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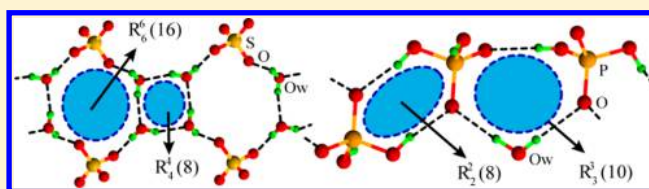
Pyridine–Urea-Based Anion Receptor: Formation of Cyclic Sulfate–Water Hexamer and Dihydrogen Phosphate–Water Trimer in Hydrophobic Environment

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S Supporting Information

ABSTRACT: A pyridine–urea-based receptor is found to stabilize cyclic sulfate–water hexamer $[(\text{SO}_4)_2-(\text{H}_2\text{O})_4]_n^{4-}$ and dihydrogen phosphate–water trimer $[(\text{H}_2\text{PO}_4)_2-\text{H}_2\text{O}]_n^{2-}$ within its hydrophobic environment upon protonation. Anion–water clusters are stabilized by H-bonding arising from urea, water, and the pyridinium moiety. Thermal stability of anion–water clusters was established by TGA, and binding constants were determined by potentiometric titration.



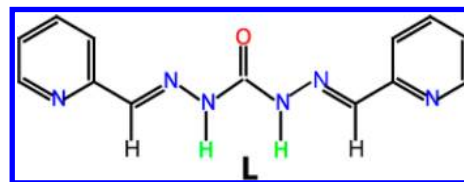
In recent times, recognition of hydrated forms of anions has attracted a great deal of attention due to their occurrence in natural and biological environments.¹ Hydrated anions are very much random and show a wide range of complicated interactions due to spontaneous formation of strong stable hydrogen bonds in an aqueous environment. As a consequence, recognition of ordered anion–water clusters is a challenging task for the researcher. Further, the formation of ordered anion–water clusters within chemical receptors allows a unique occasion to understand detailed molecular interactions in these confined environments.² In particular, there has been significant attention on understanding the ordered water clusters in hydrophobic environments³ due to their vast importance in chemical and biological interfaces.⁴ There are various types of anion–water clusters that have been reported in different designed molecular systems,⁵ explaining the structural characterization and their behavior.

Among various anions, the structural characterization of tetrahedral anion–water clusters are important due to their occurrence in natural and biological environments. In the past few years, serious attention has been given to the study of sulfate–water clusters due to its crucial role in the nucleation of ice for cloud formation, solubility of protein in our body, regulation of several metabolic and cellular processes.⁶ The deleterious effects of sulfate ion are also noted as it causes difficulties in separation from nuclear waste and hampered the vitrification process.⁷ Recently, structural properties of sulfate–water cluster and their importance have been emphasized by theoretical⁸ and experimental⁹ studies. Another tetrahedral anion phosphate also has several roles in biological systems.¹⁰ There are many reports, describing dihydrogen phosphate recognitions¹¹ but articles highlighting the recognition of hydrated dihydrogen phosphate anion(s) are very few.¹² On the other hand, the tetrahedral perchlorate anion is an environmental pollutant. Due to the high water solubility of inorganic perchlorate salts, it readily moves to aqueous medium

and causes contamination of groundwater.¹³ Therefore, recognition of hydrated forms of dihydrogen phosphate and perchlorate anions are also important.

In our continuing study on anion–water clusters,¹⁴ herein we report structural studies of tetrahedral oxanion-based cyclic anion–water clusters by a pyridine–urea functionalized receptor **L** (Scheme 1). Significantly, in the case of sulfate

Scheme 1. Pyridine–Urea Functionalized Receptor (**L**)



complex **1**, the receptor is found to stabilize a unique cyclic hexameric sulfate water cluster in its hydrophobic environment. To the best of our knowledge, solid state structural evidence of cyclic hexameric sulfate–water cluster in hydrophobic system has not been reported previously.

The receptor **L** was synthesized in good yield following the reported literature procedure.¹⁵ The receptor possesses an anion-binding urea function along with two pyridyl units (suitable for protonation). The pyridyl units not only act as protonation site but also enhance the solubility and anion binding efficiency of the receptor in aqueous medium. All the reported complexes were obtained by slow evaporation of $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (9:1) solution of **L** in the presence of respective inorganic acids.

