Anion Cluster: Assembly of Dihydrogen Phosphates for the Formation of a Cyclic Anion Octamer

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Abstract

Structural characterization of a dihydrogen phosphate complex of triprotonated tris[2-(2-thienylmethylamino)ethyl] amine shows that eight dihydrogen phosphate anions are assembled around the host by strong interactions of H-bond donors and acceptors to form a new type of cyclic anion octamer as $(H_2PO_4^-)_8$, an analogy of cyclic water octamer. The presence of an anion cluster has also been identified by electrospray ionization mass spectrometry and ^{31}P NMR experiments.

Despite having been known for many years, the term "cluster" was coined by Cotton in the early 1960s to refer to compounds containing a group of multiple metal atoms with direct metal–metal bonds known as a "metal cluster".[1–3] It is also a prevalent term to describe intermolecular bonding features between water molecules called a "water cluster" in which discrete water molecules are assembled through hydrogen bonding interactions forming a variety of chains or rings.[4–14] While a metal cluster is formed by sharing of delocalized electrons of metal atoms or ions,[3] in the case of a water cluster, molecules are held by intermolecular interactions between H-bond acceptors and H-bond donors (Scheme 1A). Another type of cluster known as an "anion cluster" has been reported in the literature, which consists of either a metal ion coordinated with anions such as $[M(A)_n]$ (where A = anion)[15–21] or an anion linked with water molecules, such as $[A(H_2O)_n]^-$.[22,23] For example, Bencini, Bianchi, Giorgi, and co-workers reported an anion cluster, $[Na(ClO_4)_6]^{5-}$

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Supporting Information

Crystallographic data in CIF format and ^1H NMR studies. This material is available free of charge via the Internet at http://pubs.acs.org.

assembled inside the cavity of a tren-based polyamine receptor, where six perchlorates were coordinated with one sodium ion in an octahedral environment.[22] Lin and co-workers characterized an oxyfluorophosphate cluster $[Ti_{10}P_4O_{16}F_{44}]^{16-}$ in which each oxygen atom of PO_4^{3-} is bonded with titanium ions.[20] Liao and co-workers isolated a crystal of $[Ru(bpy)_3]_2[I(H_2O)_6Fe(CN)_6 H_2O]$ containing an anion cluster $[I(H_2O)_6]^-$ in the empty space of the metal–organic framework.[22]

Like a water molecule, a hydrogen phosphate or dihydrogen phosphate contains both H-bond acceptors and H-bond donors (Scheme 1B); therefore, it could be an ideal species to form an anion cluster. Steed and co-workers reported dimeric hydrogen phosphate and phosphate–water chain resulting from H-bond donor–acceptor interactions in a triprotonated tris-N-(2-aminoethyl)-1,3-propanediamine diphosphate tetrahydrate.[24] A phosphate–water chain was also formed in the crystal of spermidine phosphate trihydrate.[24] Dimers of dihydrogenphosphate (Scheme 1C) with synthetic receptors were reported previously by other groups.[25,26] Light and co-workers isolated crystals of tetrabutylammonium dihydrogenphosphate with dichloromethane showing an infinite hydrogen-bonded dihydrogen phosphate chain within cationic tetrabutyl ammonium channels.[27] A similar chain was also reported by Evan and coworkers in the dihydrogen phosphate complex of 2-amino-pyridine.[26] Indeed, because of the significant impact on the environmental and biological systems, a great deal of attention has been directed toward phosphate recognition by synthetic receptors,[28–35] To the best of our knowledge, the formation of cyclic anion clusters composed of identical anions has not been reported previously. Herein, we report a phosphate complex of a tripodal receptor **L** in which one phosphate anion is encapsulated in its pseudocavity. Structural analysis shows that the ligand is wrapped by a cyclic anion cluster assembled with eight dihydrogen phosphates as $(H_2PO_4^-)_8$ (Scheme 1D). In addition, the existence of an anion cluster has also been identified by electrospray ionization mass spectrometry (ESI-MS) and ^{31}P NMR experiments.

