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PAPER

Encapsulation of divalent tetrahedral oxyanions of sulfur within the rigidified dimeric capsular assembly of a tripodal receptor: first crystallographic evidence of thiosulfate encapsulation within neutral receptor capsule†

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A simple tris(2-aminoethyl)amine based *meta*-chloro substituted tripodal thiourea receptor **L** has been extensively studied with two divalent oxyanions of sulfur, such as sulfate and thiosulfate, with identical dimensionality. The solid state crystal structure of the anion complexes with **L** reveal that the anions are encapsulated within the dimeric rigid capsular assembly of the receptor *via* N–H···anion interactions. To the best of our knowledge this is the first report on the encapsulation of thiosulfate within dimeric capsular assembly of a neutral receptor. The tight capsular sizes for both anion complexes are quite comparable, whereas the coordination mode of the anions and the hydrogen bonding parameters are significantly varied. The three dimensional solid state structural orientations of the capsular complexes are mainly governed by the Cl···Cl (for thiosulfate complex) and Cl···S (for sulfate complex) halogen bonding interactions. The solution-state binding and encapsulation of oxyanions by N–H···anion hydrogen bonding has also been confirmed by quantitative ^{1}H NMR titration and 2D NOESY NMR experiments. Both the experiments confirm that in contradiction of 2 : 1 solid state binding, in solution the studied anions are bound within the pseudocavity of the receptor with 1 : 1 binding stoichiometry. Moreover, the change in chemical shifts of thiourea –NH protons and the binding constant values suggest the receptor–sulfate interaction is more energetically favorable compared to the receptor thiosulfate interaction.

Introduction

The field of anion coordination chemistry continues to expand with new synthetic molecules capable of recognizing anions which are not only within the interest of supramolecular chemistry but also have vast significance in environmental and clinical applications.[1,2] The observations in natural anion binding systems have motivated researchers to develop several neutral receptors that employ hydrogen bonds offered by specific binding sites from amides,[3] urea/thiourea,[4] pyrroles,[5] and indole[6] functionalities for the recognition and binding of size- and shape-selective anionic guests on appropriate frameworks in various media. Acyclic receptors with multi-armed hydrogen-bonding functionality have been frequently found to coordinate with targeted anionic species *via* the formation of monomeric and dimeric capsular assemblies.[7] The most interesting features of molecular capsules is their ability to create an anion specific cavity that isolates the encapsulated guest from the bulk of the solvent media and thereby leads to the molecular sorting phenomena, when there is a possibility of formation different capsular assembly in the same solution.[8] The high solvation energies of anions must be compensated for by the host for effective anion recognition in competitive media.[9] In this context, the structure of the receptor requires a tailored design where the receptor satisfies the higher coordination numbers required for the binding of anions and hydrated anions. Tris-(2-aminoethyl)amine-based (tren-based) urea/thiourea functionalized tripodal scaffolds offer a flexible and structurally preorganized cavity, which has been widely employed in the binding and recognition of anions because of their favorable conformation for multiple hydrogen bonds that favor the formation of a stable host–guest complex.[10]

Among the various oxyanions, the harmful effect of sulfate (tetrahedral oxyanion) has been recognized as a prominent species of concern in cleanup processes of nuclear waste and hard water; *e.g.*, contamination of nuclear waste sites by this anion has been a matter of increased concern, hampering the vitrification process.[11] Because of its large standard Gibb's energy of hydration (−1080 kJ mol^{-1}), extraction of sulfate ions from an aqueous to an organic phase presents a particularly challenging task.[10b] To defeat this problem the receptor must have both exceptional affinity and selectivity for the sulfate ion. In this regard the most promising approach can be obtained from Nature's sulfate-binding protein, where sulfate isolation from the

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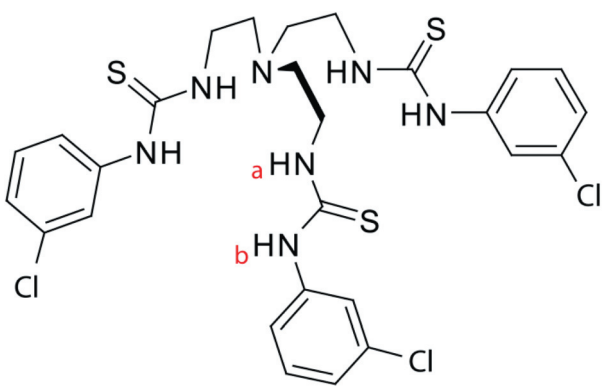
† Electronic supplementary information (ESI) available: Additional crystallographic data; characterization data; PXRD of complexes; ^{1}H NMR titration spectra. CCDC reference numbers 879915 (**1**) and 879916 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30999h

surrounding solvent is achieved by encapsulation of the anion inside hydrophobic cavities functionalized with suitable binding groups. The crystal structure of SBP reveals that an individual sulfate anion is completely encapsulated within the core of the protein (8 Å below the surface), between the two lobes of SBP through seven hydrogen bonds involving five from peptide –NH groups, one from serine –OH group, and the last from the tryptophan –NH group. In recent years the tren-based tripodal trisurea/thiourea backbone has also been found to encapsulate the sulfate ion in a 1 : 1 or 2 : 1 (host–guest) ratio, and some of them have been efficiently employed in sulfate-ion separation based on liquid–liquid anion-exchange technology or competitive crystallization techniques.[10a,e,m] In recent review, Ghosh and co-worker give a nice account of sulfate recognition and extraction by various synthetic receptors.[10l]

Another tetrahedral sulfur-containing oxyanion is thiosulfate, widely used (as the sodium salt) in different fields, for instance, the photographic industry, analytical chemistry (iodometric titration), paper making, gold extraction and also useful in a surprisingly broad range of clinical situations.[12] Moreover, sodium thiosulfate has been safely used as a therapeutic agent for a long time (almost 100 years). Nowadays it is widely used as an antidote for the treatment of cyanide poisoning,[12b] by converting cyanide to thiocyanate (excreted in the urine), catalyzed by the enzyme rhodanase and also found useful in prevention of the toxicity of cisplatin in cancer therapy. It reacts with free radicals (oxygen) to form a sodium sulfate compound which prevents the radicals from destroying or attacking the living cells. Additionally, it has also been used as potential remedy of renal diseases[12c] and anti-fungal (tinea versicolor) infections. These versatile applications of the thiosulfate anion make it an important target analyte for recognition. In this regard the slow release or transport of thiosulfate anion in the specific target site *via* encapsulation would be a promising approach in its clinical application.

In our ongoing effort in the field of anion receptor chemistry,[13] herein, we report the solid and solution state binding of two tetrahedral sulfur containing oxyanions (sulfate and thiosulfate) of a chloro-substituted tris(thiourea) receptor, **L** (Scheme 1), in DMSO. The solid state crystal structure of both the anions with **L** reveals that the anions are encapsulated within the dimeric capsular assembly of the receptor with optimal N–H···O and N–H···S hydrogen bonding coordination. The sizes of tight capsular assemblies for both anions are quite comparable, whereas the coordination mode of the anions and the hydrogen bonding parameters are noticeably varied. The three dimensional solid state structural orientations of the capsular complexes are mainly governed by the Cl···Cl and Cl···S halogen bonding interaction, which is directional in nature and has two types of preferred geometries, as nicely generalized by Desiraju and Guru Row.[14] Moreover, the receptor anion solution state interactions are also studied in detail by NMR experiments in DMSO-d_6 at RT. Interestingly, in contradiction of 2 : 1 solid state binding, the results from solution state NMR experiments confirm that both the anions are bound within the pseudocavity of the receptor **L** with 1 : 1 binding stoichiometry.



Scheme 1 Molecular structure of a tris(thiourea) receptor, **L**.

