Sulfate ion encapsulation in caged supramolecular structures assembled by second-sphere coordination†

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A tripodal tris(3-pyridylurea) receptor (L) assembles with metal sulfate salts MSO_4 (M = Mn, Zn) to afford supramolecular cages $[SO_4 \subset L_2]$ that encapsulate the SO_4^{2-} ion *via* multiple hydrogen bonds in a three-dimensional structure held by second-sphere coordination; ^{1}H NMR and negative-ion mode ESI-MS spectra reveal significantly strong sulfate binding in solution.

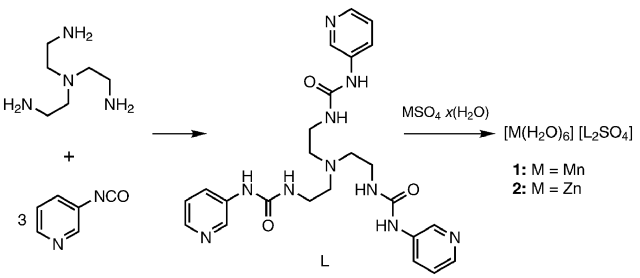
Anion complexation is an important and fast-growing subject in supramolecular chemistry.[1] Bowman-James recently induced the concept of *coordination number* of transition metal complexes to anion coordination chemistry and summarized the definition and geometrical features of anion complexation.[2] Tripodal molecules bearing amide, urea or other functions are widely used in the binding and recognition of anions due to their favorable conformation for multiple hydrogen bonds.[3] The binding and extraction of sulfate anion is of particular interest due to its biological and environmental importance and high charge density according to the Hofmeister effect, and great efforts have been put into the design of sulfate receptors.[4] However, there are only a few examples of sulfate encapsulation, including two recent reports of complete entrapping of SO_4^{2-} ion by tren-based tris(urea) ligands.[5–9] A tris(2-aminoethyl)amine-based receptor with −CN groups encapsulated SO_4^{2-} ions in a 1D MOF with a total of twelve N–H···O hydrogen bonds—the highest and saturated coordination number observed so far for sulfate.[8] Another sulfate ion encapsulation has been achieved by the neutral molecule of a similar tris(urea) receptor equipped with *p*-nitrophenyl groups.[5]

Urea-based pyridyls are a class of ligands that are capable of coordinating with metal ions and hydrogen bonding with anions.[9,10] We have previously reported the anion binding properties of some *N*-aryl-*N*′-pyridylureas and their metal complexes.[11] In an effort to achieve enhanced hydrogen bonding affinities by the cooperative formation of multiple hydrogen bonds, the work has been expanded to tris(urea) receptors. Herein we report the sulfate anion encapsulation in supramolecular assemblies $[M(H_2O)_6][SO_4 \subset L_2]$ (M = Mn, Zn) formed by $MSO_4 \cdot xH_2O$ and a tris(3-pyridylurea) ligand L.

The new receptor *N*-[2-[bis[2-[*N*′-(3-pyridyl)ureido]ethyl]-amino]ethyl]-*N*′-(3-pyridyl)urea (L) was readily synthesized from tris(2-aminoethyl)amine and pyridyl isocyanate (Scheme 1, ESI†). The solid-state structure‡ of L shows a 1D chain formed by eight bifurcated intermolecular urea···urea hydrogen bonds around each L molecule (Fig. 1), which is similar to the phenyl-substituted analog.[12] Reaction of L with 0.5 equivalent of $MSO_4 \cdot xH_2O$ in water–methanol (50 : 50 v/v) gave the crystalline products with the composition $[M(H_2O)_6][L_2SO_4]$ (M = Mn, **1**; Zn, **2**).§ The compounds are only sparingly soluble in methanol and DMSO and are insoluble in other common organic solvents. They are thermally stable up to the melting points of 163 °C for **1** and 164 °C for **2**.

Single-crystal X-ray diffraction analyses§ reveal that complexes **1** and **2** are isomorphous. Two inversion-symmetric molecules of L form a cavity that encapsulates a sulfate anion in its center *via* hydrogen bonding to the six urea groups (Fig. 2(a)). There are a total of eleven N–H···O bonds between the twelve NH groups and the four O atoms of SO_4^{2-} (when the N···O distance is set to <3.20 Å). One of the oxygen atoms (O9) accepts four hydrogen bonds, while O7 takes three, and the other two O atoms (O8 and O10) form two N–H···O contacts each. This is in contrast to the SO_4^{2-} binding by the silver MOF complex, in which each O atom accepts three, and each NH group donates one N–H···O bond, resulting in twelve hydrogen bonds.[8]

Furthermore, the asymmetric binding mode allows for several weaker interactions between SO_4^{2-} and the NH groups. If the N···O distance is restricted to <3.5 Å for hydrogen bonding, five more N–H···O contacts could be



Scheme 1 Synthesis of the ligand L and complexes **1** and **2**.

