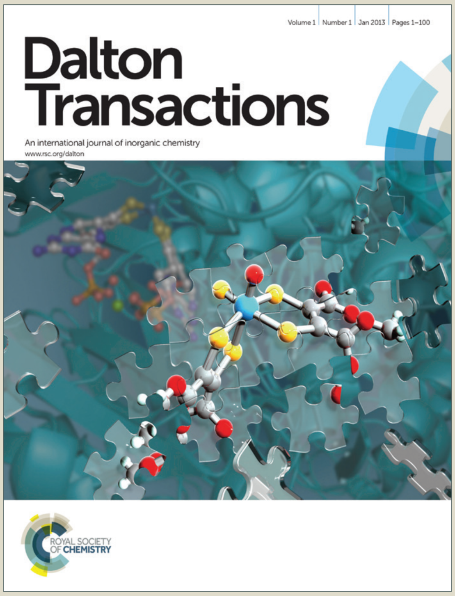
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Encapsulation of $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster in a metal organic framework of a pyridyl functionalized cyanuric acid based tris-urea

Ranjan Dutta,[a] Bidyut Akhuli[a] and Pradyut Ghosh*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

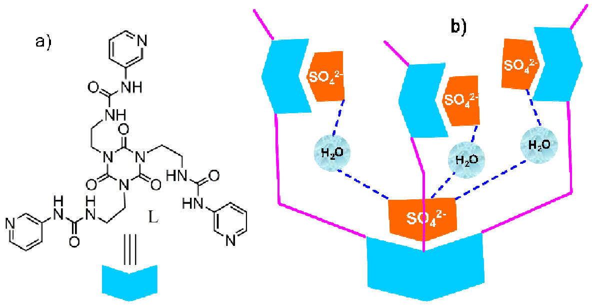
Encapsulation of hydrated sulfate in a bowl-shaped metal organic coordination polymer formed by Zn^{2+} assisted self-assembly of a 3-pyridyl terminated cyanuric acid platform based urea receptor is reported in aqueous medium. Trapping of unusual $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster in $[Zn(H_2O)_6]^{2+}$ capped self-assembled structure is characterized by single crystal X-ray crystallography. Furthermore, selective binding of SO_4^{2-} is established from ^{1}H-NMR titration study.

Recognition of hydrated anions is of great importance due to their presence in natural and biological environments.[1] High charge density and very high hydration energy of SO_4^{2-} (ΔG_h = -1080 kjmol^{-1})[2] assist the formation of different sulfate-water clusters in aqueous environment. Association of twelve hydrogen bonds from water molecules are predicted in the first hydration shell of SO_4^{2-} by theoretical calculation.[3] Sulfate-water clusters play crucial role in many environmental and biological processes such as aerosol formation, dissolution of protein in human body and regulation of various metabolic processes.[4] Same time SO_4^{2-} interferes in the vitrification process of nuclear waste and causes permanent hardness of water.[5] Thus, recognition of hydrated SO_4^{2-} is more relevant than naked SO_4^{2-} in the area of molecular recognition and self-assembly.

Various synthetic receptors having ammonium, amide, urea, indole functionalities have been employed for SO_4^{2-} recognition both in organic and aqueous medium.[6] Metal ion templated self-assembled structures provide a successful strategy for selective recognition of SO_4^{2-} via complete encapsulation.[7] Particularly, pyridyl-urea containing metallo-supramolecular structures are employed for SO_4^{2-} encapsulation either by discrete assembly or coordination polymer formation.[7c-j,m-o] In this context, Custelcean and Kaifer *et al.* have recently reported SO_4^{2-} encapsulation driven self-assembly process towards the formation of M_4L_6 cages in aqueous medium.[7h,i] However, encapsulation of hydrated-sulfate by synthetic receptors is rare in the literature. Such evidence of sulfate-water cluster recognition is reported by Das *et al.* via the isolation of a rugby ball shaped $[(SO_4)_2(H_2O)_3]^{4-}$ cluster in the dimeric capsular assembly of a tren based tris-urea receptor.[6c]

Herein we demonstrate a coordination driven self-assembly process of a cyanuric acid platform based tris-urea **L** in presence of $ZnSO_4/MgSO_4$ in aqueous methanol (1:1). Importantly, encapsulation of hydrated sulfate $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster in the self-assembled cavity is observed in case of Zn^{2+} whereas SO_4^{2-} assisted dimeric capsular assembly is observed in case of Mg^{2+}. Furthermore, we show selective binding of SO_4^{2-} over other anions by ^{1}H-NMR titration study.