Experimental

Materials and methods

All reagents were obtained from commercial sources and used as received. Solvents were distilled freshly following standard procedures. Tris(2-aminoethyl)amine (tren), 3-chlorophenyl isocyanate, and tetraalkylammonium salts were purchased from Sigma-Aldrich and used as received. Solvents for synthesis and crystallization experiments were purchased from Merck, India, and used as received.

Instruments

IR spectra were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000–400 cm^{-1}. NMR spectra were recorded on a Varian FT-400 MHz instrument. Chemical shifts were recorded in parts per million (ppm) on the scale solvent peak as reference. ESI-MS spectra were recorded in a WATERS LC-MS/MS system, Q-Tof Premier in the Central Instrument Facility (CIF) of IIT Guwahati.

X-Ray crystallography

Intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo K_α radiation (λ) 0.71073 (Å) at 298 K, with increasing ω (width of 0.3° per frame) at a scan speed of 5 s per frame. The SMART software was used for data acquisition. Data integration and reduction were performed with SAINT and XPREP software.[15] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[16] Structures were solved by direct methods using SHELXS-97[17a] and refined with full-matrix least squares on F^2 using the SHELXL-97[17b] program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to all carbon and nitrogen atoms were geometrically fixed, and the positional and temperature factors were refined isotropically. Structural illustrations have been drawn with MERCURY[18] for Windows. A summary of the crystal data and relevant refinement parameters are given in Table 1. CCDC 879915 (**1**) and 879916 (**2**) are contained the supplementary crystallographic data for this paper.†

Table 1 Crystal parameters and refinement data

Compound	Complex **1**	Complex **2**
Formula	$C_{86}{\cdot}H_{132}{\cdot}Cl_6{\cdot}N_{16}{\cdot}O_4{\cdot}S_7$	$C_{70}{\cdot}H_{100}{\cdot}Cl_6{\cdot}N_{16}{\cdot}O_3{\cdot}S_8$
Formula weight	1891.27	1682.92
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	13.8087(7)	13.7854(14)
b/Å	14.3169(7)	25.836(3)
c/Å	26.6346(14)	48.851(5)
α/°	93.887(3)	90.00
β/°	98.290(3)	95.818(6)
γ/°	97.087(3)	90.00
V/Å	5151.1(5)	17309(3)
Z	2	8
T (K)	298(2)	298(2)
μ (cm^{-1})	0.361	0.444
d_{cal}/g cm^{-3}	1.130	1.292
Cryst dimens/mm^3	0.32 × 0.028 × 0.26	0.30 × 0.29 × 0.25
No. of reflns collected	25 686	21 045
No. of unique reflns	25 645	20 954
No. of params	1092	846
R_1; wR_2 ($I > 2\sigma(I)$)	0.2527, 0.2990	0.1951, 0.3113
R(int)	0.0984	0.0945
GOF (F^2)	1.173	1.062
CCDC no.	879915	879916

NMR studies

^{1}H NMR titration studies were done to determine the binding constants of **L** for sulfate and thiosulfate in DMSO-d_6 at room temperature. Initial concentrations were $[ligand]_0$ = 5 mM, and $[anion]_0$ = 50 mM. Each titration was performed by 10–12 measurements at room temperature. The association constant K was calculated by fitting two NH signals with a 1 : 1 binding model, using the equation $\Delta\delta = ([A]_0 + [L]_0 + 1/K - (([A]_0 + [L]_0 + 1/K)^2 - 4[L]_0[A]_0)^{1/2})\Delta\delta_{max}/2[L]_0$ (where L is the ligand and A is the anion).[19] The error limit in K was less than 10%.

Synthesis and characterization

Receptors L. Tripodal receptor **L** was synthesized by slight modification of a reported literature procedure[13e] where the reaction of tris(2-aminoethyl)amine (tren) with 3-chlorophenyl isothiocyanate in a 1 : 3 molar ratio at room temperature yielded the receptor in quantitative yield. A total of 1.98 g (3 mmol) of 3-chlorophenyl isothiocyanate was dissolved in 30 mL of dry tetrahydrofuran (THF) in a 100 mL round-bottomed flask and 0.146 ml (1 mmol) of tren dissolved in 10 mL of dry THF were added dropwise over a period of 15 min with constant stirring at

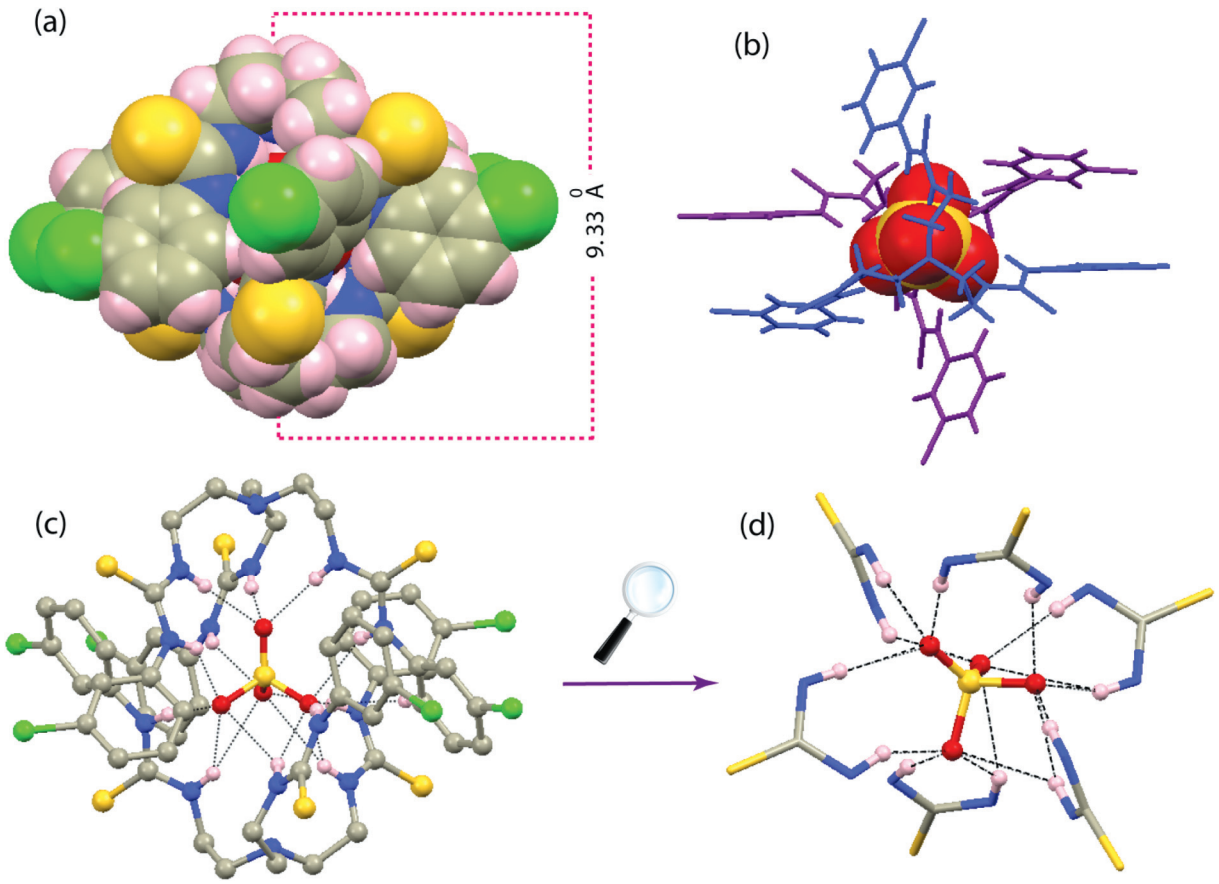


Fig. 1 (a) Space-filling representation depicting full encapsulation of the SO_4^{2-} anion. (b) Sulfate encapsulation by the crystalline self-assembled capsules **L**, Two molecules of **L**, shown as stick models and sulfate are shown as a space-filling model. (c) Ball-and-stick presentation depicting the 15 hydrogen-bonding contacts on SO_4^{2-} within the dimeric capsule of **L**. (d) Magnified view showing coordination of SO_4^{2-} with the 12 –NH groups of the dimeric capsule. TBA countercations are omitted for clarity of presentation.

room temperature. The resulting solution mixture was stirred 12 hours at room temperature. Then, the volume of the solvent (THF) was reduced *in vacuo* by using rotary evaporator, and the obtained solid product was filtered off and washed with 10 mL of dichloromethane a couple of times to remove the unreacted starting materials and impurities. The colorless precipitate was collected and dried in air and characterized by NMR, FT-IR, ESI-MS. Yield 88%.