Received: October 22, 2013

Revised: November 29, 2013

The reaction of **L** with sulfuric acid (H_2SO_4) gave the colorless complex $[\text{LH}_2\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}](1)$. X-ray structural elucidation of the complex shows that it crystallizes in the triclinic system with space group $P\bar{1}$.^{16a} The asymmetric unit contains one doubly protonated receptor, sulfate anion, and three crystalline water molecules. The receptor forms a 1:1 complex with trihydrated sulfate anions. The protonated receptor is planar and present in its anticongformation with respect to the $\text{C}=\text{O}$ bond. It forms strong H-bonding interactions with the sulfate anion and water molecules. The detailed coordination environment of SO_4^{2-} suggests that it is stabilized via ten H-bonding interactions with two receptor cations and three water molecules, comprised of three $\text{N}-\text{H}\cdots\text{O}$ (two urea NH and one PyH^+), three $\text{O}\cdots\text{H}_2\text{O}$ (lattice water), and four $\text{C}-\text{H}\cdots\text{O}$ strong bonds (three imine and one aromatic). The detailed H-bonding interactions (distance and angle) are as follows: $\text{N1}\cdots\text{O5} = 2.733(3)$ Å and $\angle\text{N1}-\text{H1N}\cdots\text{O5} = 161.0(3)^\circ$, $\text{N4}\cdots\text{O5} = 2.970(2)$ Å and $\angle\text{N4}-\text{H4N}\cdots\text{O5} = 163.5(1)^\circ$, $\text{N3}\cdots\text{O8} = 2.866(2)$ Å and $\angle\text{N3}-\text{H3N}\cdots\text{O8} = 169.0(1)^\circ$, $\text{O2w}\cdots\text{O6} = 2.781(3)$ Å and $\angle\text{O2w}-\text{H2B}\cdots\text{O6} = 175.6(2)^\circ$, $\text{O3w}\cdots\text{O6} = 2.762(3)$ Å and $\angle\text{O3w}-\text{H3A}\cdots\text{O6} = 173.0(3)^\circ$, $\text{O4w}\cdots\text{O7} = 2.689(3)$ Å and $\angle\text{O4w}-\text{H4A}\cdots\text{O7} = 162.4(2)^\circ$, $\text{C5}\cdots\text{O7} = 3.311(3)$ Å and $\angle\text{C5}-\text{H5}\cdots\text{O7} = 143.2(2)^\circ$, $\text{C6}\cdots\text{O7} = 3.385(2)$ Å and $\angle\text{C6}-\text{H6}\cdots\text{O7} = 156.6(2)^\circ$, $\text{C8}\cdots\text{O8} = 3.283(3)$ Å and $\angle\text{C8}-\text{H7}\cdots\text{O8} = 160.1(2)^\circ$, and $\text{C8}\cdots\text{O5} = 3.396(3)$ Å and $\angle\text{C8}-\text{H7}\cdots\text{O5} = 141.2(2)^\circ$. Two oxygen atoms of sulfate ion O6 and O8 behave as a bifurcated H-bond acceptor, while O5 and O7 behave as a trifurcated H-bond acceptor resulting in ten H-bonds within acceptable donor-to-acceptor distances (Figure 1). Interest-

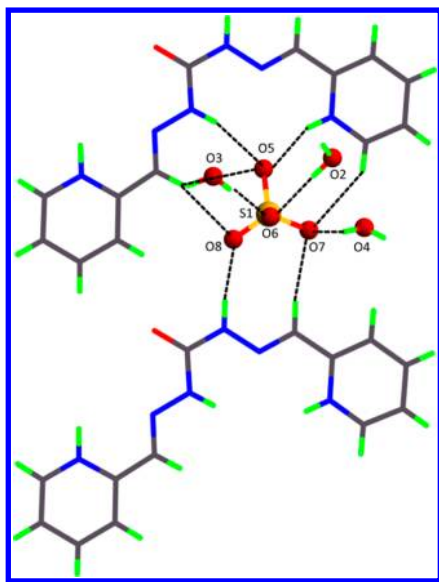


Figure 1. Coordination mode of sulfate anion in complex 1.

ingly, in complex **1**, two hydrated sulfate anions met each other in opposite directions via two H-bonding interactions between O2w and O4w water molecules, which eventually led to the formation of an unusual sulfate–water hexameric ring. The cyclic hexameric sulfate–water cluster was formed via six H-bonding interactions among two sulfate anions and four water molecules, and only two oxygen atoms of each sulfate anion are involved in H-bonding interactions in this cluster (Figure 2a). The solid-state arrangement of water molecules and sulfate anions probably helps the formation of the H-bonded sulfate–