The ligand **L** was synthesized as described earlier.[36] The phosphate complex, $[H_3\mathbf{L}(H_2PO_4)](H_2PO_4)_2$, was obtained from the reaction of **L** with phosphoric acid in water. The complex was shown to decompose at about 250 °C. This temperature corresponds to a sharp endothermic peak at 253 °C on a differential scanning calorimetry (DSC) thermogram recorded for the salt using a differential scanning calorimeter (Supporting Information). X-ray quality crystals were grown by vapor diffusion of methanol into an aqueous solution of the salt at room temperature. The structure of the phosphate complex of **L** was determined by X-ray diffraction analysis.[37]

Crystallographic analysis of the complex suggests that all three secondary amines are protonated and the charges are balanced by three $H_2PO_4^-$. One $H_2PO_4^-$ is bonded to three protonated amines through one oxygen (O1) with strong hydrogen bonds in the range of N⋯O with 2.827 (3) to 2.832 (3) Å (Figure 1A,B). The oxygen atom (O1) is encapsulated in the cavity, forming a pseudo C_3 symmetric complex. Other two anions remain between the arms of the ligand, one $H_2PO_4^-$ with a single hydrogen bond and another with two hydrogen bonds with secondary nitrogens of the tren unit. Therefore, all six protons on the charged nitrogens are utilized in H-bonding with three anions (Table 1). The coordination environment of the encapsulated $H_2PO_4^-$ is quite different than that observed in the nitrate complex of **L** reported previously.[36] In the case of nitrate complex, an almost perfect C_3 symmetric complex was formed, where one nitrate was encapsulated and held by six H-bonds with protonated secondary amines. An earlier report on the crystal structure of a phosphate complex with a phenyl substituted tripodal amine showed that the three phosphate anions were present between the tren arms, while one molecular phosphoric acid was stacked above the quasi-planar tren.[38]

Extending the structure in two-dimensional directions, the phosphate anions are found to be involved in strong hydrogen bonding interactions between H-bond donors and acceptors resulting in the formation of a cyclic phosphate octamer (Figure 1C,D) — an observation that is consistent with the result of a mass spectrum showing the appearance of an **L**-phosphate complex with eight anions (discussed later). As shown in Figure 1C, the encapsulated $H_2PO_4^-$ is connected with two $H_2PO_4^-$ from both sides via four H-bonds to form a trimeric dihydrogen phosphate. Two identical trimers (from two asymmetric units) are then further linked via two $H_2PO_4^-$ groups from both sides, forming the octameric dihydrogen phosphate as $(H_2PO_4^-)_8$. It is worth mentioning that the tripodal host is encircled by the octameric phosphate by a total of six H-bonds. As viewed in the space filling model (Figure 1D), the void space generated by the octameric dihydrogen phosphate (Figure 1E) is nicely occupied by the tripodal ligand. More interestingly, the asymmetric units are packed along the a and b axes through H-bonds to form an infinite 2D sheet composed of identical cyclic dihydrogen phosphate octamers (Figure 1F).

As listed in Table 1, the OH···O bond distances in the octameric dihydrogen phosphate are in the range of 2.494 (3) to 2.631 (3) Å. These distances are much shorter than normal hydrogen-bonding distances between acceptor and donor (OH···O 2.8 Å).[39] It is remarkable that two H-bonds O3H···O9 and O4H···O7 with distances of 2.494 (3) and 2.529 (3) Å, respectively, are considerably short, suggesting the formation of a strong trimer. These two H-bond distances with O···O < 2.55 Å could be arguably classified as low-barrier hydrogen bonds (LBHB) which are comparable to those previously reported for benzoylacetone (O···O = 2.502 Å)[40] and for yellow protein (O···O = 2.51 Å) and slightly longer than 2.45 Å observed in a tetraamidic macrocycle.[36] LBHBs are observed in biology within protein interiors and are thought to play roles in protein functions, enzymatic catalysis, and the stabilization of specific reaction intermediates in enzymes.[41,42]