Melting point: 183 °C, ^{1}H NMR (DMSO-d$_6$) δ (ppm): 9.73 (s, H–N), 7.81 (s, H–N) 7.66 (s, 1H), 7.31 (m, 2H), 7.128 (t, 1H), 3.50 (d, 2H) 2.74 (d, 2H), ^{13}C NMR (DMSO-d$_6$) δ (ppm): 41.91, 52.00, 121.11, 122.23, 123.65, 130.18, 132.77 140.95 and 180.30. FT-IR (ν, cm^{-1}): 1589 (C═C), 1556 (C═S sym), 766 (C═S, asym) 3227 (N–H), 3326 (N–H), ESI(+ve) mass spectrometry: 656.28.

Synthesis and characterization of complex 1 2TBA[2L·(SO_4^{2-})]. Sulfate-encapsulated complex **1** was obtained by mixing **L** and (n-TBA)$_2$SO$_4$/(n-TBA)HSO$_4$. In both the cases, 50 mg of **L** was dissolved in 5 mL of DMSO in a 25 mL round-bottomed flask. In the case of the (n-TBA)$_2$SO$_4$ salt, 3 mL of (n-TBA)$_2$SO$_4$ (50 wt% in water) was added at once to the 5 mL of **L** solution whereas, in other case 25 mg of n-TBAHSO$_4$ was added at a time to the 5 mL of **L**. Then in both cases, the mixtures were stirred for 1 hour at room temperature and allowed to crystallize at room temperature in open test tubes. From both the solutions, colorless crystals of the sulfate complex of **L**, [2**L**(SO4^{2-})]·2TBA (**1**), suitable for X-ray diffraction were obtained after seven–ten days. Isolated yield of **1** is (31 mg) 88%

Melting point: 184 °C, ^{1}H NMR (DMSO-d$_6$) δ (ppm): 10.36 (s, H–N), 8.69 (s, H–N) 7.82 (s, br, 3H), 7.38 (s, br, 3H), 7.17 (s, br, 3H), 7.026 (s, br, 3H) 3.50 (s, br, 6H), 3.13 (s, br, 8H) 2.59 (s, br, 6H), 1.53 (s, br, 8H) 1.28 (s, br, 8H) 0.90 (s, br, 12H) ^{13}C NMR (DMSO-d$_6$) δ (ppm): 13.49, 19.22, 23.08, 41.91, 53.29, 57.598, 120.90, 122.07, 122.91, 129.37, 132.21 141.69 and 180.24 FT-IR (ν, cm^{-1}): 1085 (SO_4^{2-}), 1604 (C═C), 1538 (C═S sym) 784 (C═S, asym), 3277 (N–H, br).

Synthesis and characterization of complex 2 2TEA[2L·($S_2O_3^{2-}$)]. Thiosulfate-encapsulated complex **2** was obtained by charging previously prepared 5 ml aqueous solution containing equimolar mixture of (n-TEA)Cl and $Na_2S_2O_3$ (10 equivalent each) into a 8 mL DMSO solution of **L** (50 mg). Then the mixture was stirred for 15 min at room temperature and warmed at 60 °C for 5 min. After cooling to room temperature, the resulting solution was filtered using a filter paper. Filtrate was collected in 20 mL test tube and allowed to crystallize at room temperature. Colorless crystals suitable for single-crystal X-ray crystallographic analysis of [2**L**($S_2O_3^{2-}$)]·2TEA are obtained after ten days. Isolated Yield of **2** is (41 mg) 65%.

Melting point: 134 °C, ^{1}H NMR (DMSO-d$_6$) δ (ppm): 10.30 (s, H–N), 8.53 (s, H–N), 7.83 (s, 3H) 7.45 (d, 3H), 7.22 (t, 3H), 7.05 (d, 3H), 3.53 (s, 6H), 3.16 (q, 8H) 2.64 (d, 6H), 1.18 (t, 12H) ^{13}C NMR (DMSO-d$_6$) δ (ppm): 7.10, 42.05, 51.47, 53.35, 121.12, 122.12, 123.04, 129.61, 132.30, 141.65 and 180.15. FT-IR (ν, cm^{-1}): 1095 ($S_2O_3^{2-}$), 1590 (C═C), 1531 (C═S sym) 778 (C═S, asym), 3277 (N–H, br).

Table 2 Hydrogen-bonding contacts on SO_4^{2-} and $S_2O_3^{2-}$ anions within the dimeric cage of **L** in complexes **1** and **2**

D–H···A	H···A	D···A	D–H···A/°
Complex **1**			
N3H···O1	2.313	3.016(9)	139.0(3)
N4H···O1	2.209	3.007(8)	154.1(4)
N5H···O1	2.63	2.977(9)	157.9(4)
N6H···O1	2.384	3.09(1)	139.9(4)
N2H···O2	2.628	3.343(9)	141.4(3)
N5H···O2	2.286	3.010(9)	141.9(4)
N6H···O2	2.651	3.388(9)	144.4(3)
N7H···O2	2.071	2.92(1)	169.3(4)
N2H···O3	2.551	3.275(9)	142.4(3)
N3H···O3	2.068	2.92(1)	170.8(4)
N4H···O3	2.501	3.21(1)	140.7(4)
N7H···O3	2.333	3.041(9)	139.9(4)
N2H···O4	2.023	2.923(9)	177.7(4)
N4H···O4	2.22	3.05(1)	163.2(4)
N6H···O4	2.03	2.89(1)	179.1(4)
N9H···O5	2.11	2.82(1)	140.7(4)
N10H···O5	2.70	3.39(1)	138.1(4)
N11H···O5	2.076	2.833(9)	146.4(5)
N13H···O5	2.140	2.881	144.2(5)
N10H···O6	2.154	2.89(1)	143.2(4)
N12H···O6	2.357	3.13(1)	151.0(5)
N13H···O6	2.277	3.131(9)	171.7(5)
C36H···O6	2.386	3.16(1)	140.3(5)
N9H···O7	2.065	2.918(9)	171.9(4)
N10H···O7	2.625	3.40(1)	150.3(4)
N11H···O7	2.655	3.330(9)	136.2(4)
N12H···O7	2.098	2.92(1)	160.0(5)
N14H···O7	2.310	3.142(9)	162.9(6)
N10H···O8	2.263	3.10(1)	163.2(4)
N11H···O8	2.131	2.97(1)	164.1(5)
N14H···O8	2.214	3.00(1)	151.0(6)
Complex **2**			
N4–H···O1	2.358	3.16(1)	154.4(6)
N5H···O1	2.208	3.05(1)	164.3(7)
N7H···O1	2.312	3.03(2)	141(1)
N12H···O1	2.102	2.94 (1)	162.8(7)
N3H···O2	2.112	2.97(7)	172.4(7)
N5H···O2	2.694	3.36(1)	134.6(6)
N2H···O2	2.580	3.34(1)	147.3(7)
N14H···O2	2.239	3.02(1)	151.6(7)
C18H···O2	2.679	3.51(2)	149(1)
N9H···O3	2.228	3.00(1)	149.8(7)
N11H···O3	2.192	2.96(1)	148.9(7)
N12H···O3	2.705	3.40(1)	138.4(7)
N13H···O3	2.249	3.04(1)	153.4(6)
N14H···O3	2.645	3.41	148.4(7)
N3H···S8	2.938	3.46(1)	121.2(7)
N6H···S8	2.457	3.29(1)	163(1)
N7H···S8	2.890	3.67(2)	152(1)
N10H···S8	2.486	3.30(1)	156.9(7)