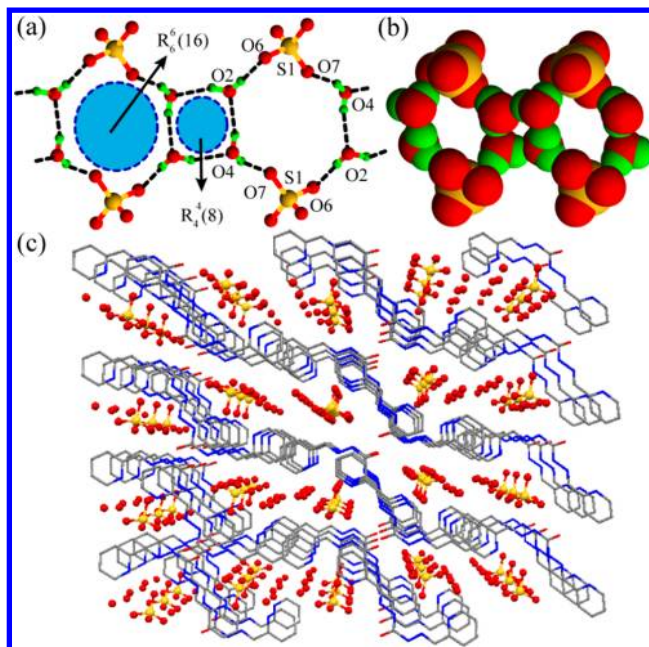


Figure 2. (a) Depicting infinite chain of fused sulfate–water hexamer $[(\text{SO}_4)_2-(\text{H}_2\text{O})_4]_n^{4+}$ and water tetramer. (b) Space-filling representation of two fused rings. (c) Showing the hydrophilic sulfate–water assembly entrapped by hydrophobic environment of the cationic receptor.

water network. It is noted that the hexameric ring is not planar and forms a classical chair conformation where four water molecules lie in the plane and two sulfate anions are present above and below of plane (Figure S21 of the Supporting Information). The hexameric sulfate–water ring is mainly stabilized by strong H-bonding interactions with urea NH and PyH^+ functions of the protonated receptors. The H-bonding interactions involved in the cyclic sulfate–water cluster are $\text{O2w}\cdots\text{H2B}\cdots\text{O6}$ [$\text{O2w}\cdots\text{O6} = 2.781(3)$ Å, $\angle\text{O2w}-\text{H2B}\cdots\text{O6} = 175.6(2)^\circ$] and $\text{O4w}\cdots\text{H4A}\cdots\text{O7}$ [$\text{O4w}\cdots\text{O7} = 2.689(3)$ Å, $\angle\text{O4w}-\text{H4A}\cdots\text{O7} = 162.4(2)^\circ$] that gave the $R_6^6(16)$ motif. Further, it also interacts with the water molecules of neighbor clusters through H-bonding, which subsequently led to the formation of 1D polymeric aggregates of sulfate–water clusters in the hydrophobic pocket of the receptors along the crystallographic b axis (Figure 2a). The infinite polymeric aggregates were made by repeating two fused rings (Figure 2b), of which one is the sulfate–water hexamer and the other one is a water tetramer. Close inspections of the distance and angle of this water tetramer confirmed it to be a nearly square array. In addition, crystal packing viewed along the a axis generates a hydrophilic sulfate–water channel surrounded by the hydrophobic receptor (Figure 2c). The presence of a H-bonded hydrated sulfate anion in complex **1** has also been confirmed by solid-state FT-IR analysis. The presence of a moderate signal at 3435 cm^{-1} and a strong signal $\sim 1100\text{ cm}^{-1}$ in complex **1** attributed to the stretching frequencies of the water and sulfate anion, respectively, which are absent in the free receptor (Figure S11 of the Supporting Information). Simulated PXRD of the sulfate complex **1** nearly matches with the experimental PXRD pattern (Figure S17 of the Supporting Information).

On protonation with phosphoric acid, **L** yielded complex $[\text{2LH}\cdot 2\text{H}_2\text{PO}_4\cdot 3\text{H}_2\text{O}]$ (**2**). Single crystal X-ray analysis of dihydrogen phosphate complex **2** reveals that it is in a monoprotonated state, form 1:1 colorless complex with

