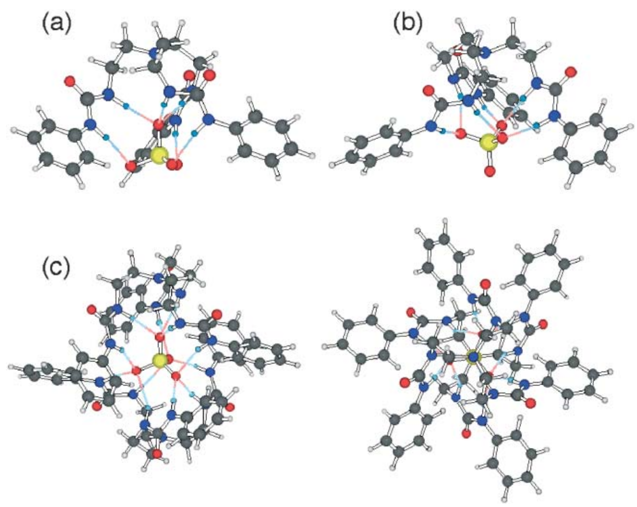


Fig. 1 Molecular model of **1a**·SO_4^{2-}. a) Axial binding with the urea groups positioned on the three edges radiating from a common oxygen atom of sulfate. b) Facial binding with the urea groups positioned on the three edges of the same triangular face of sulfate, which is 2.3 kcal/mol higher in energy than the axial mode. c) Sulfate encapsulation by concurrent axial–facial binding by two ligands.

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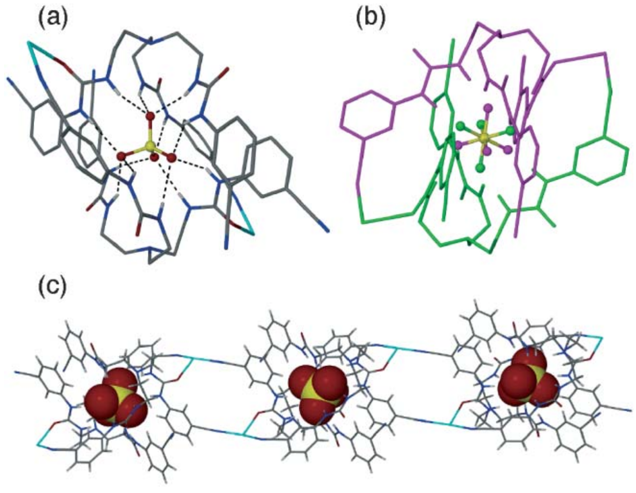

Fig. 2 Crystal structure of **2**. a) Sulfate encapsulation *via* twelve hydrogen bonds from six urea groups. b) Coordination cage with the two ligands related by inversion symmetry depicted in green and magenta. The sulfate sits on the crystallographic inversion center and is rotationally disordered over two positions. c) 1D coordination polymer with the framework shown as stick model and the sulfate anions shown as space filling model.

Crystallization of **1b** from water/acetone in the presence of half equivalent of Ag_2SO_4 yielded a coordination polymer with the composition $[Ag_2(\mathbf{1b})_2](SO_4)\cdot(\text{acetone})_{1.5}\cdot(H_2O)_{3.7}$ (**2**), as indicated by elemental analysis, ^{1}H NMR spectroscopy in DMSO (ESI), and single-crystal X-ray diffraction.‡ The framework is insoluble in water and common organic solvents (except DMSO), and is thermally stable up to 192 °C, at which temperature it melts with decomposition. The urea NH protons in the NMR spectrum of **2** are shifted downfield by 0.84 and 0.48 ppm relative to **1b**, suggesting relatively strong hydrogen bonding of the sulfate, and a Job's plot revealed a 2 : 1 ligand to sulfate binding stoichiometry.[12] Molecular modeling (MMFF94) showed that the sulfate can accommodate two molecules of **1a**, with the six urea groups chelating the anion in a C_3-symmetrical complex (Fig. 1c). Crystal structure analysis of **2** confirmed the 2 : 1 sulfate binding by **1b**, with one ligand coordinating in the axial mode and the other in the facial mode (Fig. 2), resulting in a total of twelve hydrogen bonds (Table 1). The two ligands are additionally held together by CN···Ag and urea(O)···Ag coordination bonds, as well as π···π interactions between the phenyl rings, essentially forming a molecular cage that encapsulates the sulfate in its center. The cages are interlinked *via* CN···Ag coordination bonds to form a one-dimensional coordination polymer,[13] with the Ag nodes being tetracoordinated by two –CN groups, one urea, and a water molecule. Compared to the molecular model, however, the ligand deviates from the ideal C_3 symmetry, apparently as a result of the silver coordination and crystal packing effects. Furthermore, the cage is centrosymmetric, as required by the space group symmetry, with the sulfate sitting on the crystallographic inversion center. Lacking a proper inversion center the tetrahedral sulfate anion is rotationally disordered over two positions, with the eight O atoms with half occupancy defining the corners of a cube.