Results and discussion

For a receptor to bind with the anionic guests, it should, in principle, possess preorganized directional H-bond donors tailored on a suitable platform/framework. Receptor **L** possesses a highly organized tripodal scaffold with three hydrogen-bonding thiourea functions appropriate for anion encapsulation *via* their optimal hydrogen bonding coordination. Efforts are made to find out the binding similarities and dissimilarities of receptor **L** towards two divalent tetrahedral oxyanions of sulfur (sulfate and thiosulfate) both in the solid and solution state. From the viewpoint of anion coordination chemistry, crystallization has

traditionally been a route to understand the structural details of the anion complexes formed, primarily by single-crystal XRD analysis. Fortunately, we were able to isolate single crystals of both sulfate and thiosulfate complexes of the receptor **L**, suitable for X-ray crystallographic analysis from individual solutions of **L** in presence of the respective anions. It is interesting to observe that both the anions are entrapped within the rigid supramolecular dimeric capsular assembly of the receptor **L** *via* N–H···anion interactions.

Structural description of complex 1

We attempted to grow single crystal of complexes of **L** with both HSO_4^- and SO_4^{2-} by charging their excess *n*-TBA salt. Interestingly in both cases the colorless crystals of the sulfate complex of **L** crystallize with good yield. They crystallize in the triclinic space group $P\bar{1}$. Two identical symmetric molecules of **L** flipped inward toward each other in a face-to-face fashion ($d_{N1\cdots N1}$ = 9.334 (6) Å) form a micro-cavity that encapsulates a sulfate anion (disordered, eight half occupied oxygen atoms) in its centre *via* hydrogen bonding to the six thiourea groups (Fig. 1). The asymmetric unit of complex **1** contains two symmetry-independent capsular units, exhibiting conformational isomorphism, their occurrence generally controlled by kinetic and thermodynamic crystal stability because these factors are mostly considered to be the consequences of interrupted crystallization. Both the capsular units are almost identical. In the first capsular unit the encapsulated sulfate anion is stabilized by a total of fifteen hydrogen bonding interactions between the twelve NH groups of two **L** moieties and four O atoms of SO_4^{2-}. Three out of the four oxygen atoms O1, O2 and O3 accept four hydrogen bonds each, while O4 accepts three hydrogen bonds in a trifurcated fashion. Apart from these hydrogen bonding interactions, there are also some weak C_{Phenyl}–H···O interactions present, which give extra stabilization to the encapsulated sulfate anion. Moreover, a close inspection of the hydrogen-bond parameters, especially the N–H···O angle *vs.* H···O distances, reveal that in the strong hydrogen bonding interaction region of $d_{H\cdots O} < 2.5$ Å and $d_{N\cdots O} \leq 3.2$ Å there are thirteen contacts (Fig. 5a). The second capsular unit present in the crystal lattice is quite similar to the first one, only the receptor anion hydrogen bonding parameters are slightly varied (Table 2). A similar type of sulfate encapsulation in a metal free system by tris thiourea based receptors was previously reported by Gale and co-workers.[10i] Interestingly, the sulfate-encapsulated dimeric cages are interlinked with one another through halogen-bonding interactions between the sulfur atom of the thiourea group and the *meta*-substituted chloride atom of the phenyl ring, with a separation distance of 3.482 (3) Å (*x*,*y*,*z*), and which subsequently form a 1D chain capsular assembly along the crystallographic *a* axis. Two such 1D arrays of capsular assemblies are further interconnected with one another *via* TBA cations by C–H···S interactions, and generate hexagonal networks of sulfate-encapsulated dimeric cages around each capsular unit along the *b* axis (Fig. 2). These added interactions contribute to the high stability of 1 (MP = 184). Moreover the presence of hydrogen bonded sulfate anions in complex **1** has also been confirmed by solid-state FT-IR analysis. The stretching frequency of –NH in complex **1** (ν 3277 cm^{-1}) shows a notable shift of 65 cm^{-1} with subsequent broadening of the peak in comparison to that of **L** (ν 3341 cm^{-1}), supporting the existence of strong N–H···O hydrogen bonds between **L** and the SO_4^{2-} anion. Furthermore, the presence of a moderate signal at 2873 cm^{-1} and a strong signal 1085 cm^{-1} in complex **1** can be attributed to the C–H stretching frequencies of the TBA groups and symmetric stretching frequency of the sulfate anion (Fig. S8, ESI†). Characteristically, the broad intense symmetric absorption band at ~1085 cm^{-1} is generally used to identify the presence of sulfate in individual complexes. The powder X-ray diffraction studies on bulk crystals obtained from both in the presence of SO_4^- and HSO_4^- matches closely with the simulated diffraction pattern obtained from the single-crystal structure of complex **1** suggesting that, even in the presence of HSO_4^-, the sulfate complex of the receptor **L** crystallizes (Fig. S13, ESI†).

Moreover, the formation of the sulfate complex even in presence of HSO_4^- anions can be attributed to the coordination

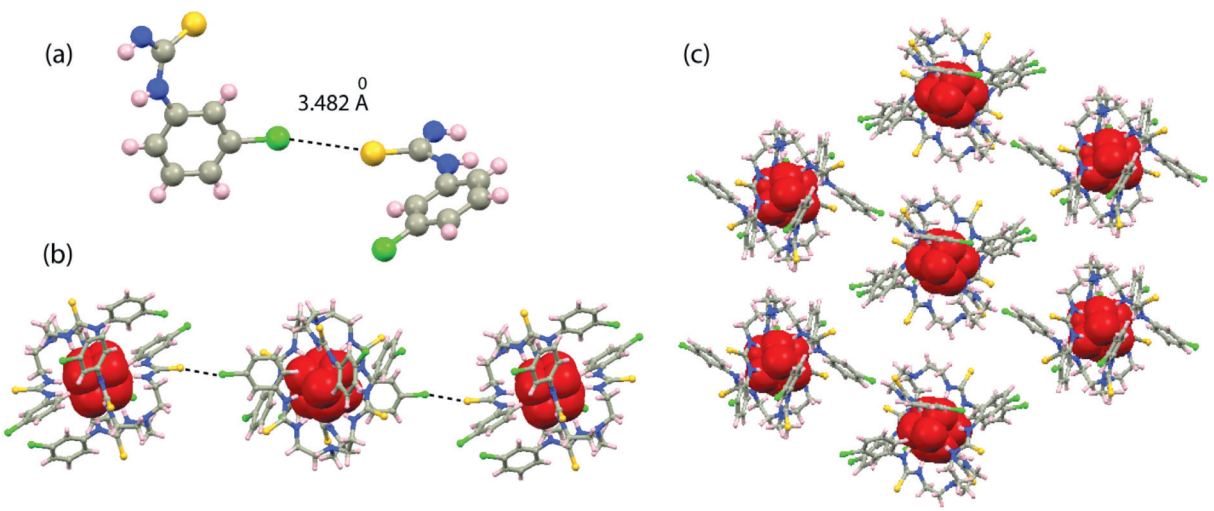


Fig. 2 (a) The Cl···S halogen bonding interaction between two capsular units in complex **1**. (b) Halogen bonding directed 1D capsular assembly along crystallographic *a* axis. (c) Crystal packing in complex **1**, as viewed down the crystallographic *b* axis.