Tripodal urea receptor **L** (Scheme 1a) is synthesized by the reaction of tripodal amine and 3-pyridyl isocyanate in moderate yield (Scheme 1S, ESI†). Slow evaporation of MeOH/H_2O (1:1) solution of **L** and $ZnSO_4$,$7H_2O$, results crystals of complex **1** with the composition $[\mathbf{L}_3Zn_3(SO_4)_4][Zn(H_2O)_6][(H_2O)_{18}]$ in high yield (~75%). However, crystals of dimeric capsules of complex **2** $[\mathbf{L}_2SO_4][Mg(H_2O)_6][(H_2O)_2]$ are obtained by slow evaporation of a MeOH/H_2O solution of **L** and $MgSO_4$. Complex **1** contains large amount of solvents in the unit cell and crystallographic parameters are given in Table 1S, ESI†.



Scheme 1. a) Molecular structure of **L** and b) pictorial representation of four hydrated SO_4^{2-} encapsulation in the bowl shaped secondary building unit.

Direct coordination of pyridyl nitrogen donor (Py-N) of **L** to Zn^{2+} generates the coordination polymer **1**, which propagates in three dimensions (Fig. 1a). Each bowl shaped secondary building unit (SBU) of **1** contains one central C_{3v}-symmetric receptor unit (**L**) at the bottom of the bowl, other three receptor units at the three sides of the bowl, three hexa-coordinated Zn^{2+}, four encapsulated SO_4^{2-} and one $[Zn(H_2O)_6]^{2+}$ cation (Scheme 1b). Each Py-N atom of the central **L** is coordinated to one Zn^{2+} each, thus forms a C_{3v}-symmetric cleft which encapsulates one SO_4^{2-} in its centre *via* N-H···O interactions (Table 2S, ESI†). Remaining coordination sites of Zn^{2+} are fulfilled by the coordination of two Py-N atoms of two side **L** units, one Py-N atom of another SBU and two water molecules (**O9** and **O10**) (Figure 7S, ESI†). Thus a bowl shaped SBU is generated where encapsulation of three reaming SO_4^{2-} anions are achieved in the cavity formed by three side-**L** units. In most of the sulfate assisted self-assembled structures encapsulation of a single SO_4^{2-} are observed in the solid state.[7g-j]

Thus, complex **1** represents a unique example of simultaneous encapsulation of as many as four SO_4^{2-} in a supramolecular assembly (Fig. 1b). Now each of four encapsulated SO_4^{2-} are interconnected by bridging water molecules *via* O-H···O interactions to form the $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster (Fig. 1c). Further insight into the coordination details of $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster reveals one O atom (**O6**) of the central SO_4^{2-} is solely H-bonded to three –NH groups (**N4-H4**) of central **L** unit.

