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Article

Aqueous Chemistry of Chlorocyclophosphazenes: Phosphates $\{PO_2\}$, Phosphamides $\{P(O)NHR\}$, and the first Phosphites $\{PHO\}$ and Pyrophosphates $\{(PO)_2O\}$ of These Heterocycles

Joanne Ledger, Ramamoorthy Boomishankar,† and Alexander Steiner*

Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom.
†Present address: Department of Chemistry, Indian Institute of Technology, Guwahati, North Guwahati, Assam-781039, India.

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Cyclotriphosphazenes have been functionalized with various oxo-groups at one of the ring phosphorus atoms. Starting from geminal dichlorides (**A**) which are equipped with amino groups at the other two phosphorus atoms $\{(Z'_2P)_2N_3PCl_2$ (Z' = NHCy) and $(Z''P)_2N_3PCl_2$ (Z'' = $\{EtN(C_3H_6)NEt\}$), respectively$\}$, phosphate (**B**), pyrophosphate (**C**), phosphamide (**D**), and phosphite (**E**) derivatives have been prepared. The zwitterionic phosphate $(Z'_2P)_2N_3H_2PO_2$ **B** is obtained via the 4-dimethylamino pyridine (dmap)-catalyzed hydrolysis of **A** in a biphasic mixture of aqueous KOH and tetrahydrofuran (thf). **B** contains a PO_2 moiety neighboring two protonated ring nitrogen sites. It crystallizes as the tetrahydrate $(Z'_2P)_2N_3H_2PO_2 \cdot 4H_2O$, which consists of a double helix: A helical chain of hydrogen bonded zwitterions is intertwined with a helical chain of water molecules. The reaction of **A** with only dmap in $CHCl_3$ produces the dication $[(Z'_2P)_2N_3P(dmap)_2]^{2+}$, which binds two dmap ligands at one phosphorus atom. The tetrahydrate dehydrates at 160 °C in vacuo under formation of the pyrophosphate $\{(Z'_2P)_2N_3HPO\}_2O$ **C**, which contains a O═P−O−P═O residue linking the two phosphazene rings. When heated in a mixture of aqueous KOH, primary amine, and thf, **A** undergoes a concurrent aminolysis-hydrolysis reaction, which gives the phosphamide $(Z_2P)_2N_3HP(O)NHR$ **D** featuring a P(=O)NHR residue. The corresponding reaction of **A** with α,α′-diamino-*p*-xylene in a 2:1 ratio leads to the formation of $\{(Z'_2P)_2N_3HP(O)NHCH_2\}_2C_6H_4$, in which two phosphamide moieties are linked by a xylylene bridge. Phosphites **E** containing PHO moieties are obtained via reduction of the dichloride with potassium and subsequent treatment with KOH. The product consists of a hexameric potassium complex, which features a central K_6O_6 double cube arrangement and contains the anionic ligand $[(Z''P)_2N_3PHO]^-$ that offers two bidentate N−P−O coordination sites. Addition of NH_4Cl yields the neutral phosphite $(Z''P)_2N_3HPHO$. The title compounds are amphiphilic featuring hydrophilic NH and PO_x moieties and hydrophobic alkyl groups. In addition, they show amphiprotic behavior via protonation/deprotonation at ring N atoms.

Introduction

Cyclophosphazenes are versatile inorganic ring systems owing to the great stability of the phosphorus nitrogen backbone and the ability to undergo substitution of side groups with retention of the ring structure. The phosphazene ring has been equipped with various substituents, such as OR, NHR, and NR_2 groups. Their R groups can be tailored in numerous ways to fulfill specific electronic and steric requirements. A wide variety of additional functional groups have been added to the substituents, which include metal coordination sites, hydrogen bond donors and acceptors as well as ionic end groups.[1] In particular, $Cl_6P_3N_3$ **1** has served as an important starting compound for numerous cyclotriphosphazene derivatives. Its six-membered ring offers a rigid platform for multifunctional molecular arrangements, including multisite ligands for metal complexes,[2] coordination polymers,[3] supramolecular building blocks,[4] core moieties for dendrimers,[5]

*To whom correspondence should be addressed. E-mail: a.steiner@liverpool.ac.uk.

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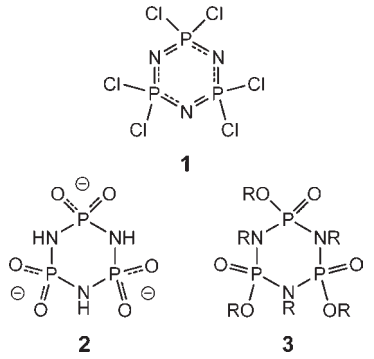
Chart 1

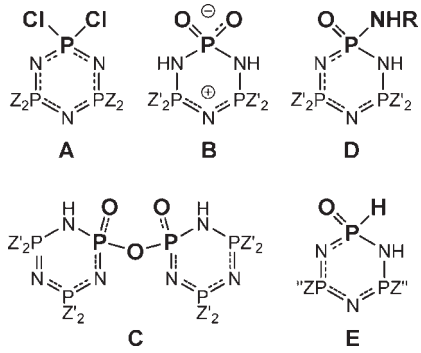


1 **2** **3**

oligopeptide,[6] and multiporphyrin assemblies,[7] as well as molecular components for inclusion compounds,[8] mesophases,[9] and micelles.[10]