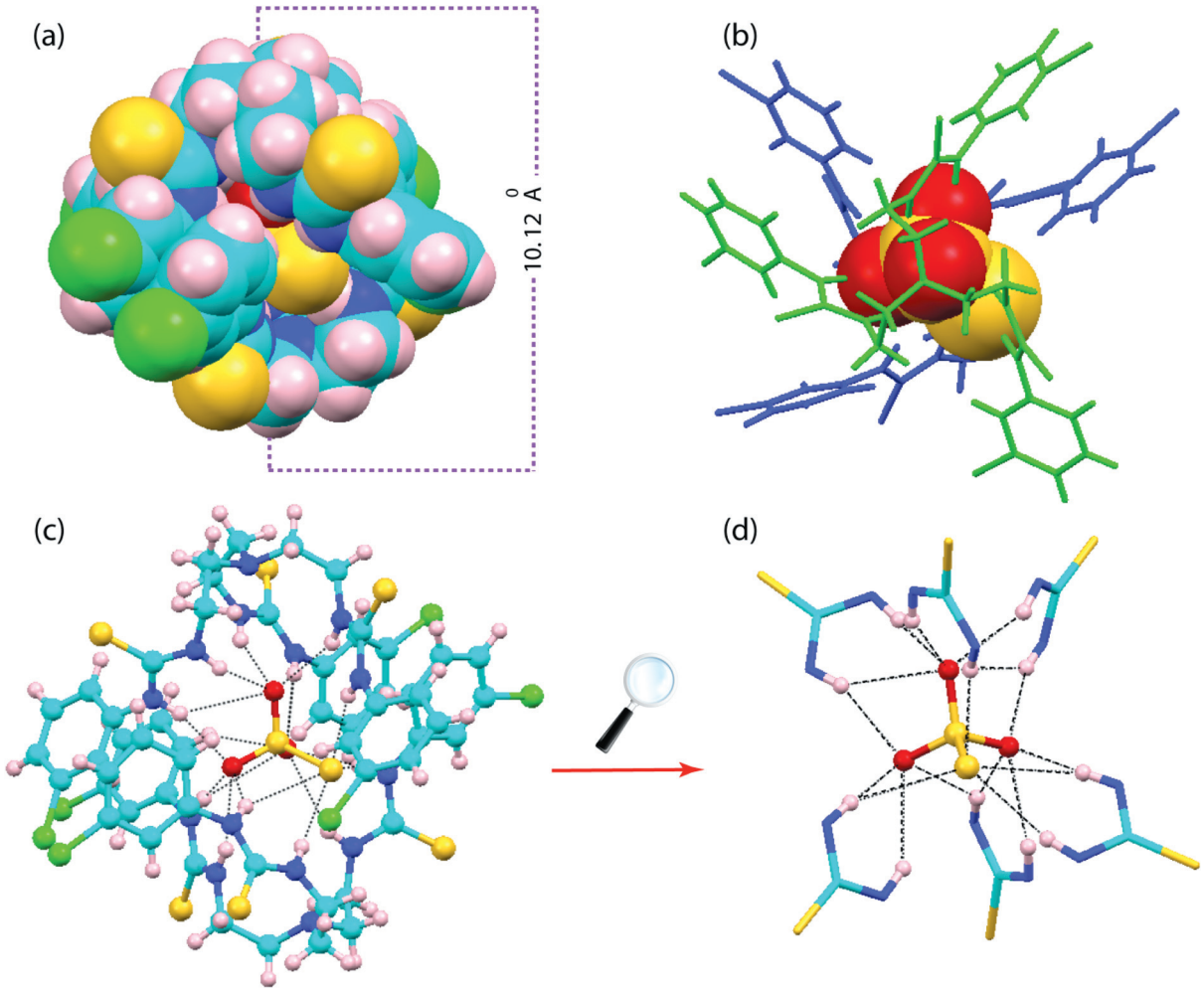


Fig. 3 (a) Space-filling representation depicting full encapsulation of the $S_2O_3^{2-}$ anion. (b) Thiosulfate encapsulation by the crystalline self-assembled capsules **L**, Two molecules of **L**, shown as stick models, and thiosulfate are shown as a space-filling model. (c) Ball and stick presentation depicting the 14 hydrogen-bonding contacts on $S_2O_3^{2-}$ within the dimeric capsule of **L**. (d) Magnified view showing coordination of $S_2O_3^{2-}$ with the 12 –NH groups of the dimeric capsule. TEA countercations are omitted for clarity of presentation.

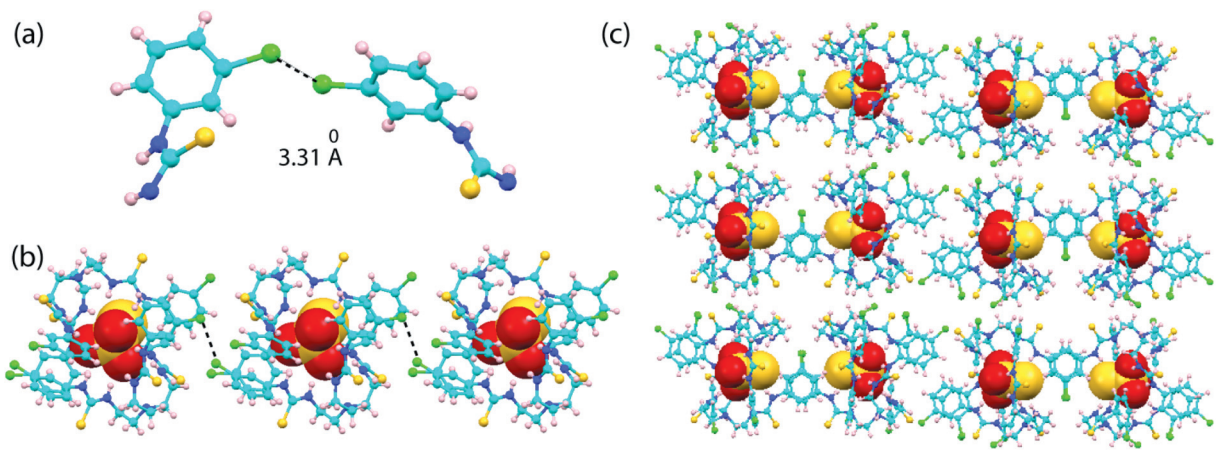


Fig. 4 (a) The Cl···Cl halogen bonding interaction between two capsular units in complex **2**. (b) Halogen bonding directed 1D capsular assembly along the crystallographic *a* axis (c) Crystal packing in complex **2**, as viewed down the crystallographic *bc* plane.

induced proton transfer between the free and bound anions; such solution-state deprotonations of the protonated state of an anion, *viz*., $H_2PO_4^-$, HCO_3^-, and HSO_4^- are quite well known in the literature.[10d] Essentially the formation of several hydrogen-