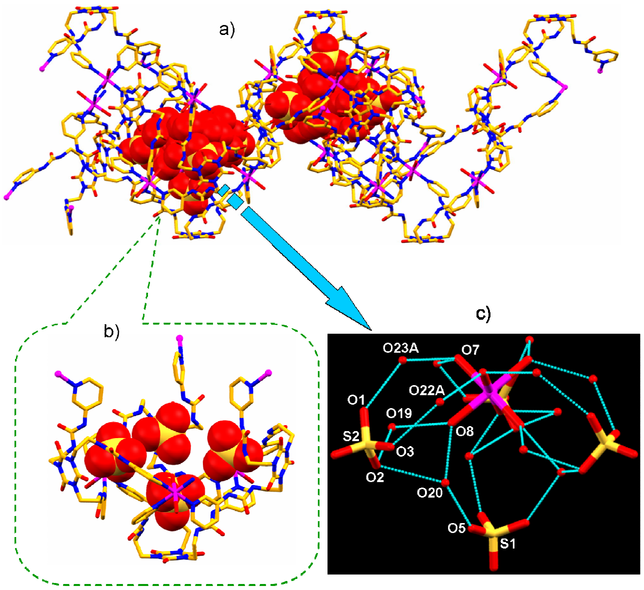


Fig. 1 a) View of $[Zn(H_2O)_6]^{2+}$ capped hydrated SO_4^{2-}, $[(SO_4)_4(H_2O)_{12}]^{8-}$ encapsulation in the cavity of metal-organic coordination polymer **1**; b) view of four SO_4^{2-} encapsulation in the bowl shaped SBU of **1**; c) close-up view of $[Zn(H_2O)_6]^{2+}$ capped hydrated SO_4^{2-}, $[(SO_4)_4(H_2O)_{12}]^{8-}$. All the hydrogens and lattice solvents are omitted for clarity.

Whereas each of the three remaining O atoms (**O5**) are H-bonded to one –NH group (**N5–H5A**) each. Furthermore, each **O5** is connected to O atom (**O2**) of each side SO_4^{2-} via a bridging water molecule (**O20**) (Figure 8S, ESI†). This bridging water molecule is further H-bonded to $[Zn(H_2O)_6]^{2+}$ cation. **O4** of the each side SO_4^{2-} are H-bonded to three –NH groups namely **N1–H1**, **N10–H10** and **N13–H13** of side **L** unit. Three remaining O atoms namely **O1**, **O2** and **O3** are H-bonded to one –NH group each namely **N12–H12, N2–H2** and **N9–H9** respectively (Figure 8S, ESI†). In addition **O1** and **O3** are connected to $[Zn(H_2O)_6]^{2+}$ through two disordered bridging water molecules namely **O23A** and **O22A** respectively. Whereas, **O2** is connected to $[Zn(H_2O)_6]^{2+}$ via a bridging water molecule **O19**. Furthermore, **O19** is connected to **O20** via **O9**. Thus, $[Zn(H_2O)_6]^{2+}$ capped $[(SO_4)_4(H_2O)_{12}]^{8-}$ cluster is recognized in the cavity of the bowl shaped SBU. Detail H-bonding interactions of $[(SO_4)_4(H_2O)_{12}]^{8-}$ with the receptor functionalities (C=O group of **L**) are provided in the ESI† (Figure 9Sb). Further, packing diagram of **1** shows a porous channel running along *c* axis (Figure 10S, ESI†). In contrast, tren based 3-pydridyl urea is reported to form SO_4^{2-} encapsulated dimeric capsular assembly irrespective of the counter cations, where the cation exists as $[M(H_2O)_6]^{2+}$ species [M = Zn^{2+}, Cd^{2+}, Mg^{2+}, Co^{2+}, Mn^{2+}].[7c] ESI-MS(negative mode) analysis of **1** shows peaks at 715.96 and 976.91 corresponding to monovalent $[\mathbf{L}+HSO_4]^-$ and divalent $[\mathbf{L}_3+SO_4]^{2-}$ species respectively (Figure 11S, ESI†). The bulk purity of **1** is verified by PXRD analysis of crystals of **1**, which matches well with the simulated pattern (Figure 12S, ESI†). Further, the solvent content of complex **1** is verified by thermogravimetric analysis (TGA), where a weight loss of 18.039% is observed ~130°C. This experimental weight loss corroborate with the calculated value (18.19%) from the crystal structure of **1** (Figure 13S, ESI†). Comparative IR study of **L** and **1** also confirms presence of SO_4^{2-} with a new peak at 1120 cm^{-1} (Figure 14S, ESI†), corresponding to the stretching frequency of SO_4^{2-}.

