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Decameric Water Clusters Shaped as Two Parallel Cyclic Pentamers with Staggered Conformation Stabilize Supramolecularly Bonded Infinite Chains of $H_2PO_4^-$ Ions

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A laterally nonsymmetric aza-cryptand on acidification with H_3PO_4 affords an H-bonded infinite chain of $H_2PO_4^-$ ions. These chains are aligned parallel through H-bonding interactions with discreet decameric water clusters leaving large void spaces. Diprotonated cryptand molecules occupy these voids through supramolecular interactions. The crystal data for the compound are: triclinic space group $P\bar{1}$, a = 12.765(5), b = 13.254(2), c = 13.817(4) Å, V = 2137.3(14) Å^3, Z = 2, $R1$ = 0.0582, $wR2$ = 0.1339, S = 1.092.

Introduction

The phosphate ion is an essential nutrient in biosystems and is transported by a phosphate-binding protein (PBP) that forms a strong H-bond with the mono- or dibasic form of phosphate.[1] Phosphate groups are frequently found with enzyme substrates or co-factors. It is not clear whether water plays any role in the translocation of inorganic phosphate across the cell membrane or in the formation of enzyme–substrate complexes. In DNA, water molecules are concentrated in six hydration sites per phosphate group and the positions as well as the occupancies of these sites are dependent on the conformation and nature of the nucleotide in addition to the type of DNA itself.[1] A water molecule exhibits uncertainty over the number of H-bonding interactions and their fluctuations with other water molecules−both of which are responsible for the anomalous behavior of bulk water. However, this diversity of H-bonding interactions is very important in the biological world as it can enforce a delicate balance among several possible conformations of an enzyme essential for its functional role(s). Recent years have witnessed both theoretical[2–5] and experimental[6–8] scrutiny of a number of small water clusters in different surroundings to investigate the development of properties of the condensed phase in a step-wise manner. We present here the structure of water decamers in the confinement of infinite H-bonded quasi-parallel chains of dibasic phosphates. Theoretical calculation[9] by Buck et al. had suggested that the minimum energy conformation for the decamer was as an octameric cube with two water molecules fused at one of the edges, while a more recent calculation showed two fused parallel pentamers to be energetically the most stable.[10] An ice-like diamondoid decamer[11] has been identified in a self-assembled metal-organic cage,[11d] while a water decamer in the form of two fused parallel cyclic pentamers with staggered conformation has been characterized[11c] in an organic host built from 5-hydroxyisophthalic acid and 18-crown-6. Supramolecular associations of water molecules forming a 3D structure with voids are potentially important for entrapment of molecules of interest if the water molecules can be removed without drastically altering the overall structure.

Results and Discussion

Compound **1** is isolated as colorless crystals when an aza-cryptand (Scheme 1) is dissolved in water by dropwise addition of phosphoric acid. In the asymmetric unit (Figure 1), diprotonated cryptand, two $H_2PO_4^-$ anions, and seven water molecules are found. One of the water molecules (Ow7) is H-bonded inside the cryptand cavity, while another (Ow6) is H-bonded to the cryptand from outside. This molecule (Ow6) acts as an H-bond acceptor to one of the protonated amino nitrogen atoms of the cryptand arm with the N···O distance of 2.789 Å. This water molecule also forms an H-bond with $H_2PO_4^-$. The five remaining water molecules (Ow1–Ow5) describe a quasi-planar cyclic structure that eventually forms a decameric unit with five other centrosymmetrically related water molecules (Figure 2). The two pentameric cycles are oriented parallel to each other with a staggered conformation. Although this is a higher energy structure, it is stabilized by the environment. The $H_2PO_4^-$ anions form infinite H-bonded chains that run almost parallel to one another and the water deca-

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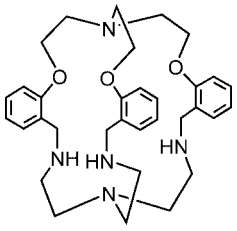
mers connect these chains through strong H-bonding interactions (Table 1) forming almost rectangular voids (approximate dimension 13.2×7.5 Å) that are occupied by cryptand molecules (Figure 3). The water molecule Ow4 of the cyclic pentamer acts as an H-bond acceptor to the cryptand, while the remaining four are H-bonded to the $H_2PO_4^-$ chains. The cryptand shows only weak interactions with the phosphate chains and the water molecules act as a glue holding together both the phosphate chains and the cryptands leading to the supramolecular assembly (Figure 4). The two parallel pentamers are connected at two positions



Scheme 1. Illustration of the laterally nonsymmetric aza-cryptand L.