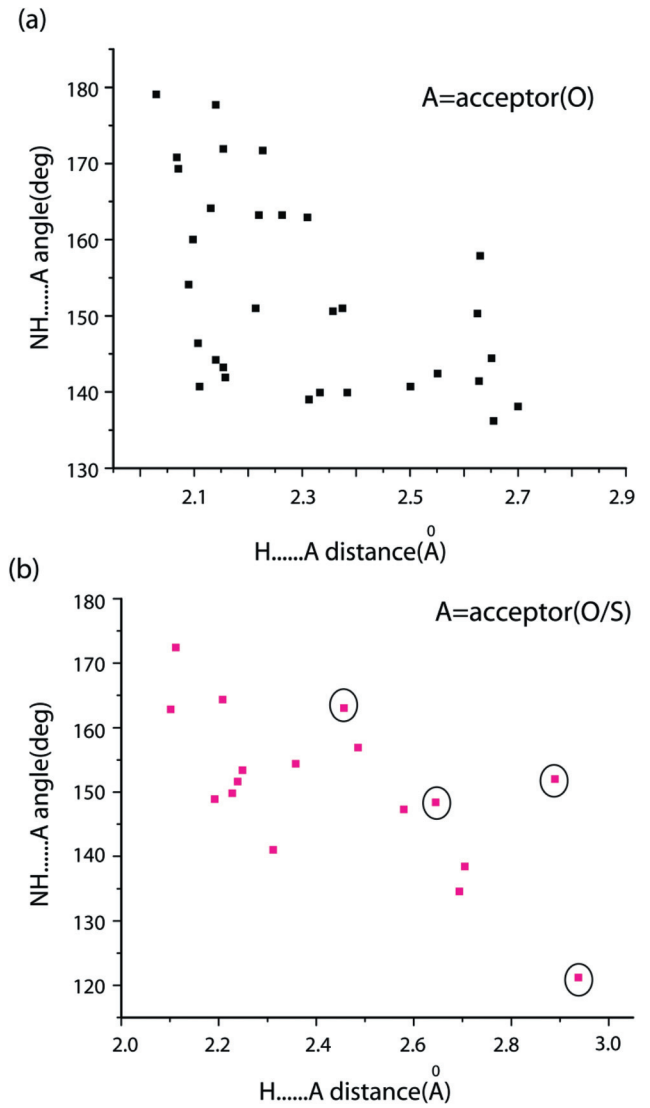


Fig. 5 (a) The scatter plot of the N–H···A angle *vs.* H···A distance of the hydrogen bonds for: (a) complex **1**; and (b) complex **2**. A = Acceptor (O\S); circled points indicate N–H···S interactions.

bonding interactions with the receptor significantly lowers the pK_a of the bound guest, which is eventually deprotonated by the free guest species present in solution.

Structural description of complex 2

The complex **2** was synthesized from the reaction between DMSO solutions of **L** and previously prepared aqueous mixture of TEACl and $Na_2S_2O_3$. Interestingly, the thiosulfate complex of **L** with a TEA counter cation was crystallized from slow evaporation of reaction mixture, suggesting geometric and electrostatic complementarity between $S_2O_3^{2-}$ and **L** that prefers the formation of a thiosulfate complex rather than a chloride complex. It is worth mentioning here that efforts were also made to crystallize an $S_2O_3^{2-}$ complex in presence of only $Na_2S_2O_3$, but these were not fruitful presumably because the thiosulfate encapsulated receptor segment does not prefer hydrophilic Na^+ or the hydrated Na^+ cation. This is also supported by the presence of a TEA counter cation instead of an Na^+ cation or hydrated Na^+ cation in the crystal lattice of complex **2**, while, it was crystallized from the mixture of both the Na^+ and TEA cations. The complex **2** crystallizes in the monoclinic system with centrosymmetric space group *C*2/*c*. Structural elucidation reveals two inversion-symmetric molecules of **L** are flipped inward toward each other in a face to face fashion [$d_{(N1\cdots N8)}$ = 10.12 (1) Å; (Fig. 3), with one ligand coordinating in the axial mode and the other in the facial mode, and thereby creating a micro cage supramolecular structure that encapsulates a thiosulfate anion in its centre *via* N–H···O and N–H···S hydrogen bonds by the six thiourea groups and the two receptors are assembled by π···π interactions of the chloro-phenyl rings (C1g···C6g = 3.755 Å and C2g···C5g = 3.996 Å). The capsular size of complex **2** (10.12 Å) is slightly larger (~0.8 Å) compared to complex **1** (9.33 Å), which may attributed to the larger size and lower charge density of the thiosulfate anion compared to sulfate. In addition to this, close inspection of complex **2** reveals that the N–H atoms of the thiourea functionalities are more directed towards three oxygen atoms of the encapsulated thiosulfate anion, resulting in the outer S8 atom of the thiosulfate anion being slightly out of the capsular cage, probably due to the

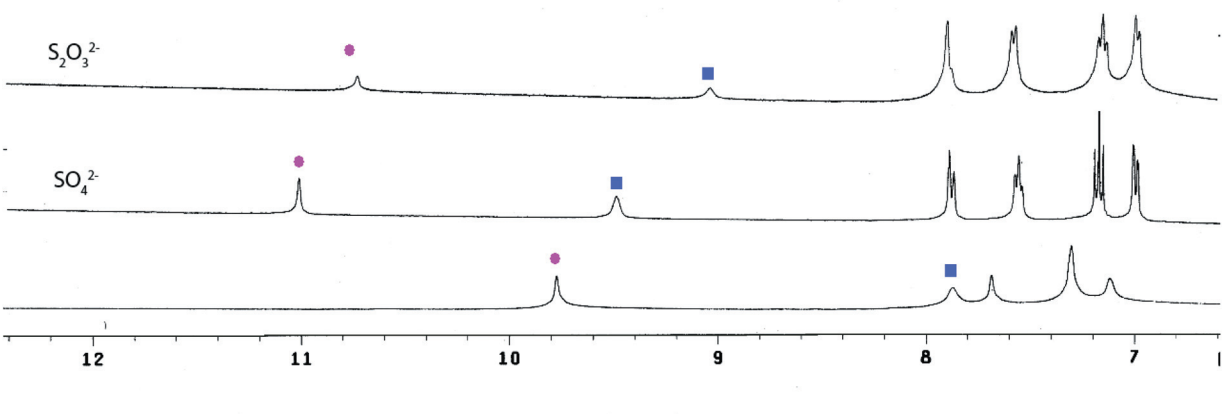


Fig. 6 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **L** and maximum observable shifts of thiourea –NH resonances upon the addition of excess (5 equiv.) SO_4^{2-} and $S_2O_3^{2-}$ anions.

larger S7–S8 bond distance and the lower charge density over the S8 atom compared to the three oxygen atoms. The TEA counter cations of complex **2** are disordered, and one TEA counter cation equally shares two positions in the asymmetric unit. There are thirteen N–H···O and four N–H···S hydrogen bonds of six thiourea groups that are responsible for stabilizing the encapsulated thiosulfate anion (Fig. 4). Two out of three oxygen atoms O1, and O2 accepts four hydrogen bonds each, while O3 accepts five hydrogen bonds. A correlation of the N–H···O angle *vs.* H···O distance (Fig. 5a) shows that in the strong hydrogen bonding interaction region of $d_{H\cdots O} < 2.5$ Å and $d_{N\cdots O} \leq 3.2$ Å, there are nine contacts stabilizing three oxygen atoms of the encapsulated thiosulfate anion. When compared to N–H···O interactions, the N–H···S interactions are relatively weak. The average values of the N···S distance and N–H···S angle are 3.43 Å and 148.2°, respectively. To the best of our knowledge this is the first report on the full encapsulation of thiosulfate anion within dimeric capsular assembly of a neutral receptor, although the first encapsulated thiosulphate complex within protonated cryptant host was previously reported by Nelson and co-workers.[20]

The thiosulfate-encapsulated dimeric cages are interlinked with one another through Cl···Cl (3.31(1) Å, 1/2 + *x*,1/2 + *y*,*z*) halogen bonding interactions, forming a 1D chain polymeric structure along the crystallographic *a* axis. Two such 1D arrays of capsular assemblies are further interconnected with one another by weak C–H···S interactions, forming a 2D layer structure along the crystallographic *b* axis (Fig. 4). Moreover, the presence of a hydrogen bonded thiosulfate anion in complex **2** has also been confirmed by solid-state FT-IR analysis. Analogous to complex **1** here also a significant shift (55 cm^{-1}) with subsequent broadening in the –NH signal compared to that of **L** is observed, indicating the presence of strong N–H···anion interaction between the thiourea functionalities of **L** and the thiosulfate anion. Additionally, the presence of a moderate signal at 1075 cm^{-1} can be attributed to the stretching frequency corresponding to the thiosulfate anion (Fig. S11, ESI†). As the complex **2** crystallizes in presence of more than one anion, therefore, it is required to verify the homogeneity of the isolated bulk crystal. The powder X-ray diffraction studies on isolated bulk crystals match perfectly with the simulated diffraction pattern obtained from the single-crystal structure of complex **2**, indicating the homogeneity of the isolated crystals of the thiosulfate capsules (Fig. S14, ESI†).