However, crystallographic analysis of $MgSO_4$ complex of **L** i.e. **2** reveals encapsulation of SO_4^{2-} in the dimeric capsular assembly of **L** (Fig. 2a). Twelve strong N-H···O interactions are involved to encapsulate the SO_4^{2-} inside the dimeric capsule (Fig. 2b). In this case Mg^{2+} cation exists as $[Mg(H_2O)_6]^{2+}$ species which hold the capsule via H-bonding interaction with –C=O group of **L** and Py-N atom through a bridging water (**O14**). Similar structural features are found in both the Mg-capsules derived from tren and cyanuric platform based 3-pyridyl urea except the H-bonding pattern of $[Mg(H_2O)_6]^{2+}$ cation. Capsular dimension of **2** is measured as 9.71 Å compared to the 9.65 Å in its tren analogue.[7c] Hydrogen bonding parameters and interactions of $[SO_4\mathbf{L_2}]^{2-}$ capsule with six $[Mg(H_2O)_6]^{2+}$ cations through second-sphere coordination are provided in the supporting information (Figure 15S & 16S, ESI†). Comparative IR spectra of **L** and **2** shows characteristics peak of SO_4^{2-} at 1095 cm^{-1} (Figure 17S, ESI†)

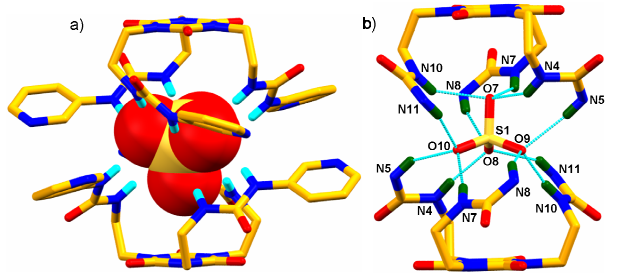


Fig. 2 a) View of complex **2** showing complete encapsulation of SO_4^{2-} in the dimeric capsular assembly of **L**; b) close-up view of twelve N-H···O interactions in **2**. Non-acidic hydrogens and countercation are omitted for clarity.

Solution state complexation study of **L** and $ZnSO_4$ is investigated by titrating a solution of **L** with $ZnSO_4$ in DMSO-d_6. Significant downfield shift of NHa (Δδ ~ 1.2 ppm) and NHb (Δδ ~ 1.4 ppm) protons are observed upon addition of ~1 equiv. of $ZnSO_4$ (Fig. 3a, Figure 18S, ESI†). Job's plot analysis by monitoring the chemical shift of NHa proton reveals 1:1 association between **L** and SO_4^{2-} in solution (Fig. 3b). This 1:1 association of **L** and SO_4^{2-} in solution is same as that of solid state biding pattern in **1**. Binding constant calculation shows *log K* value 5.47 for **L** with $ZnSO_4$ in DMSO-d_6. However, no such changes in chemical shift are observed for **L** with $Zn(AcO)_2$, $Zn(NO_3)_2$, $ZnCl_2$ and $Zn(ClO_4)_2$ as evident from qualitative ^{1}H-NMR analysis in DMSO-d_6 (Figure 19S, ESI†). Moreover, solution state binding of **L** and $ZnSO_4$ is verified by ITC study by titrating a solution of **L** with $ZnSO_4$ in DMSO (Fig. 4). The observed exothermic binding profile with 1:1 (host/guest) stoichiometry (n = 0.87±0.01) further support the ^{1}H-NMR data. The estimated kinetic and thermodynamic parameters (K, TΔS, ΔH and ΔG) of the above experiment are provided in the ESI† (Figure 20S).

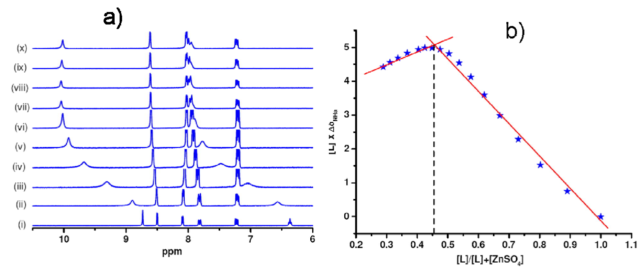


Fig. 3 (a) ^{1}H-NMR spectral changes of **L** with added $ZnSO_4$ in DMSO-d_6 ([**L**] is varied from 4.43 mM to 3.28 mM by the addition of aliquots of 34.08 mM $ZnSO_4$). Ratio of concentration [**L**]/[SO_4^{2-}]: (i) 0, (ii) 0.12, (iii) 0.37, (iv) 0.62, (v) 0.86, (vi) 1.11, (vii) 1.35, (viii) 1.72, (ix) 2.22, and (x) 2.71. (b) Job's plot for **L** with $ZnSO_4$.