Table 1. Hydrogen bond parameters in compound **1**.

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	∠D–H···A [°]
Ow1-H···Ow2	0.825(5)	2.088(1)	2.892(2)	164.6(2)
Ow2-H···Ow5′	0.907(1)	1.982(2)	2.864(4)	183.84(4)
Ow3-H···Ow2	0.815(2)	2.082(3)	2.894(1)	174.14(5)
Ow4-H···Ow3	0.931(4)	1.822(5)	2.747(3)	171.62(6)
Ow4-H···Ow5	0.923(3)	1.822(3)	2.728(4)	166.67(5)
Ow5-H···Ow1	0.862(3)	1.829(2)	2.736(2)	172.13(1)
Ow6-H···O4	0.817(1)	1.996(3)	2.809(4)	173.24(5)
Ow7-H···N1	0.807(4)	2.264(1)	3.068(3)	174.91(2)
Ow7-H···N5	0.929(5)	1.857(4)	2.782(4)	173.12(5)
Ow1-H···O6	0.888(1)	1.935(4)	2.801(3)	164.78(3)
Ow2-H···O9	0.897(3)	1.936(2)	2.806(1)	162.83(6)
Ow3-H···O4	0.880(3)	1.937(2)	2.813(2)	173.08(1)
Ow5-H···O11	0.815(4)	1.939(3)	2.744(4)	169.35(5)
N3–H···Ow7	0.901(4)	1.955(3)	2.845(4)	169.33(5)
N3–H···Ow4	0.900(1)	1.856(4)	2.682(1)	151.57(2)
N4–H···Ow6	0.900(3)	1.919(3)	2.789(2)	162.15(5)
N4–H···Ow7	0.900(4)	1.895(2)	2.782(4)	168.12(3)
O5–H···O6	0.918(2)	1.675(2)	2.588(3)	172.98(5)
O7–H···O11	0.788(4)	1.809(3)	2.595(1)	174.48(2)
O8–H···O4	0.845(3)	1.821(1)	2.653(2)	167.96(5)
O10–H···O9	0.888(4)	1.692(3)	2.572(4)	170.42(5)

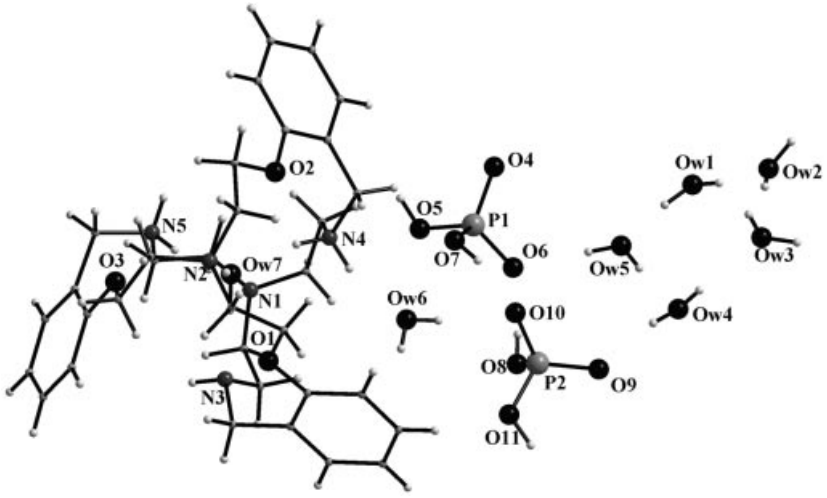


Figure 1. Asymmetric unit showing the diprotonated cryptand molecule with $H_2PO_4^-$ anions and seven water molecules.