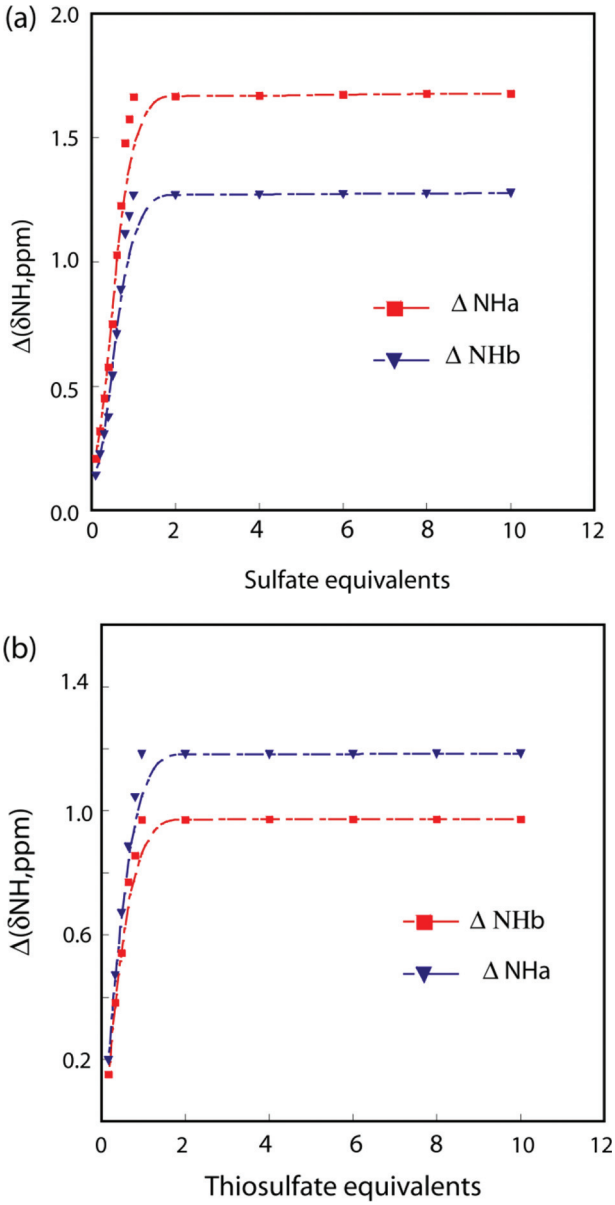


Fig. 7 ^{1}H NMR titration curves of **L** with (a) SO_4^{2-} and (b) $S_2O_3^{2-}$ anions in DMSO-d_6 at RT. Net changes in the chemical shifts of –NH are shown against the increasing amount of anion (50 mM). H_a = CH_2NHCS and H_b = CSNHAr.

Anion binding study by ^{1}H NMR spectroscopy

It is now well known in the field of supramolecular chemistry that the behavior of molecules/receptors in dilute or very dilute solution is really quite dissimilar from their behavior in molecular capsules in the solid state. Therefore, to find the mode of receptor–anion interaction in solution we have carried out qualitative as well as quantitative ^{1}H NMR titration and NOESY experiments in DMSO-d_6 at RT. Fig. 6 illustrates the qualitative test of both the anions, which shows the changes in chemical shift observed upon addition of 5 equivalents of each anion at once to the tris(thiourea) receptor **L** in DMSO-d_6 at RT. This preliminary study reveals the most substantial shifts have been observed for the thiourea protons (–NH_a and –NH_b), indicating that the –NH functions of the thiourea groups provide suitable sites of interaction between the receptor and anions in solution.

^{1}H NMR titration of receptor **L** with [*n*-TBA]SO_4^{2-} shows that upon gradual addition of standard SO_4^{2-} solution a large downfield shift of thiourea –NH resonances ($\Delta\delta$ –NH_a = 1.666 ppm; $\Delta\delta$ –NH_b = 1.267 ppm) and a small but important change in the chemical shift with subsequent splitting of the aryl –CH protons $\Delta\delta$ = 0.227, could be explained by the fact that the sulfate anion also significantly interacts with the C–H protons in solution (Fig. S6, ESI†). The considerably larger shift of –NH_a ($\Delta\delta$ = 1.66 ppm) relative to –NH_b signals ($\Delta\delta$ = 1.267 ppm) indicates there is an obvious discrepancy between the –NH_a···sulfate and –NH_b···sulfate binding modes, whereas, no such binding discrepancy of –NH protons was found in the solid state structure

of complex **1**. The change in the chemical shift of the –NH resonances of the NMR spectra, as recorded with an increasing amount of sulfate anion in solution at room temperature, gave the best fit for a 1 : 1 binding model (log K = 4.54), which are well consistent with the report of Gale for fluoride-substituted tris(thiourea) receptors.[10i] The 1 : 1 binding stoichiometry in DMSO-d_6 were further verified by the Job's plot analysis. The maximum change in the chemical shift during titrations for **L** is obtained when the mole fraction of sulfate anion has reached about 0.5, which suggests a host–guest binding in a 1 : 1 stoichiometry (Fig. S7, ESI†). Despite this, the crystal structure obtained for complex **1** revealed 2 : 1 complex stoichiometry.

Furthermore, ^{1}H NMR titration of **L** with standard sodium thiosulfate solution also occurs downfield shift of thiourea –NH resonances ($\Delta\delta$ –NH_a = 1.18 ppm; $\Delta\delta$ –NH_b = 0.97 ppm). Interestingly the degree of downfield shift of both the –NH resonances is lesser compared to the sulfate anion (Fig. 6). Here also there is a considerably larger shift of –NH_a ($\Delta\delta$ = 1.18 ppm) relative to the –NH_b signals ($\Delta\delta$ = 0.97 ppm), indicating –NH_a···anion interactions are more energetically favorable than NH_b···anion interactions (Fig. S10, ESI†). However, the solid state crystal structure of complex **2** shows equal participation from both the thiourea protons toward the thiosulfate anion within the rigid dimeric capsular cage of **L**. Moreover, the significant shift with concomitant splitting of the aryl –CH protons indicates that thiosulfate induces a change of the electronic environment of the phenyl rings of the receptor **L**. The association constants (log K) of **L** with $S_2O_3^{2-}$ were calculated from