H_2PO_4^- anion.^{16b} The asymmetric unit of complex 2 contains two symmetry independent monoprotonated receptors, two different symmetric H_2PO_4^- ions, and three lattice water molecules. Similar to complex 1, both the receptors are planar and present in its anticonformation with respect to the $\text{C}=\text{O}$ bond. It forms H-bonding interactions with H_2PO_4^- anions and water molecules. The coordination environments of two crystallographically nonequivalent H_2PO_4^- anions are different. Interestingly, extending the H-bonding contacts on H_2PO_4^- anions in complex 2 shows that one water molecule (O1w) acts as a bridging H-bond donor between two symmetry independent H_2PO_4^- anions and forms an unusual water bridge cyclic trimer $[\text{H}_2\text{PO}_4-\text{H}_2\text{O}-\text{H}_2\text{PO}_4]^{2-}$, while two of the same symmetric H_2PO_4^- anions form cyclic dimer $[\text{H}_2\text{PO}_4-\text{H}_2\text{PO}_4]^{2-}$ via complementary strong H-bonding interactions and resulted structural motif R_3^3 (10) and R_2^2 (8), respectively (Figure 3). The detailed H-bonding parameters involved in the

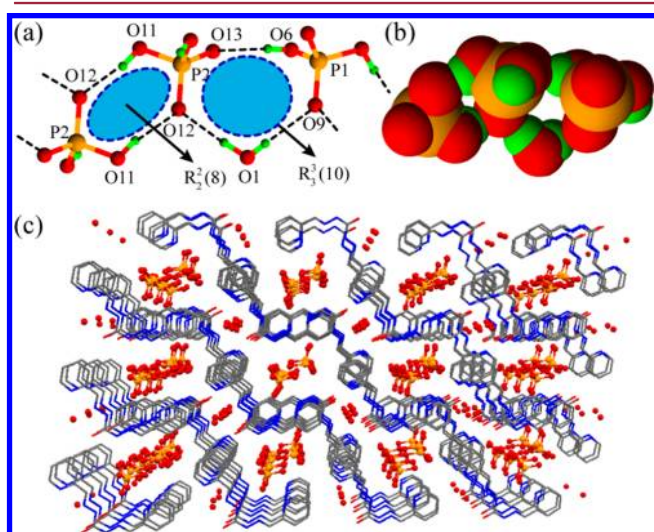


Figure 3. (a) Showing an alternative arrangement of cyclic trimeric and dimeric rings of hydrated H_2PO_4^- anions in complex 2. (b) Space-filling model of two interconnected cyclic ring motifs of H_2PO_4^- anions. (c) Showing the different hydrophilic channel made of dihydrogen phosphate–water and water molecules surrounded by the hydrophobic environment.

cyclic trimer and dimer are as follows: $\text{O1w}\cdots\text{O9} = 2.829(7)$ Å and $\angle\text{O1w}-\text{H1B}\cdots\text{O9} = 177.0(9)^\circ$; $\text{O1w}\cdots\text{O12} = 2.777(6)$ Å and $\angle\text{O1w}-\text{H1A}\cdots\text{O12} = 174.0(7)^\circ$; $\text{O6}\cdots\text{O13} = 2.580(5)$ Å and $\angle\text{O6}-\text{H6O}\cdots\text{O13} = 158.0(2)^\circ$; $\text{O7}\cdots\text{O9} = 2.531(4)$ Å and $\angle\text{O7}-\text{H7O}\cdots\text{O9} = 170.0(2)^\circ$; and $\text{O11}\cdots\text{O12} = 2.571(5)$ Å and $\angle\text{O11}-\text{H11O}\cdots\text{O12} = 168.7(2)^\circ$. Full H-bonding details are given in Table S2 of the Supporting Information. These two cyclic ring motifs are arranged in alternative fashion and ultimately led to the formation of an interesting polymeric assembly of hydrated H_2PO_4^- anions in the hydrophobic environment of complex 2 along the a axis. These cyclic anionic rings are mainly stabilized by strong H-bonding interactions with urea NH and PyH^+ functions of the protonated receptor(s). Probably the geometry of the monoprotonated receptor and the unique H-bonding dual (donor and acceptor) nature of the H_2PO_4^- anion play crucial roles in the formation of the polymeric assembly of hydrated H_2PO_4^- anions in complex 2. Moreover, the detailed coordination environments of H_2PO_4^- anions show that the $\text{H}_2\text{P}(1)\text{O}_4^-$ is stabilized via ten H-bonds while $\text{H}_2(2)\text{PO}_4^-$ is stabilized via eleven H-bonds

(Figure 4). In the case of $\text{H}_2(1)\text{PO}_4^-$, oxygen atoms O7 and O8 form two H-bonds, each in bifurcated fashion, while O6 and