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† Electronic supplementary information (ESI) available: Synthesis and crystal structure of the ligand L, IR spectrum of **1**, ^{1}H NMR, ESI-MS and IR spectra of **2**, hydrogen bond parameters for **2**, and crystallographic data. See DOI: 10.1039/b719019k

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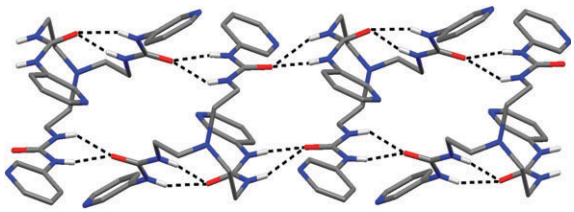

Fig. 1 The solid-state structure of L showing the 1D chain formed by intermolecular urea···urea hydrogen bonds.

added, especially for the 'unsaturated' sulfate oxygen atoms, O8 and O10 (Table 1, Fig. 3). These supplementary contacts may provide additional stability for the sulfate binding of the host, as confirmed by ESI-MS studies described below. A correlation of N–H···O angle *vs.* H···O distance (Fig. 3) shows that in the region of $d_{H\cdots O} < 2.5$ Å, which corresponds to N···O distances shorter than 3.2 Å, only one contact has an N–H···O angle smaller than 140°. In the weak interaction region ($2.5 < d_{H\cdots O} < 2.8$ Å and $3.2 < d_{N\cdots O} < 3.5$ Å), the angles are around 130–140°.

The metal ions lie on an inversion center and exist as hexaaqua complex $[M(H_2O)_6]^{2+}$ in the assemblies **1** and **2**, and the $[SO_4^{2-} \subset L_2]$ units are held together into a three-dimensional structure by interacting with $[M(H_2O)_6]^{2+}$ cations. Interestingly, the pyridyl N donors of the ligand are not coordinated to the metal ions directly, but are involved in second-sphere coordination with a water molecule of $[M(H_2O)_6]^{2+}$ through O–H···N hydrogen bonding. There is also an O–H···O contact between the same H_2O molecule and

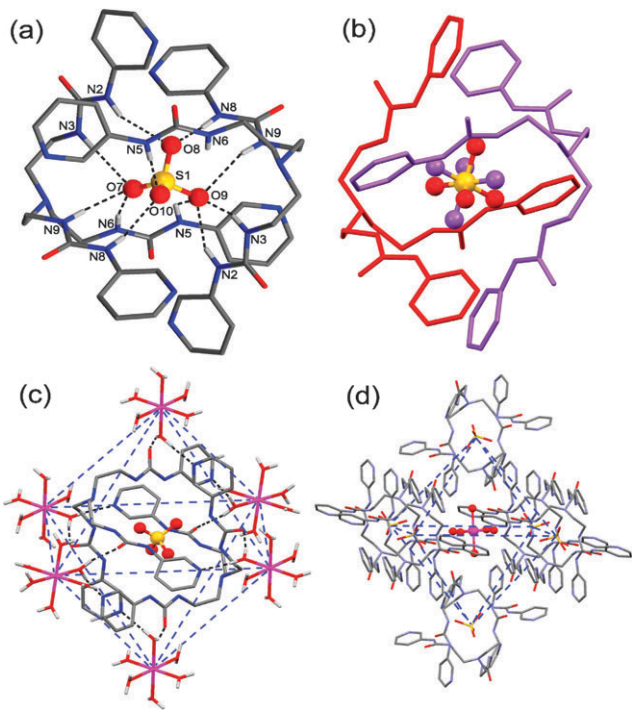

Fig. 2 Crystal structure of **1**. (a) The hydrogen-bonded $[SO_4 \subset L_2]^{2-}$ capsule. (b) Two inversion-related L molecules and the disordered sulfate ion. (c) Interaction of $[SO_4 \subset L_2]^{2-}$ with six $[Mn(H_2O)_6]^{2+}$ cations through second-sphere coordination. (d) $[Mn(H_2O)_6]^{2+}$ at the center of an octahedron formed by six $[SO_4 \subset L_2]^{2-}$ capsules.