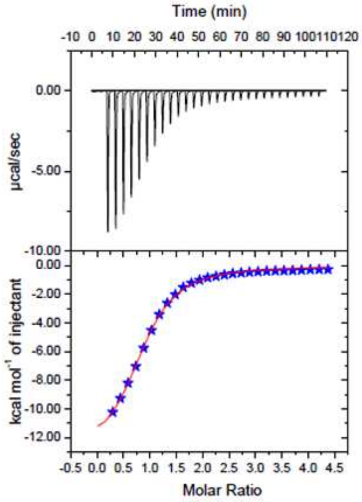


Fig. 4 ITC profile for the titration **L** (0.1212 mM) with $ZnSO_4$ (2.5 mM) in DMSO at 298K.

Competitive crystallization of **L** with $ZnSO_4$,$7H_2O$ in presence of 10 equivalent of $NaNO_3$ in MeOH/H_2O (1:1) yields crystals of **1** in high yield as determined by FTIR (Figure 21S, ESI†) and X-ray structural study.

In summary, we have demonstrated a unique example of hydrated sulfate cluster, $[(SO_4)_4(H_2O)_{12}]^{8-}$ recognition in a self-assembled metal-organic coordination polymer derived from a 3-pyridyl attached cyanuric acid platform based tripodal urea and Zn^{2+} in aqueous medium. Encapsulation of as many as four SO_4^{2-} is demonstrated in the cavity of the bowl shaped secondary building unit of the coordination polymer.

PG thanks Department of Science and Technology (DST), India, for financial support through a Swarnajayanti Fellowship. R.D. would like to acknowledge IACS, Kolkata for research fellowship. B.A. acknowledges CSIR, India for SRF. X-ray crystallography study is performed at the DST-funded National Single Crystal X-ray Diffraction Facility at the Department of Inorganic Chemistry, IACS.

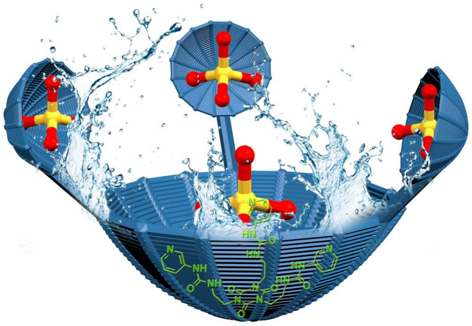
Notes and references

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Kolkata 700032. India. E-mail: icpg@iacs.res.in*

† Electronic Supplementary Information (ESI) available: Synthesis and characterization of **L** and complex **1**,**2**; ^{1}H-NMR and ITC profile; Crystallographic tables for complex **1-2**; hydrogen bonding parameters of **1** and **2**; TGA, PXRD plot for **1**. CCDC numbers: **1024314** (complex **1**) and **1024315** (complex **2**)