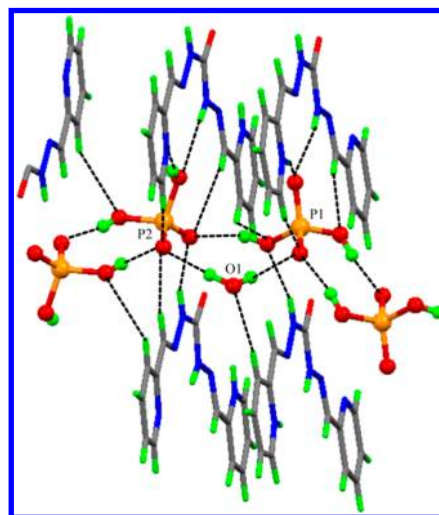


Figure 4. Stabilization of the infinite chain of hydrated H_2PO_4^- anions via H-bonding interactions with a cationic receptor.

O9 form three H-bonds each in trifurcated fashion. Whereas for $\text{H}_2(2)\text{PO}_4^-$, O10 and O11 form two H-bonds each in bifurcated fashion, while the trifurcated and tetrafurcated mode of H-bonding interactions are observed for O13 and O12, respectively. Structural study in-depth shows among three crystallized water molecules only one directly involved in H-bonding with H_2PO_4^- anions, but the other two water molecules (O2w and O3w) interact with the $\text{C}=\text{O}$ (carbonyl) and pyridine moiety shown in Figure S23 of the Supporting Information. But in the case of the sulfate complex 1, all three water molecules interact with the sulfate anion. The packing diagram along the c axis shows dihydrogen phosphate–water and water molecules that lie in two different hydrophobic pockets, forming anion–water and water channel, respectively (Figure 3c). The vibrational stretching frequency of complex 2 indicates a broad band centered around 3440 cm^{-1} and a sharp peak ranging from 1120 to 1157 cm^{-1} that can be attributed to the O–H and P–O bond, suggesting the presence of the water molecule and H_2PO_4^- anion (Figure S12 of the Supporting Information). The bulk phase purity of the complex was also confirmed by PXRD study, where the simulated and experimental patterns closely match with each other (Figure S18 of the Supporting Information).

The complex 3 crystallizes in the $\text{P}\bar{1}$ space group, and X-ray structure reveals that the doubly protonated receptor forms 1:2 (receptor:anion) light yellow complex.^{16c} The asymmetric unit contains one doubly protonated receptor, two perchlorate anions, and two lattice water molecules. In contrast to complexes 1 and 2, here in complex 3, the ClO_4^- anion does not form any cyclic anion–water ring; rather, it forms an infinite $[(\text{ClO}_4)_2-\text{H}_2\text{O}]_n^{2-}$ chain via H-bonding participation with the water molecule (O2w) (Figure S25 of the Supporting Information). The hydrogen atoms of O2w are dynamic in nature and shared among three neighbored ClO_4^- ions. The O2w water molecule H-bonded with the ClO_4^- ion by $\text{O2w}\cdots\text{O5} = 3.016(5)$ Å, $\text{O2w}\cdots\text{O8} = 2.766(6)$ Å, and $\text{O2w}\cdots\text{O9} = 2.929(5)$ Å interactions and serves as the H-bond acceptor with urea NH [$\text{N3}\cdots\text{O2w} = 2.816(4)$ Å]. Structural view shows while one water molecule (O2w) interacts with the ClO_4^- ion,

the other water molecule (O3w) connects the two planar protonated receptors through H-bonding interactions with C=O and PyH⁺ and form squarelike geometry resulting an H-bonding R₂²(6) motif (Figure S26 of the Supporting Information). The bonding parameters in square motif are O3w...O1 = 2.840(4) Å, ∠O3w—H3A...O1 = 150.0(6)° and O3w...O1 = 3.009(4) Å, ∠O3w—H3B...O1 = 134.0(5). The coordination environments of two ClO₄[−] anions are different. The Cl(1)O₄[−] is seven- and Cl(2)O₄[−] is ten-coordinated via several N—H...O (urea and PyH⁺) (O...H₂O and C—H...O interactions (Figure S27a of the Supporting Information). Notably, for Cl(2)O₄[−], one oxygen atom O4 lies perfectly perpendicular to the pyridinium moiety of the receptor and forms the anion-π interaction with a distance of 3.212 Å (Figure S27b of the Supporting Information). The details of H-bonding parameters are tabulated in Table S2 of the Supporting Information. The protonated receptor in complex 3 forms hydrophobic layers and perchlorate–water are entrapped between the layers forming hydrophilic chains (Figure S29 of the Supporting Information). The broad band centered around 3444 cm^{−1} and 1083–1138 cm^{−1} in the FT-IR spectrum of 3 can be attributed to the O—H and Cl—O stretching frequency (Figure S13 of the Supporting Information). Closely matched experimental and simulated PXRD patterns of complex 3 confirmed the bulk phase purity of the complex (Figure S19 of the Supporting Information).