The interaction of **L** with dihydrogen phosphate was further investigated by ESI-MS (positive ion mode) experiments. As shown in Figure 2, the peak at m/z 435.2 corresponds to the free ligand [H**L**]$^+$. Afterward, new peaks appeared at 534.4, 632.6, 730.5, 828.4, 926.0, 1022.1, 1120.1, and 1220.0 with an interval of almost 98, which corresponds to the molecular weight of phosphoric acid — an indication of an anion cluster formation in the gaseous phase. It is assumed that during the ionization process each $H_2PO_4^-$ in the cluster accepts one proton to produce [H**L**$(H_3PO_4)_n$]$^+$, so that the overall charge of the ionic species is +1. In the mass spectrum, the highest peak at m/z 730.5 (100%), which corresponds to the host with three dihydrogen phosphates, suggests the formation of a 3 strong trimer — an observation that is consistent with the crystallographic results showing a strong trimer due to the presence of two considerably strong H-bonds (O3H···O9 = 2.494 (3) and O4H···O7 = 2.529 (3) Å). The peak appearing at 1220.0 is due to the formation of an octamer [H**L**$(H_3PO_4)_8$]$^+$, which is in agreement with the results of the X-ray structure.

In order to evaluate the interaction of **L** with dihydrogen phosphate, the ^{1}H NMR studies were carried out using the tosylate salt of [H$_3$**L**](Ts)$_3$ with TBAH$_2$PO$_4$ in CDCl$_3$. However, the addition of the anion gave an immediate precipitation in the NMR tube, hampering the determination of the binding constant. After the addition of 1.5 equiv of $H_2PO_4^-$, all signal intensities of the tren unit gradually decreased and almost disappeared, while those for tosylates remained the same (see Supporting Information). This observation suggests during the complexation process ([H$_3$**L**]$^{3+}$·3Ts$^-$ + 3TBA$^+$·$H_2PO_4^-$ = [H$_3$**L**(H_2PO_4)]$(H_2PO_4)_2$ + 3TBA$^+$·Ts$^-$), the reaction product [H$_3$**L**(H_2PO_4)]$(H_2PO_4)_2$ is quite insoluble in CDCl$_3$. However, the other product TBA$^+$·Ts$^-$ is soluble in CDCl$_3$ showing clear NMR signals with the intensity unchanged, which is an indication of the high affinity of [H$_3$**L**]$^{3+}$ for dihydrogen phosphate. As reported previously, the host was found to be soluble in the

presence of halides and nitrate in $CDCl_3$, showing the binding affinity (in log K) in the order of NO_3^- (2.50) > Br^- (2.06) > Cl^- (2.03) > F^- (2.00) > ClO_4^- (1.74) > I^- (1.70).

Efforts were also made to examine the binding behavior of $[H_3L](Ts)_3$ by ^{31}P NMR spectroscopy using 0.01 M $TBAH_2PO_4$ in DMSO-d_6. In order to avoid the dilution effect, the host solution (0.1 M) was prepared containing $TBAH_2PO_4$ (0.01 M), and all the peaks were calibrated against 85% H_3PO_4 aqueous solution filled in a sealed capillary tube. The host solution was added gradually to the guest solution while ^{31}P NMR was recorded for each sample. As shown in Figure 3, one peak emerged at 1.45 ppm for the free phosphate. This peak continued to shift downfield to a 1.85 ppm, when the $[Host]_0/[Guest]_0$ (= R') ratio was 0.33 or $[Guest]_0/[Host]_0$ (= R) was 3.04. Interestingly, further addition of the host (R' > 0.33) to the anion solution resulted in an upfield shift of "P" resonance. The shift change with an increase of $H_3[L](Ts)_3$ is displayed in Figure 4. A previous report of Sessler demonstrated the upfield shift of phosphorus resonance in the ^{31}P NMR due to the complexation of protonated sapphyrins with phosphate.[43] In our case, the two opposite trends of downfield shifts (R' < 0.33) and upfield shift (R' > 0.33) in the ^{31}P NMR spectra (see Figure 4) could be related to the clustering effect and normal anion binding effect. This assumption was further supported by the fact that the NMR shift changes in the range of R' = 0.33 to 3.75 (where R > 3.0) was found to fit nicely with a 1:1 binding model[44] (inset in Figure 4). The upfield trend of NMR shifts of $H_2PO_4^-$ with R' < 0.3 (where more than 3 equiv of $H_2PO_4^-$ are present) to the host is possibly due to the shielding of the phosphorus nucleus resulting from the phosphate cluster as observed in the crystal structure.