1 A. Lee, P. A. Dawson and D. Markovich, *Int. J. Biochem. Cell Biol.*, 2008, **37**, 1350; (b) D. T. Richens, *The Chemistry of Aqua Ions*; Wiley: Chichester, West Sussex, England, 1997.
2 Y. *J.* Marcus, *Chem. Soc. Faraday Trans.*, 1991, **87**, 2995–2999.
3 B. Gao and Z. Liu, *J. Chem. Phys.*, 2004, **121**, 8299.
4 (a) F. Hofmeister, *Archives of Experimental Pathology and Pharmacology*, 1887, **24**, 247; (b) J. W. Pflugrath and F. A. Quiocho, *Nature*, 1985, **314**, 257-260; (c) G. Y. Stokes, A. M. Buchbinder, J. M. Gibbs-Davis, K. A. Scheidt and F. M. Geiger, *Vib. Spectrosc.*, 2009, **50**, 86-98.
5 (a) *The Problem with Anions in the DOE Complex. In Fundamentals and Applications of Anion Separations*; B. A. Moyer, R. P. Singh, Eds.; Kluwer Academic: New York, 2004; p 107114; (b) B. A. Moyer, R. Custelcean, B. P. Hay, J. L. Sessler, K. Bowman-James, V. W. Day and S. –O. Kang, *Inorg. Chem.*, 2013, **52**, 3473-3490.
6 (a) S. O. Kang, M. A. Hossain, D. Powell and K. Bowman-James, *Chem. Commun.*, 2005, 328–330; (b) D. Curiel, A. Cowley and P. D. Beer, *Chem. Commun.*, 2005, 236–238; (c) D. A. Jose, D. K. Kumar, B. Ganguly and A. Das, *Inorg. Chem.*, 2007, **46**, 5817-5819; (d) I. Ravikumar, P. S. Lakshminarayanan, M. Arunachalam, E. Suresh and P. Ghosh, *Dalton Trans.*, 2009, 4160-4168; (e) J. S. Mendy, M. Pilate, T. Horne, V. W. Day and M. A. Hossain, *Chem. Commun.*, 2010, **46**, 6084–6086, (f) I. Ravikumar and P. Ghosh, *Chem. Soc. Rev.*, 2012, **41**, 3077-3098.
7 (a) C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Am. Chem. Soc.*, 2004, **126**, 5030-5031; (b) R. Custelcean, B. A. Moyer and B. P. Hay, *Chem. Commun.*, 2005, 5971–5973; (c) R. Custelcean, P. Remy, P. V. Bronnesen, D. Jiang and B. A. Moyer, *Angew. Chem. Int. Ed.*, 2008, **47**, 1866-1870; (d) B. Wu, J. Liang, J. Yang, C. Jia, X. –J. Yang, H. Zhang, N. Tang and C. Janiak, *Chem. Commun.*, 2008, 1762-1764; (e) R. Custelcean, A. Bock and B. A. Moyer, *J. Am. Chem. Soc.*, 2010, **132**, 7177-7185; (f) A. Rajbanshi, B. A. Moyer and R. Custelcean, *Cryst. Growth Des.*, 2011, **11**, 2702-2706; (g) R. Custelcean, J. Bosano, P. V. Bronnesen, V. Kertesz and B. P. Hay, *Angew. Chem. Int. Ed.*, 2009, **48**, 4025-4029; (h) R. Custelcean, P. V. Bronnesen, N. C. Duncan, X. Zhang, L. A. Watson, G. V. Berkel, W. B. Parson and B. P. Hay, *J. Am. Chem. Soc.*, 2012, **134**, 8525-8534; (i) S. Yi, V. Brega, B. Captain and A. E. Kaifer, *Chem. Commun.*, 2012, **48**, 10295-10297; (j) R. Custelcean, P. V. Bronnesen, B. D. Raoch and N. C. Duncan *Chem. Commun.*, 2012, **48**, 7438-7440; (k) G. Mezei, P. Baran and R. G. Raptis, *Angew. Chem. Int. Ed.*, 2004, **43**, 574-577; (l) I. R. Fernando, S. A. Surmann, A. A. Urech, A. M. Poulsen and G. Mezei, *Chem. Commun.*, 2012, **48**, 6860-6862; (m) Z. Yang, B. Wu, X. Huang, Y. Liu, S. Li, Y. Xia, C. Jia and X. –J. Yang, *Chem Commun.*, 2011, **47**, 2880-2882; (n) S. Banerjee, N. N. Adarsh and P. Dastidar *Eur. J. Inorg. Chem.*, 2010, 3770-3779; (o) B. Akhuli and P. Ghosh, *Dalton Trans.*, 2013, **42**, 5818-5825; (p) R. Custelcean, *Chem. Commun.*, 2013, **49**, 2173-2182; (q) J. Pang, F. Jiang, D. Yuan, J. Zheng, M. Wu, G. Liu, K. Su and M. Hong, *Chem. Sci.*, 2014, doi: 10.1039/C4SC01973C.

Graphical Abstract



Encapsulation of four sulfates in hydrated form is demonstrated in the coordination driven self-assembly of a tripodal urea receptor.