We performed thermogravimetric analysis (TGA) to examine the thermal stability of all the complexes. The weight loss 7.8% (calcd 8.5%) in complex 1 corresponding to two water molecules was removed at 116 °C, while one water molecule is retained up to 145 °C and released along with the decomposition of the complex, which suggests that the water molecules involved in the cyclic sulfate–water cluster released first and then the removal of strongly bounded water molecules (by PyH⁺ moiety and sulfate anion) took place. In the case of complex 2, though the coordination environments of three water molecules are different, we did not observe any gradual loss of water, but rather the TGA study exhibited a facile weight loss of 6.70% (calcd 6.86%) at 120 °C, indicating the removal of all three water molecules simultaneously. The complex 3 holds the water molecules weakly as observed from the TGA study where weight loss 6.85% (calcd 7.12%) related to two water molecules released early at 92 °C (Figures S14–S16 of the Supporting Information).

The protonation constant of L and binding constant of [LH₂]²⁺ with tetrahedral anions were determined by potentiometric method in the water/methanol (9:1) medium (Figure 5). The distribution curve showed [LH₂]²⁺ predominates at a pH lower than 3.8. Upon addition of base, it starts to lose the

proton and the monoprotonated species exists up to pH 4.5. The further increase in pH shows the abundance of the neutral receptor L, which predominates after pH 6.5. The binding affinity of [LH₂]²⁺ toward several tetrahedral oxyanions showed that the log K value for SO₄^{2−}, H₂PO₄[−], and ClO₄[−] are 0.49, 0.35, and 0.08, respectively. These values suggest that the receptor interacts with SO₄^{2−} and H₂PO₄[−] ions strongly compared to the perchlorate ion (Table S3 and S4 of the Supporting Information).

In summary, we have presented the formation of the stable infinite sulfate–water chain containing chairlike sulfate–water hexamer [(SO₄)₂–(H₂O)₄]_n^{4−}, infinite chain of dihydrogen phosphate–water trimer [(H₂PO₄)₂–H₂O]_n^{2−}, and a simple perchlorate–water chain by a pyridinium–urea functionalized hydrophobic system. The presence of an anion binding urea group and pyridyl units (protonation site) in the planar receptor play a crucial role in stabilizing anion water clusters/hydrated anions. Thermal stability of the oxyanion–water cluster was established by TGA, and the binding constant of the receptor with anions was determined by potentiometric titration in aqueous medium.

Our studies of hydration of oxyanions in the hydrophobic environment in protic solvent are relevant to biological systems where high hydrophobic patches are present in a highly protic medium. This result could open the opportunity of study of the complex behavior of anions in the aqueous phase. Mainly the hydration phenomena of multiple charged anions (SO₄^{2−}) may be the key result for elucidation of sulfate–water interaction patterns observed in chemical and environmental issues. Further study requires the exploitation of the precise orientation of water molecules around oxyanions in the designed system theoretically or experimentally.

■ ASSOCIATED CONTENT

§ Supporting Information

Experimental, characterization data and crystallographic details; figures; and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

G.D. acknowledges CSIR (01/2727/13/EMR-II) and Science & Engineering Research Board (SR/S1/OC-62/2011) New Delhi, India, for financial support and CIF IITG and DST-FIST for providing the instrument facilities. N.H. and A.B. thank IITG for fellowships.

■ REFERENCES

- (1) (a) Lee, A.; Dawson, P. A.; Markovich, D. *Int. J. Biochem. Cell Biol.* **2008**, *37*, 1350. (b) Marcus, Y. *Ion Solvation*; Wiley: Chichester, West Sussex, England, 1986. (c) Richens, D. T.; *The Chemistry of Aqua Ions*; Wiley: Chichester, West Sussex, England, 1997.
- (2) (a) Cametti, M.; Rissanen, K. *Chem. Commun.* **2009**, 2809. (b) Hudnall, T. W.; Chiu, C.-W.; Gabbai, F. P. *Acc. Chem. Res.* **2009**, *42*, 388.
- (3) (a) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Chem. Commun.* **2004**, 2220. (b) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671.