In conclusion, we have structurally identified a very unusual anion cluster of octameric dihydrogen phosphate in a simple tripodal amine–phosphate complex. The positively charged host stabilizes the anionic cluster by providing H-bond donors to the anions, where the tren unit is encircled by the octamer as $(H_2PO_4^-)_8$ assembled by the strong interactions of H-bond donors and acceptors of dihydrogen phosphate similar to a cyclic water octamer.[7] The results from ESI-MS and ^{31}P NMR studies further support the formation of the phosphate cluster. Although there are numerous examples of cyclic water clusters as well as metal clusters that have been structurally characterized, to the best of our knowledge, the formation of a cyclic anion cluster with identical anions has not been published before. Through this finding, we have unveiled a new class of anion clusters with anions containing both H-bond donors and acceptors, where anions play the topological role of the water molecules.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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37. Crystal data for $[H_3L(H_2PO_4)](H_2PO_4)_2$: $M = 728.65$, hexagonal, $a = 9.2366(10)$ Å, $c = 63.693(6)$ Å, $V = 4705.9(8)$ Å^3, $T = 90.0(5)$ K, space group $P6_5$, $Z = 6$, $\mu(CuK_\alpha) = 4.18$ mm^{-1}, 20 434 reflections measured, 5413 independent reflections ($R_{int} = 0.0283$). The final R_1 values were 0.0261 ($I > 2\sigma$ (I)) and 0.0261 (all data). The final $wR(F^2)$ values were 0.0657 ($I > 2\sigma$ (I)) and 0.0657 (all data). The space group was confirmed by refinement of the Flack parameter to $x = 0.040(15)$ for 2490 Friedel pairs. Two of the thiophene rings are disordered.

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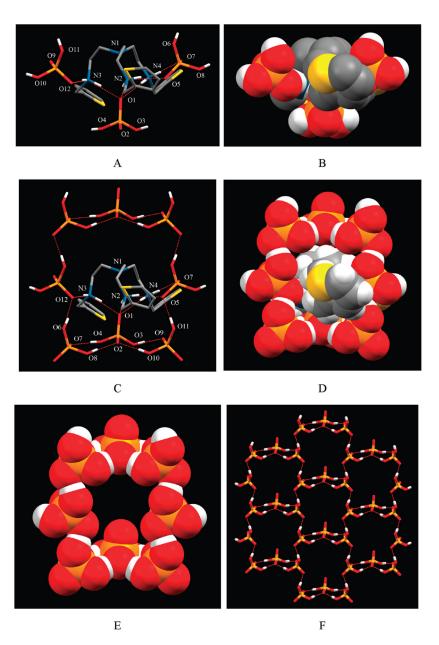44. Schneider HJ, Kramer R, Simova S, Schneider U. J Am Chem Soc. 1988; 110:6442–6448.