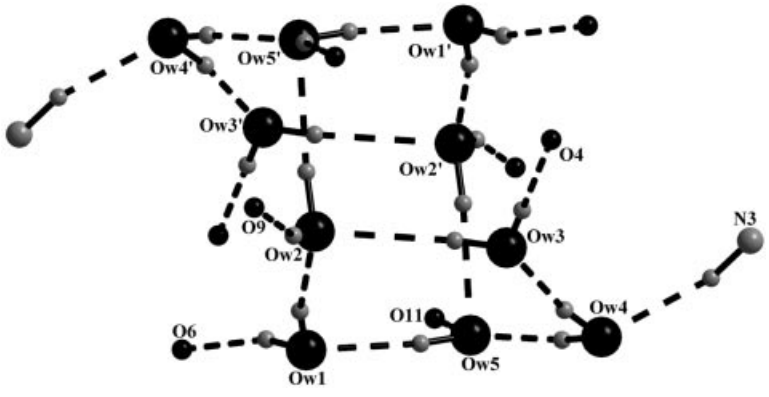


Figure 2. Perspective view of the $(H_2O)_{10}$ cluster showing the H-bonding interactions.

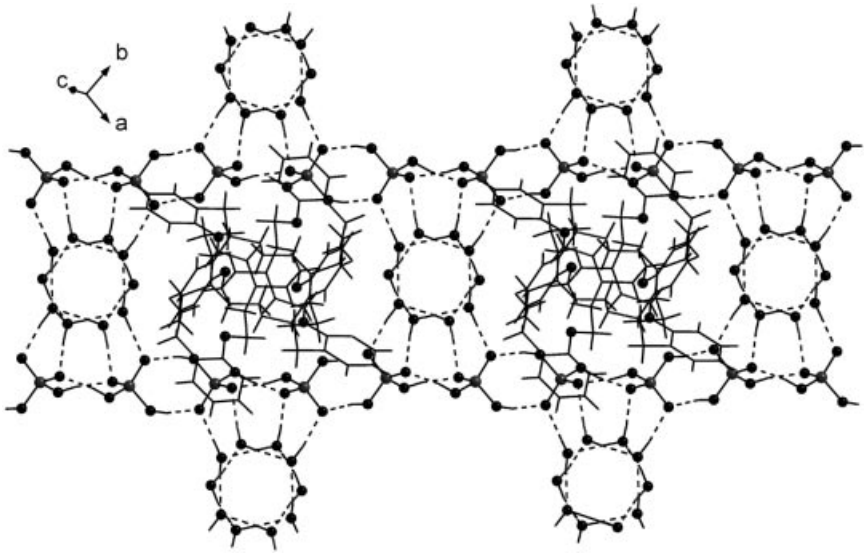


Figure 3. View showing chains of $H_2PO_4^-$ anions connected by water decamers with cryptand molecules occupying voids.

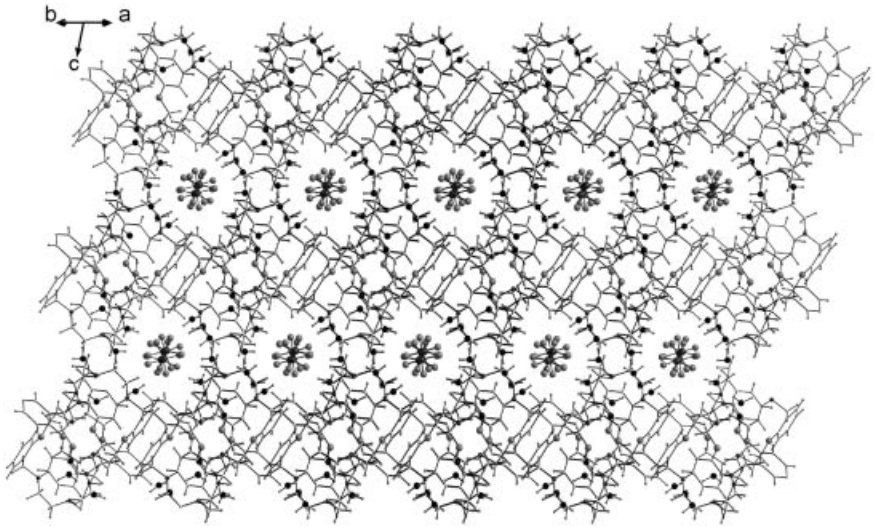


Figure 4. Self-assembled structure of compound **1** viewed along the phosphate chains.