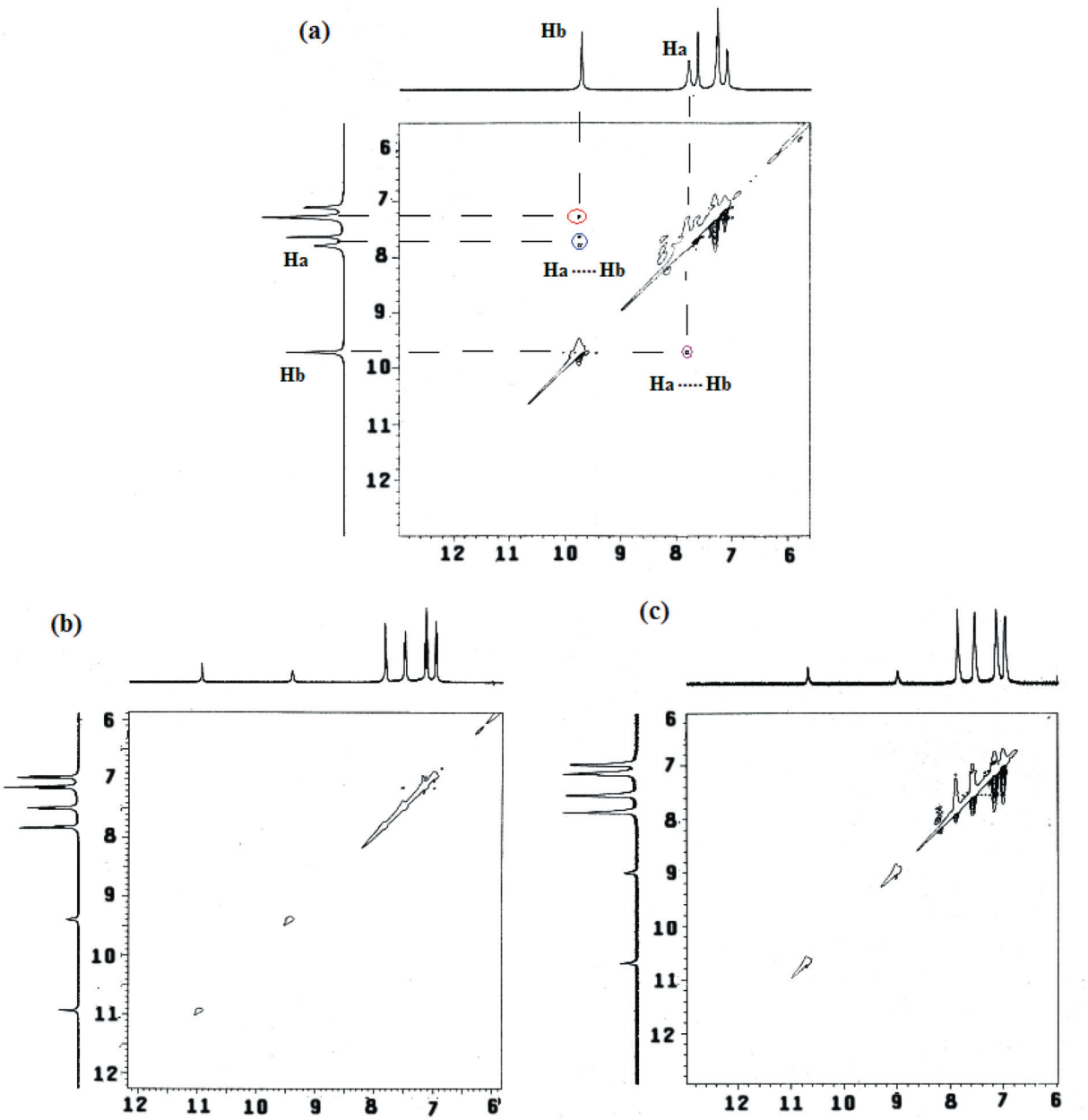


Fig. 8 2D NOESY NMR experiments of: (a) free receptor **L**; (b) **L** in presence of 1 equiv. of sulfate anion; and (c) **L** in presence of 1 equiv. of thiosulfate anion. All the spectra are taken in DMSO-d_6 at 298K.

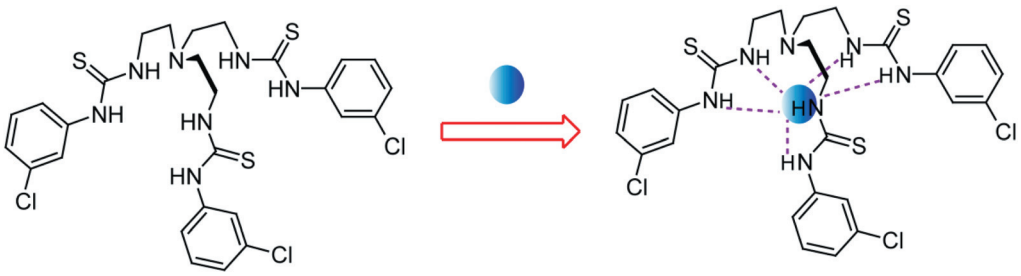


Fig. 9 Proposed binding mode of the receptor **L** for sulfate and thiosulfate anion in solution.

quantitative titration experiment and found to be log $K = 3.35$ by considering the 1 : 1 binding model, because no data fit for the Job plot experiment was obtained due to complex precipitation during the titration experiment. The comparatively large $\Delta\delta$ values for thiourea protons and the higher binding constant value of the sulfate anion can be attributed to the smaller size and higher charge density of sulfate anion compared to thiosulfate (Fig. 7).

The mode of receptor–anion interactions and the anion-induced electronic and conformational changes of the receptor can be illustrated by the 2D NOESY NMR experiment, which is a traditional and useful tool in the field of supramolecular host–guest chemistry. Therefore, for improved understanding of the solution state binding nature of the receptor toward the anions, we have carried out 2D NOESY NMR experiments both for free receptor (**L**) and anion complexes in DMSO-d_6 at RT (Fig. 8). The free receptor molecule shows a significantly strong NOESY signal between the thiourea protons $-NH_a$ and $-NH_b$. Interestingly, the through-space NOE signals are considerably weakened in both complexes, and completely absent upon addition of one equivalent of the respective anions (sulfate and thiosulfate), indicating a conformational change of **L** due to encapsulation of the anions in a 1 : 1 binding stoichiometry. A similar type of anion-encapsulation-induced change in NOESY spectra was previously reported by Hossain and Schneider for tren-based (urea) receptors.[10k, 19] In contradiction of the 2 : 1 solid state binding, the results from NMR experiments confirm that in solution the studied anions are bound to the pseudocapsular cavity of **L** with 1 : 1 binding stoichiometry (Fig. 9).

Conclusions

In conclusion, we have demonstrated the detailed solid and solution state binding comparison of two divalent oxyanions of sulfur with similar dimensionality (sulfate and thiosulfate) with a tris(thiourea) receptor **L**. The solid state crystal structures for the anion complexes reveal that the SO_4^{2-} and $S_2O_3^{2-}$ are encapsulated within the dimeric capsular assembly of the receptor by satisfying their optimal coordination through N–H···O and N–H···S hydrogen bonds with 1 : 2 stoichiometries. It was found the mode of encapsulation and capsular sizes for both anion complexes are quite comparable. To the best of our knowledge, this is the first crystallographic evidence of the full encapsulation of thiosulfate anion within dimeric capsular assembly of a neutral receptor. The three-dimensional solid-state crystal packing of the capsular complexes are mainly governed by the Cl···Cl (for the thiosulfate complex) and Cl···S (for the sulfate complex) halogen bonding interactions, giving added stabilization to the anion complexes. The solution-state binding and encapsulation of oxyanions by N–H···anion hydrogen bonding has also been confirmed by quantitative ^{1}H NMR titration and 2D NOESY NMR experiments. The change in the chemical shifts of the thiourea –NH protons and the binding constant values suggests the receptor binds more strongly to sulfate anions compare to thiosulfate. Furthermore, the 2D NOESY NMR and Job's plot experiments suggest that in solution the anions SO_4^{2-} and $S_2O_3^{2-}$ are encapsulated in the pseudocapsular cavity of **L** with 1 : 1 binding stoichiometry, indicating an obvious disagreement of the binding mode from that observed in their solid state crystal structures.

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