Figure 1.
Crystal structure of $[H_3\mathbf{L}(H_2PO_4)](H_2PO_4)_2$ showing one $H_2PO_4^-$ with three NH···O as a perspective view (A) and space filling model (B); cyclic dihydrogen phosphate octamer encircling the tripodal receptor as a perspective view (C) and space filling model (D); cyclic dihydrogen phosphate octamer as a space filling model (E), and assembly of dihydrogen phosphate octameric units in a lattice framework (F).
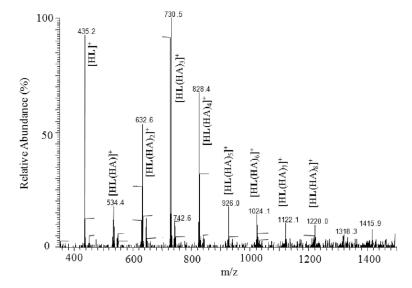
Figure 2.
ESI-MS (positive ion mode) spectrum of the dihydrogen phosphate complex in water.
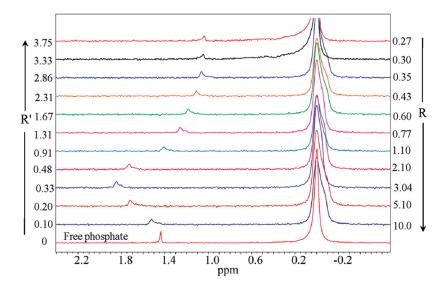
Figure 3.
^{31}P NMR spectra of TBAH$_2$PO$_4$ (0.01M) with an increasing addition of H$_3$[**L**](Ts)$_3$ ([R' = [Host]$_0$/[Guest]$_0$ and $R = 1/R'$ = [Guest]$_0$/[Host]$_0$), showing the peak movement of "P" resonance in DMSO-d_6 at room temperature.
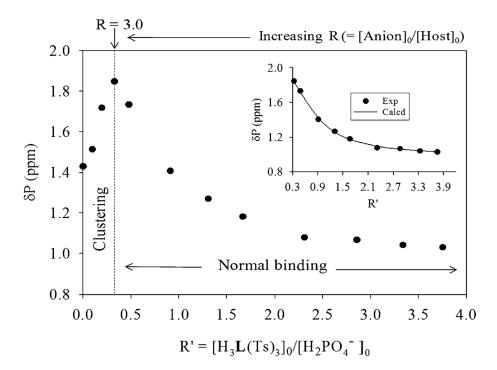
Figure 4.
The change in ^{31}P NMR signals of $TBAH_2PO_4$ (0.01 M) with an increasing addition of $H_3[L](Ts)_3$ in DMSO-d_6 at room temperature.

Scheme 1.
Tripodal Receptor (L); H-Bond Donor and Acceptor Groups in (A) Water and
Dihydrogenphosphate (B); Dihydrogen Phosphate Dimer (C); Cyclic Dihydrogen Phosphate
Octamer (D)

Table 1

Hydrogen Bonding Parameters (Å, °)[a]

D–H⋯O	D⋯O	∠DHO
N2–H21N⋯O5	2.757 (3)	164.9
N2–H22N⋯O1	2.832 (3)	167.4
N3–H31N⋯O12	2.756 (3)	173.7
N3–H32N⋯O1	2.755 (3)	158.2
N4–H41N⋯O1	2.827 (3)	151.7
N4–H42N⋯O7	2.795 (3)	176.8
O3–H3O⋯O9[i]	2.494 (3)	171 (4)
O4–H4O⋯O7[ii]	2.529 (3)	173 (4)
O6–H6O⋯O12[iii]	2.576 (3)	169 (4)
O8–H8O⋯O2[iii]	2.621 (3)	173 (4)
O10—H10O⋯O2[iv]	2.631 (3)	178 (4)
O11–H11O⋯O5[iv]	2.576 (3)	176 (4)

[a]Symmetry codes:

[i] = x - 1, y, z;

[ii] = x + 1, y + 1, z.

[iii] = x - 1, y - 1, z.

[iv] = x + 1, y, z.