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## Encapsulation of $[(SO_4)_4(H_2O)_{12}]^{8-}$ clusters in a metal organic framework of pyridyl functionalized cyanuric acid based tris-urea<sup>†</sup>

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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 an unusual  $[(SO_4)_4(H_2O)_{12}]^{8-}$  cluster in a  $[Zn(H_2O)_6]^{2+}$  capped self-assembled structure is characterized by single crystal X-ray crystallography. Furthermore, selective binding of  $SO_4^{2-}$  is established from the <sup>1</sup>H-NMR titration study.

Recognition of hydrated anions is of great importance due to their presence in natural and biological environments.<sup>1</sup> High charge density and very high hydration energy of  $SO_4^{2-}$  ( $\Delta G_h =$ -1080 kJ mol<sup>-1</sup>)<sup>2</sup> assist the formation of different sulfatewater clusters in the aqueous environment. Association of twelve hydrogen bonds from water molecules are predicted in the first hydration shell of  $SO_4^{2-}$  by theoretical calculation.<sup>3</sup> Sulfate-water clusters play a crucial role in many environmental and biological processes such as aerosol formation, dissolution of proteins in the human body and regulation of various metabolic processes.<sup>4</sup> At the same time  $SO_4^{2-}$  interferes in the vitrification process of nuclear waste and causes permanent hardness of water.<sup>5</sup> 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, and indole functionalities have been employed for  $SO_4^{2-}$ recognition both in organic and aqueous media.<sup>6</sup> Metal ion templated self-assembled structures provide a successful strategy for selective recognition of  $SO_4^{2-}$  *via* complete encapsulation.<sup>7</sup> Particularly, pyridyl–urea containing metallo-supramolecular structures are employed for  $SO_4^{2-}$  encapsulation either by discrete assembly or coordination polymer formation.<sup>7c–j,m–o</sup> In this context, Custelcean and Kaifer *et al.* have recently reported the  $SO_4^{2-}$  encapsulation driven self-assembly process towards the formation of  $M_4L_6$  cages in aqueous medium.<sup>7h,i</sup> However, encapsulation of hydrated sulfates 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.<sup>6c</sup>

Herein we demonstrate a coordination driven self-assembly process of a cyanuric acid platform based tris-urea L in the presence of  $ZnSO_4$ -MgSO<sub>4</sub> in aqueous methanol (1:1). Importantly, encapsulation of the hydrated sulfate [(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>8-</sup> cluster in the self-assembled cavity is observed in the case of  $Zn^{2+}$  whereas  $SO_4^{2-}$  assisted dimeric capsular assembly is observed in the case of Mg<sup>2+</sup>. Furthermore, we show selective binding of  $SO_4^{2-}$  over other anions by the <sup>1</sup>H-NMR titration study.

Tripodal urea receptor L (Scheme 1a) is synthesized by the reaction of tripodal amine and 3-pyridyl isocyanate in



**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.



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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Synthesis and characterization of L and complexes 1 and 2; <sup>1</sup>H-NMR and ITC profiles; crystallographic tables for complexes 1 and 2; hydrogen bonding parameters of 1 and 2; TGA and PXRD plots for 1. CCDC 1024314 (complex 1) and 1024315 (complex 2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02877e

moderate yield (Scheme 1S, ESI<sup>†</sup>). Slow evaporation of the MeOH-H<sub>2</sub>O (1:1) solution of L and ZnSO<sub>4</sub>·7H<sub>2</sub>O results in crystals of complex 1 with the composition  $[L_3Zn_3(SO_4)_4]$ - $[Zn(H_2O)_6][(H_2O)_{18}]$  in high yield (~75%). However, crystals of dimeric capsules of complex 2  $[L_2SO_4][Mg(H_2O)_6][(H_2O)_2]$  are obtained by slow evaporation of a MeOH-H<sub>2</sub>O solution of L and MgSO<sub>4</sub>. Complex 1 contains a large amount of solvents in the unit cell and crystallographic parameters are given in Table 1S, ESI.<sup>†</sup>

Direct coordination of the 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 forming a  $C_{3v}$ -symmetric cleft which encapsulates one SO42- in its centre via N-H···O interactions (Table 2S, ESI<sup>†</sup>). The remaining coordination sites of Zn<sup>2+</sup> are filled 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) (Fig. 7S, ESI<sup>†</sup>). Thus a bowl shaped SBU is generated where encapsulation of three remaining  $SO_4^{2-}$ 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 SO42- is observed in the solid state.7g-j Thus, complex 1 represents a unique example of simultaneous encapsulation of as many as four SO<sub>4</sub><sup>2-</sup> anions in a supramolecular assembly (Fig. 1b). Now each of the four encapsulated SO<sub>4</sub><sup>2-</sup> anions are interconnected by bridging water molecules



**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 the 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.

*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 the  $[(SO_4)_4(H_2O)_{12}]^{8-}$  cluster reveals that one O atom (O6) of the central  $SO_4^{2-}$  is solely H-bonded to three –NH groups (N4–H4) of the central L unit.