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

N–H···O	H···O	N···O	∠N–H···O
N2–H2A···O8	2.24	3.034(3)	154
N2′–H2A···O9	2.17	2.970(3)	155
N3–H3A···O7	2.28	3.135(4)	173
N3′–H3A···O9	2.39	3.140(3)	146
N5–H5A···O9	2.36	2.986(3)	130
N5′–H5A···O10	1.96	2.822(3)	179
N6–H6A···O7	2.11	2.950(3)	166
N8–H8A···O10	2.18	2.946(3)	148
N8′–H8A···O8	2.08	2.908(3)	161
N9–H9A···O7	2.27	3.124(4)	175
N9′–H9A···O9	2.42	3.168(3)	146
N5–H5A···O7	2.56	3.282(4)	142
N5′–H5A···O8	2.73	3.252(3)	120
N6′–H6A···O8	2.70	3.340(3)	133
N6′–H6A···O10	2.76	3.444(3)	138
N9′–H9A···O8	2.65	3.355(3)	140

[a] Primed atoms related by symmetry code $-x, 1-y, 1-z$.

a carbonyl O atom of another ligand. Thus, each $[SO_4^{2-} \subset L_2]$ cage is located in the center of an octahedron formed by six $[M(H_2O)_6]^{2+}$ cations *via* six O_w–H···N and six O_w–H···O interactions (Fig. 2(c)). Meanwhile, each $[M(H_2O)_6]^{2+}$ cation also sits at the center of an octahedron with six $[SO_4^{2-} \subset L_2]$ moieties as the nodes (Fig. 2(d)). The S atom of the tetrahedral sulfate anion also resides on an inversion center, with the eight half-occupied O atoms defining the corners of a cube (Fig. 2(b)). The extended 3D solid-state structure of the second-sphere assemblies in this work is quite different from the two known examples of sulfate entrapment with similar tris(urea) ligands, both of which feature 1D structures.[5,8]

^{1}H NMR spectrum of the Zn(II) compound **2** shows significant downfield chemical shifts ($\Delta\delta$ 1.01 and 0.74 ppm) for the two urea NH protons relative to L in DMSO-d_6. Titration of $ZnSO_4 \cdot 7H_2O$ to the solution of L in DMSO-d_6 resulted in a binding constant of 6.42 (log K), which is considerably larger than those reported for other receptors, *e.g.* 4.50 for a macrocyclic tetraamide[7] and 4.97 for a tripodal receptor.[5] The changes of the NH signals of L upon addition of $ZnSO_4 \cdot 7H_2O$ are shown in Fig. 4.

Negative-ion mode ESI-MS spectra of **1** (Fig. 5) and **2** displayed anionic peaks at m/z 1109.8 for the monovalent $[2L + SO_4 + H]^-$ and m/z 554.6 for divalent $[2L + SO_4]^{2-}$,

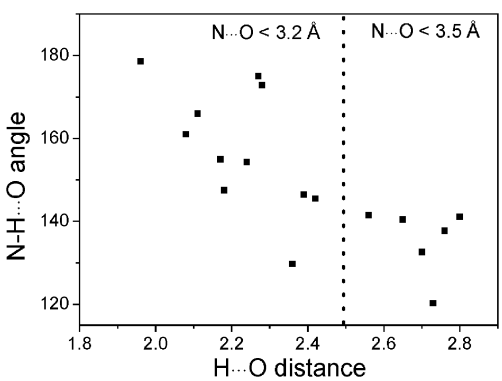

Fig. 3 The scatterplot of N–H···O angle *vs.* H···O distance of the hydrogen bonds (including the weaker contacts) in **1**. Similar plot for **2** is given in ESI.†

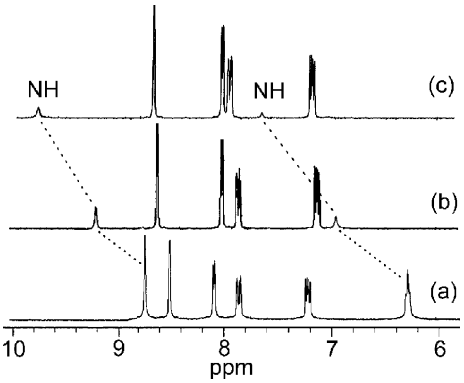

Fig. 4 Downfield shifts of the urea NH groups upon addition of $ZnSO_4$ to the solution of L in DMSO-d_6. (a) L; (b) L + 0.25 equiv. $ZnSO_4$; (c) L + 0.5 equiv. $ZnSO_4$. Note: the intensity of the NH signals decreases due to exchange with water molecules of $ZnSO_4{\cdot}7H_2O$.

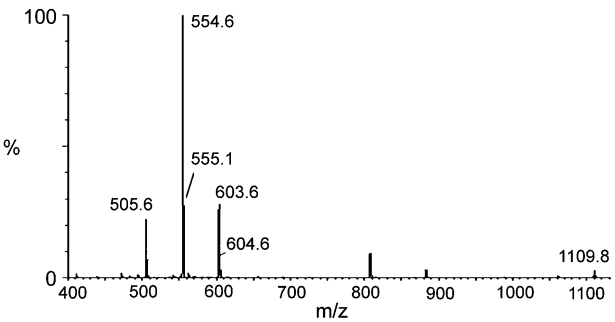

Fig. 5 Negative-ion mode ESI-MS spectrum of **1**.

which agree well with the calculated values of 1109.5 and 554.2, respectively. These data further proved that sulfate ion is chelated tightly in the molecular capsules in solution.