through H-bonding and these four O atoms exhibit tetra-coordination while the rest are tri-coordinated. Such hydrogen-bond-deficient water molecules are, however, present[12,13] at the surface of liquid water or hexagonal ice. A wide range of O···O distances are observed (2.736–2.894 Å) in the present cluster as the water molecules adjust to the surroundings.

In the FTIR spectrum of compound **1**, a broad peak appears centering around 3420 cm^{-1} attributable[14] to the water cluster. Thermal analysis of compound **1** shows that it begins to lose weight after ca. 50 °C without showing any plateau region.

Conclusion

In conclusion, we have characterized a novel water decamer in the shape of two parallel five-membered staggered rings. These decamers glue quasi-parallel diphosphate chains resulting in large voids that are occupied by cryptand molecules.

Experimental Section

Materials: All the reagent-grade chemicals were used without purification unless otherwise specified. Triethanolamine, salicylaldehyde, tris(2-aminoethyl)amine, and sodium borohydride were obtained from Aldrich. Sodium hydroxide, anhydrous sodium sulfate, phosphoric acid, and thionyl chloride were received from S. D. Fine Chemicals (India). Thionyl chloride and all the solvents were freshly distilled prior to use.

Physical Measurements: Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}): Perkin–Elmer Model 1320; thermogravimetric analysis (heating rate of 5 °C/min): Mettler Toledo Star System. Microanalysis data for the compound were obtained from CDRI, Lucknow.

Synthesis of $[LH^{+2}{\cdot}2H_2PO_4^{-2}{\cdot}7H_2O]$ (1): The cryptand L was synthesized as reported previously.[15] The cryptand was dissolved in water by dropwise addtion of phosphoric acid, and the resulting solution, upon slow concentration at room temperature, afforded pale yellow rectangular parallelepiped crystals of $[LH^{+2}{\cdot}2H_2PO_4^{-2}{\cdot}7H_2O]$ (**1**) in 60% (0.530 g) yield. $C_{33}H_{65}N_5O_{18}P_2$ (881.84): calcd. C 44.94, H 7.43, N 7.94; found C 44.91, H 7.52, N 8.01.

X-ray Structural Studies: The X-ray data were collected with a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (0.71069 Å). Data collection and its reduction were achieved with SMART (version 5.628) and SAINT (version 6.45). The structure was solved by direct methods and refined on F^2 using the SHELX-97 package.[16] All the H atoms bonded to water O were located in the difference Fourier maps. The non-hydrogen atoms were refined anisotropically. The H atoms were not refined. Crystal data for **1**: pale yellow, rectangular parallelepiped, crystal dimensions $0.19 \times 0.15 \times 0.12$ mm, triclinic, $P\bar{1}$, $Z = 2$, $a = 12.765(5)$, $b = 13.254(2)$, $c = 13.817(4)$ Å, $V = 2137.3(14)$ Å^3, $\rho_{cald.} = 1.37$ g cm^{-3}, $T = 100$ K, $\mu = 0.18$ mm^{-1}, $\theta_{max} = 28.32°$. A total of 14357 reflections collected, of which 7784 were unique, $R1 = 0.0582$, $wR2 = 0.1339$, GOOF = 1.092 for $I > 2\sigma(I)$, residual electron density: 0.512 and –0.548 e Å^{-3}. CCDC-287356 contains the supplementary crystallographic data for this paper. These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figure showing the water clusters viewed along the phosphate chains.

Acknowledgments

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