Whereas each of the three remaining O atoms (O5) are Hbonded to one -NH group (N5-H5A) each. Furthermore, each **O5** is connected to the O atom (**O2**) of each side  $SO_4^{2-}$  via a bridging water molecule (O20) (Fig. 8S, ESI<sup>†</sup>). This bridging water molecule is further H-bonded to the  $[Zn(H_2O)_6]^{2+}$  cation. **O4** of the each side  $SO_4^{2-}$  is 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 (Fig. 8S, ESI<sup>†</sup>). 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, the  $[Zn(H_2O)_6]^{2+}$  capped  $[(SO_4)_4(H_2O)_{12}]^{8-}$  cluster is recognized in the cavity of the bowl shaped SBU. Detailed 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 (Fig. 9Sb<sup>†</sup>). Furthermore, the packing diagram of 1 shows a porous channel running along the c axis (Fig. 10S, ESI<sup> $\dagger$ </sup>). In contrast, tren based 3-pydridyl urea is reported to form SO<sub>4</sub><sup>2-</sup> encapsulated dimeric capsular assembly irrespective of the counter cations, where the cation exists as  $[M(H_2O)_6]^{2+}$  species  $[M = Zn^{2+}, Cd^{2+}, Cd^{2$ Mg<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>].<sup>7c</sup> ESI-MS(negative mode) analysis of 1 shows peaks at 715.96 and 976.91 corresponding to monovalent  $[L + HSO_4]^-$  and divalent  $[L_3 + SO_4]^{2-}$  species respectively (Fig. 11S, ESI<sup>†</sup>). The bulk purity of 1 is verified by PXRD analysis of crystals of 1, which matches well with the simulated pattern (Fig. 12S, ESI<sup>†</sup>). Furthermore, the solvent content of complex 1 is verified by thermogravimetric analysis (TGA), where a weight loss of 18.039% is observed at ~130 °C. This experimental weight loss corroborates with the calculated value (18.19%) from the crystal structure of 1 (Fig. 13S, ESI<sup>+</sup>). A comparative IR study of L and 1 also confirms the presence of  $SO_4^{2-}$  with a new peak at 1120 cm<sup>-1</sup> (Fig. 14S, ESI<sup>†</sup>), corresponding to the stretching frequency of  $SO_4^{2-}$ .

However, crystallographic analysis of the MgSO<sub>4</sub> complex of L *i.e.* 2 reveals encapsulation of SO<sub>4</sub><sup>2-</sup> in the dimeric capsular assembly of L (Fig. 2a). Twelve strong N-H···O interactions are involved to encapsulate the SO<sub>4</sub><sup>2-</sup> inside the dimeric capsule (Fig. 2b). In this case the Mg<sup>2+</sup> cation exists as  $[Mg(H_2O)_6]^{2+}$  species which hold the capsule *via* H-bonding interactions with the -C=O group of L and the Py-N atom through a bridging water molecule (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 the  $[Mg(H_2O)_6]^{2+}$  cation. The capsular dimension of 2 is measured as 9.71 Å compared to 9.65 Å in its tren analogue.<sup>7c</sup> Hydrogen bonding parameters and interactions of the  $[SO_4L_2]^{2-}$  capsule with six  $[Mg(H_2O)_6]^{2+}$  cations through second-sphere coordination are provided in the ESI (Fig. 15S and 16S, ESI<sup>+</sup>).



**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 countercations are omitted for clarity.



**Fig. 3** (a) <sup>1</sup>H-NMR spectral changes of L with added ZnSO<sub>4</sub> in DMSOd<sub>6</sub> ([L] is varied from 4.43 mM to 3.28 mM by the addition of aliquots of 34.08 mM ZnSO<sub>4</sub>). Ratio of concentration [L]/[SO<sub>4</sub><sup>2-</sup>]: (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<sub>4</sub>.

Comparative IR spectra of L and 2 show a characteristic peak of  $SO_4^{2-}$  at 1095 cm<sup>-1</sup> (Fig. 17S, ESI<sup>†</sup>).

A solution state complexation study of L and ZnSO<sub>4</sub> is performed by titrating a solution of L with  $ZnSO_4$  in DMSO- $d_6$ . A significant downfield shift of NHa ( $\Delta \delta \sim 1.2$  ppm) and NHb  $(\Delta \delta \sim 1.4 \text{ ppm})$  protons are observed upon addition of ~1 equiv. of ZnSO<sub>4</sub> (Fig. 3a, Fig. 18S, ESI<sup>†</sup>). Job's plot analysis by monitoring the chemical shift of NHa protons 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 the same as that of the solid state binding pattern in 1. Binding constant calculation shows a log K value of 5.47 for L with ZnSO<sub>4</sub> in DMSO $d_6$ . However, no such changes in chemical shift are observed for L with Zn(AcO)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, ZnCl<sub>2</sub> and Zn(ClO<sub>4</sub>)<sub>2</sub> as evident from qualitative <sup>1</sup>H-NMR analysis in DMSO- $d_6$  (Fig. 19S, ESI<sup>†</sup>). Moreover, solution state binding of L and ZnSO<sub>4</sub> is verified by the ITC study by titrating a solution of L with ZnSO<sub>4</sub> in DMSO (Fig. 4). The observed exothermic binding profile with 1:1 (host-guest) stoichiometry ( $n = 0.87 \pm 0.01$ ) further supports the <sup>1</sup>H-NMR data. The estimated kinetic and thermodynamic parameters (K,  $T\Delta S$ ,  $\Delta H$  and  $\Delta G$ ) of the above experiment are provided in the ESI (Fig. 20S<sup>†</sup>).

Competitive crystallization of L with  $ZnSO_4 \cdot 7H_2O$  in the presence of 10 equivalents of NaNO<sub>3</sub> in MeOH-H<sub>2</sub>O (1:1) yields crystals of **1** in high yield as determined by FTIR (Fig. 21S, ESI<sup>†</sup>) and X-ray structural studies.



Fig. 4  $\,$  ITC profile for the titration L (0.1212 mM) with ZnSO4 (2.5 mM) in DMSO at 298 K.

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  $SO_4^{2-}$  anions is demonstrated in the cavity of the bowl shaped secondary building unit of the coordination polymer.

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## Notes and references

- 1 (a) 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, Arch. Exp. Pathol. Pharmacol., 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, ed. B. A. Moyer and R. P. Singh, 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 Chem. Commun., 2005, 5971-5973; B. Р. Hay, (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, 5, 4163-4166.