Binding of L with other anions was also tested by ^{1}H NMR spectroscopy. Addition of half equivalent of Zn(II) salt, *e.g.* $Zn(ClO_4)_2$, $Zn(NO_3)_2$ or $Zn(OAc)_2$ to a 10 mM solution of L in DMSO-d_6 resulted in only minor changes (0.00–0.09 ppm) of the two NH protons relative to the receptor L. Compared to the sulfate ion, these anions show much weaker interaction with the tris(urea) ligand in solution.

In summary, we designed a tris(3-pyridylurea) receptor (L) that constructs cages to encapsulate sulfate ion. Aggregation of the molecular capsules $[SO_4^{2-} \subset L_2]$ through second-sphere coordination of transition metals $[M(H_2O)_6]^{2+}$ with the pyridyl functions of L leads to a three-dimensional structure. ^{1}H NMR spectroscopy and negative-ion mode ESI-MS spectrometry show that the binding of sulfate ion is rather strong and the capsules can exist in solution with a considerable stability.

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Notes and references

‡ *Synthesis* of **1**: A methanol solution (20 mL) of L (50.6 mg, 0.10 mmol) and an aqueous solution (5 mL) of $MnSO_4$ (7.6 mg, 0.05 mmol) were mixed and heated for 10 min with stirring. A small amount of precipitate was removed and the filtrate was allowed to evaporate slowly for several days to give pink crystals (54.1 mg, 85%); mp 163 °C. Anal. found: C 44.91, H 5.32, N 21.67; calc. for $Mn(H_2O)_6L_2SO_4$ ($C_{48}H_{72}MnN_{20}O_{16}S$): C 45.32, H 5.70, N 22.02%. *Synthesis* of **2**: The zinc compound was synthesized by slow diffusion of a methanol solution of L (25.3 mg, 0.05 mmol) into an H_2O–MeOH solution of $ZnSO_4{\cdot}7H_2O$ (7.2 mg, 0.025 mmol). Colorless crystals were obtained after a week. Yield (22.8 mg, 71%); mp 164 °C. Anal. found: C 45.26, H 5.37, N 21.54; calc. for $Zn(H_2O)_6L_2SO_4$ ($C_{48}H_{72}ZnN_{20}O_{16}S$): C 44.95, H 5.66; N 21.84%. See ESI† for IR and NMR data.

§ *Crystal data* for L: $C_{24}H_{30}N_{10}O_3{\cdot}0.3H_2O$ (511.98), colorless block, monoclinic, space group $C2/c$, a = 25.496(2), b = 9.7959(8), c = 20.339(2) Å, β = 94.159(2)°, V = 5066.5(7) Å^3, T = 293(2) K, Z = 4, D_c = 1.342 g cm^{-3}, F_{000} = 2168, μ = 0.094 mm^{-1}, 14978 refl. collected, 6001 unique (R_{int} = 0.0401), 3192 obs. ($I > 2\sigma(I)$); $R1$ = 0.0527, $wR2$ = 0.1242. *Crystal data* for **1**: $C_{48}H_{72}MnN_{20}O_{16}S$ (1272.26), pale-pink block, monoclinic, space group $P2_1/n$, a = 12.516(3), b = 18.505(4), c = 13.186(3) Å, β = 91.38(3)°, V = 3053(1) Å^3, T = 293(2) K, Z = 2, D_c = 1.384 g cm^{-3}, F_{000} = 1338, μ = 0.332 mm^{-1}, 17 921 refl. collected, 6945 unique (R_{int} = 0.0246), 4886 obs. ($I > 2\sigma(I)$); $R1$ = 0.0362, $wR2$ = 0.0886. *Crystal data* for **2**: $C_{48}H_{72}ZnN_{20}O_{16}S$ (1282.69), colorless block, monoclinic, space group $P2_1/n$, a = 12.453(1), b = 18.414(2), c = 13.124(1) Å, β = 91.499(1)°, V = 3008.5(5) Å^3, Z = 2, D_c = 1.416 g cm^{-3}, F_{000} = 1348, μ = 0.525 mm^{-1}, 18 094 refl. collected, 7126 unique (R_{int} = 0.0342), 4687 obs. ($I > 2\sigma(I)$); $R1$ = 0.0388, $wR2$ = 0.0905. CCDC 670346–670348. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719019k

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