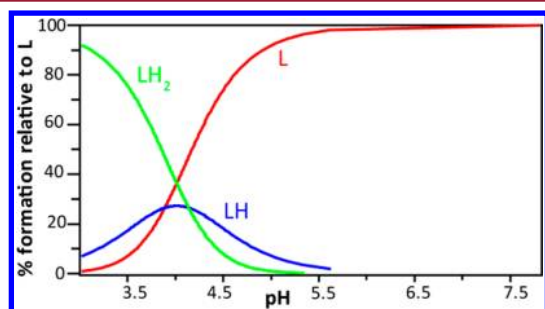


Figure 5. Species distribution curve for protonation of L.

(c) Li, Y.; Jiang, L.; Feng, T.-B.; Lu, X.-L. *Cryst. Growth Des.* **2008**, *8*, 3689.

(4) (a) Sleight, S. H.; Tame, J. R. H.; Dodson, E. J.; Wilkinson, A. J. *Biochemistry* **1997**, *36*, 9747. (b) Peters, J.; Baumeister, W.; Lupas, A. J. *Mol. Biol.* **1996**, *257*, 1031.

(5) (a) Cametti, M.; Rissanen, K. *Chem. Soc. Rev.* **2013**, *42*, 2016. (b) Bakhoda, A.; Khavasi, H. R.; Safari, N. *Cryst. Growth Des.* **2011**, *11*, 933. (c) MacGillivray, L. R.; Atwood, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 2592. (d) Wang, Q.-Q.; Day, V. W.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 2119. (e) Chakraborty, S.; Dutta, R.; Arunachalam, M.; Ghosh, P. *Dalton Trans.* **2014**, DOI: 10.1039/c3dt52694a.

(6) (a) Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D. *Science* **2001**, *294*, 2119. (b) Hofmeister, F. *Archives of Experimental Pathology and Pharmacology* **1987**, *24*, 247. (c) Lee, A.; Dawson, P. A.; Markovich, D. *Int. J. Biochem. Cell Biol.* **2005**, *37*, 1350. (d) Pflugrath, J. W.; Quiocho, F. A. *Nature* **1985**, *314*, 257.

(7) (a) *Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Department of Energy Sites*; National Research Council, National Academies Press: Washington, D.C., 2001; p 55. (b) *The Problem with Anions in the DOE Complex. In Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer Academic: New York, 2004; p 107114.

(8) (a) Asmis, K. R.; Neumark, D. M. *Acc. Chem. Res.* **2012**, *45*, 43. (b) Yu, J.-J.; Zhang, Y.-H.; Li, Z.-S. *J. Phys. Chem. B* **2012**, *116*, 12597. (c) Zhou, J.; Santambrogio, G.; Brummer, M.; Moore, D. T. *J. Chem. Phys.* **2006**, *125*, 111102. (d) Bush, M. F.; Saykally, R. J.; Williams, E. R. *J. Am. Chem. Soc.* **2007**, *129*, 2220. (e) Lambrecht, D. S.; Clark, G. N. I.; Head-Gordon, T.; Head-Gordon, M. *J. Phys. Chem. A* **2011**, *115*, 11438. (f) O'Brien, J. T.; Prell, J. S.; Bush, M. F.; Williams, E. R. *J. Am. Chem. Soc.* **2010**, *132*, 8248.

(9) (a) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Inorg. Chem.* **2007**, *46*, 5817. (b) Xia, Y.; Wu, B.; Liu, Y.; Yang, Z.; Huang, X.; He, L.; Yang, X.-J. *CrystEngComm* **2009**, *11*, 1849.

(10) (a) Amendola, V.; Boiocchi, M.; EstebanGomez, D.; Fabbri, L.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3*, 2632. (b) Sessler, J. L.; Cho, D.-G.; Lynch, V. J. *Am. Chem. Soc.* **2006**, *128*, 16518. (c) Hirsch, A. K. H.; Fischer, F. R.; Diederich, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 338.

(11) (a) Bazzicalupi, C.; Bencini, A.; Lippolis, V. *Chem. Soc. Rev.* **2010**, *39*, 3709. (b) Hargrove, A. E.; Nieto, S.; Zhang, T.; Sessler, J. L. *Chem. Rev.* **2011**, *111*, 6603. (c) Rajbanshi, A.; Wan, S.; Custelcean, R. *Cryst. Growth Des.* **2013**, *13*, 2233. (d) Baker, N. A. C.; McGaughey, N.; Fletcher, N. C.; Chernikov, A. V.; Horton, P. N.; Hursthouse, M. *Dalton Trans.* **2009**, 965. (e) Li, Y.; Jiang, L.; Feng, X.-L.; Lu, T.-B. *Cryst. Growth Des.* **2008**, *8*, 3689.