Table 1 Hydrogen bonding parameters (Å, °) for SO_4^{2-} binding in **2**

D–H···A	H···A	D···A	< D–H–A
N1–H1···O1	2.28	2.9393	132
N1–H1···O3	2.24	3.1110	170
N2–H2···O2	2.09	2.9636	170
N2–H2···O4	2.27	2.8516	124
N3–H3···O1	2.08	2.9266	162
N3–H3···O2	2.37	3.1741	152
N4–H4···O4	2.25	3.0015	143
N4–H4···O3	2.12	2.9901	168
N5–H5···O1	2.11	2.9072	151
N5–H5···O4	2.24	3.0598	156
N6–H6···O3	2.17	3.0097	160
N6–H6···O2	2.28	3.0440	146

Attempts to cocrystallize **1b** with other soluble silver salts containing different anions of various shape and basicity, such as $AgBF_4$, $AgNO_3$, $AgMeSO_3$, or AgOAc, under the same conditions as in **2**, failed to produce coordination polymers, and only crystals of the free ligand could be obtained. Crystal structure analysis§ revealed that **1b** forms 1D chains in the solid state, with each ligand molecule forming five urea···urea hydrogen bonds (ESI). ^{1}H NMR spectroscopy indicated that these anions interact significantly more weakly with **1b** compared with SO_4^{2-}. Accordingly, addition of one equivalent of $AgBF_4$, $AgNO_3$, $AgMeSO_3$, or AgOAc to a DMSO solution of **1b** induced downfield chemical shifts for the two urea NH protons of 0.00 and 0.00 ppm for BF_4^-, 0.02 and 0.01 ppm for NO_3^-, 0.21 and 0.08 ppm for $MeSO_3^-$, and 0.18 and 0.26 ppm for AcO^-, which are significantly smaller than the observed analogous shifts caused by sulfate (*vide supra*). As a better alternative to the significantly reduced interaction with BF_4^-, NO_3^-, $MeSO_3^-$ or AcO^-, **1b** prefers to self-associate in the solid state through the formation of multiple urea···urea hydrogen bonds that engage all available NH protons. We also note here that no cocrystallization was observed when $(Me_4N)_2SO_4$ was used as a sulfate source, which indicates that silver coordination and MOF formation are critical in stabilizing the $(\mathbf{1b})_2\cdot SO_4^{2-}$ complex relative to the free ligand in the solid state.

In summary, we reported here the design of an MOF host functionalized with urea binding sites that provide a coordinatively saturated environment for sulfate through the unprecedented formation of twelve complementary hydrogen bonds. Although the exclusive encapsulation of sulfate prevented anion exchange in this system, this study provides insight for future design of solid-state materials for recognition and selective separation of targeted anions.

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Notes and references

‡ Crystal data for **2**: $C_{30}H_{34}N_{10}O_7S_{0.5}Ag$, M = 770.57, colorless plate, 0.15 × 0.12 × 0.05 mm^3, triclinic, space group *P*-1 (No. 2), a = 10.3995(12), b = 13.5437(15), c = 14.6455(17) Å, α = 66.289(2), β = 76.241(2), γ = 87.576(2)°, V = 1831.2(4) Å^3, Z = 2, D_c = 1.398 g/cm^3, F_{000} = 790, Bruker SMART APEX, MoKα radiation, λ = 0.71073 Å, T = 173(2) K, $2\theta_{max}$ = 56.7°, 22524 reflections collected, 9083 unique (R_{int} = 0.0326). Final $GooF$ = 1.252, R_1 = 0.0659, wR_2 = 0.1448, R indices based on 8139

reflections with $I > 2\sigma(I)$ (refinement on F^2), 465 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.635$ mm^{-1}. CCDC 281962. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511809c

§ Crystal data for **1b**: $C_{30}H_{30}N_{10}O_3$, $M = 578.64$, colorless block, 0.21 × 0.07 × 0.07 mm^3, triclinic, space group *P*-1 (No. 2), $a = 13.0827(18)$, $b = 13.993(2)$, $c = 18.274(3)$ Å, $\alpha = 73.362(3)$, $\beta = 85.694(3)$, $\gamma = 63.147(2)°$, $V = 2853.9(7)$ Å^3, $Z = 4$, $D_c = 1.347$ g/cm^3, $F_{000} = 1216$, Bruker SMART APEX, MoKα radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $2\theta_{max} = 50.0°$, 20199 reflections collected, 10021 unique ($R_{int} = 0.0651$). Final $GooF = 0.997$, $R_1 = 0.0752$, $wR_2 = 0.1920$, R indices based on 5694 reflections with $I > 2\sigma(I)$ (refinement on F^2), 794 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.092$ mm^{-1}. CCDC 281963. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511809c

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