(12) Dalapati, S.; Alam, M. A.; Jana, S.; Guchhait, N. *CrystEngComm* **2012**, *14*, 6029.

(13) (a) Macmillan, D. K.; Dalton, W. R.; Bendar, A. J.; Waisner, S. A.; Arora, P. N. *Chemosphere* **2007**, *67*, 344. (b) *Interim Drinking Water Health Advisory For Perchlorate*; EPA 822-R-08-025; USEPA: Washington, D.C., 2008.

(14) (a) Hoque, M. N.; Basu, A.; Das, G. *Cryst. Growth Des.* **2012**, *12*, 2153. (b) Basu, A.; Das, G. *Chem. Commun.* **2013**, 49, 3997. (c) Gogoi, A.; Das, G. *Cryst. Growth Des.* **2012**, *12*, 4012. (d) Hoque, M. N.; Basu, A.; Das, G. *Supramol. Chem.* **2013**, DOI: 10.1080/10610278.2013.844811.

(15) Barragán, F. J.; Rosa, d. I.; Ariza Gómez, J. L.; Pino, F. *Mikrochim. Acta* **1984**, *82*, 171.

(16) Crystallographic data and structure refinement parameters of (a) $[\text{LH}_2\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}]$ (1): FW = $\text{C}_{13}\text{H}_{20}\text{N}_6\text{O}_8\text{S}$; MW = 420.42; triclinic; space group $P\bar{1}$, $a = 8.0541(8)$ Å, $b = 8.3073(8)$ Å, $c = 14.7666(13)$ Å, $\alpha = 85.767(7)^\circ$, $\beta = 87.441(8)^\circ$, $\gamma = 66.606(9)^\circ$, $V = 904.18(16)$ Å³, $Z = 2$, $\rho(\text{cal}) = 1.544$ g/cm³, $\mu(\text{Mo K}\alpha) = 0.237$ mm⁻¹, $T = 298(2)$ K, R_1 ; wR_2 [$I > 2\sigma(I)$] = 0.0482; 0.1108, R_1 ; $wR_2(\text{all}) = 0.0706$ and 0.1290; residual electron density = 0.249/−0.353 (e/Å³); goodness-of-fit = 1.033; reflection collected = 7190; independent reflection = 4045; CCDC no. = 927368. (b) $[\text{2LH}\cdot 2\text{H}_2\text{PO}_4\cdot 3\text{H}_2\text{O}]$ (2): FW = $\text{C}_{26}\text{H}_{36}\text{N}_{12}\text{O}_{13}\text{P}_2$; MW = 786.61; triclinic; space group $P\bar{1}$, $a = 9.009(2)$ Å, $b = 14.1152(17)$ Å, $c = 15.276(4)$ Å, $\alpha = 116.185(17)^\circ$,

$\beta = 97.676(19)^\circ$, $\gamma = 93.033(14)^\circ$; $V = 713.9(6)$ Å³; $Z = 2$, $\rho(\text{cal}) = 1.524$ g/cm³; $\mu(\text{Mo K}\alpha) = 0.210$ mm⁻¹; $T = 298(2)$ K, R_1 ; wR_2 [$I > 2\sigma(I)$] = 0.0825; 0.2470, R_1 ; $wR_2(\text{all}) = 0.1316$ and 0.3407; residual electron density = 0.904/−1.225 (e/Å³); goodness-of-fit = 1.068; reflection collected = 13692; independent reflection = 8787; CCDC no. = 943362. (c) $[\text{LH}_2\cdot 2\text{ClO}_4\cdot 2\text{H}_2\text{O}]$ (3): FW = $\text{C}_{13}\text{H}_{18}\text{Cl}_2\text{N}_6\text{O}_{11}$, MW = 505.23, triclinic, space group $P\bar{1}$, $a = 7.5545(4)$ Å, $b = 8.7273(4)$ Å, $c = 16.7176(9)$ Å, $\alpha = 79.566(3)^\circ$, $\beta = 80.063(3)^\circ$, $\gamma = 70.872(3)^\circ$, $V = 1016.49(9)$ Å³, $Z = 2$, $\rho(\text{cal}) = 1.651$ g/cm³, $\mu(\text{Mo K}\alpha) = 0.392$ mm⁻¹, $T = 298(2)$ K, R_1 ; wR_2 [$I > 2\sigma(I)$] = 0.0623; 0.1987, R_1 ; $wR_2(\text{all}) = 0.0800$; 0.2118, residual electron density = 0.670/−0.365 (e/Å³); goodness-of-fit = 1.033; reflection collected = 9861; independent reflection = 4163, CCDC no. = 927369.