Although a great deal of work has focused on the modification of the molecular periphery of cyclophosphazenes, the direct functionalization of the phosphazene ring has received less attention. Structurally characterized phosphazenes that contain oxo-functions (P═O) at the ring are rare and limited to esters {=P(O)OR} and phosphamides {=P(O)NHR}.[11] These compounds were mainly obtained by fortuitous hydrolysis of PCl moieties, which gives a P═O bond and at the same time protonates an adjacent ring nitrogen site under elimination of 1 equiv of HCl. Compared to other compounds with P−Cl bonds the hydrolysis of **1** is slow and requires an auxiliary base. The discovery that traces of water initiate the ring-opening polymerization of **1** yielding polyphosphazenes $\{Cl_2PN\}_n$ spurred interest in the hydrolytical behavior of **1**.[12] Monitoring the hydrolysis by ^{31}P NMR showed that the reaction bifurcates to give vicinal and geminal isomers of the partially hydrolyzed species.[13] The complete replacement of chloro groups produces the trimetaphosphimate ion **2**, which is the only structurally characterized phosphorus nitrogen ring system that contains dioxo phosphate moieties

Chart 2



A **B** **D** **C** **E**

$[PO_2]^-$. The trianionic ligand is a versatile building block for solid state compounds.[14] In addition, a number of oxo-derivatives of fully saturated phosphorus nitrogen rings (phosph(V)aza*n*es) have been described. Trioxophosph(V)azanes $(RNP(O)OR)_3$, **3** are generated by either thermal rearrangement of cyclotriphosphazenes $(RO)_6P_3N_3$[15] or oxidation of the corresponding cyclotriphosph(III)azanes $(RNPOR)_3$.[16] Likewise, oxo-derivatives of cyclodiphosph(V)azanes are obtained by either controlled oxidation or hydrolysis of cyclodiphosph(III)azanes.[17]

Herein, we present simple preparative routes to cyclotriphosphazenes that feature oxo-functions at one of the ring phosphorus atoms, while the other two phosphorus atoms are protected by amino groups. The resulting compounds show amphiphilic properties and thus promise applications as ligands, surfactants, and supramolecular building blocks. Starting from geminal dichlorides **A** (here Z_2 represents amino groups, $Z'_2 = (NHCy)_2$ and $Z'' = \{EtN(C_3H_6)NEt\}$ respectively) we have developed simple synthetic routes to the zwitterionic phosphate **B**, the pyrophosphate **C**, the phosphamide **D**, and the phosphite **E** (Chart 2).

Results and Discussion

Synthesis. Geminal dichloro cyclotriphosphazenes **A** are commonly obtained either by stoichiometric reactions of **1** with 4 equiv of a primary amine equipped with branched alkyl groups[18] or by treatment of **1** with ethylene or propylene diamines.[19] Here, we have employed the

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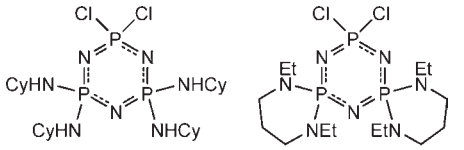
Chart 3



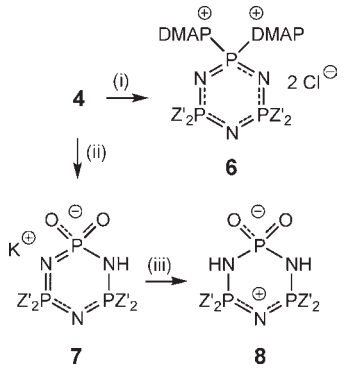
4 **5**

cyclohexyl amino derivative **4** for the synthesis of compounds **B**, **C**, and **D**, while the spirocyclic *N*,*N*′-diethyl propylene diamino derivative **5** was used to generate phosphites **E** (Chart 3).

We anticipated that the hydrolysis of the dichloride **4** would be a convenient route to phosphate **B**. However, the PCl_2 moiety remained unscathed even when **4** was refluxed for several days in a biphasic mixture of tetrahydrofuran (thf) and aqueous KOH. The reaction proceeded very slowly (10% conversion after 1 day) in the presence of a phase-transfer catalyst ($[Bu_4N]Br$). Also, refluxing **4** in a biphasic mixture of aqueous HCl and thf failed to hydrolyze the P−Cl bonds, but only protonated the ring nitrogen atom located opposite to the PCl_2 group (see Supporting Information for the crystal structure of [**4**H]Cl·thf). The reluctance of the P−Cl bonds to hydrolyze in the presence of hot hydroxide solution is surprising considering the generally observed moisture sensitivity of P−Cl bonds.[19] To our knowledge there are no reports of P−Cl bonds that withstand prolonged exposure to concentrated aqueous alkaline hydroxide solutions at elevated temperature. In search for a suitable catalyst for the hydrolysis of **4** we have tested 4-dimethylamino pyridine (dmap). Apart from being a strong nucleophile that catalyzes a plethora of substitution reactions[20] it also forms stable adducts with a variety of phosphorus compounds.[21] Recently, we have reported that **1** reacts with 6 equiv of dmap in superheated chloroform to form a crystalline material that contains $[(dmap)_6P_3N_3]^{6+}$ ions.[22]

During the course of the present study we found that **4** reacts with 2 equiv of dmap when refluxed in chloroform for 1 day yielding the dicationic dmap adduct $[(dmap)_2(CyNH)_4P_3N_3]^{2+}$ **6** (Scheme 1). The ^{31}P NMR spectrum of **6** showed the characteristic AX_2 signal pattern of cyclotriphosphazenes containing two magnetically equivalent ^{31}P nuclei in the phosphazene ring {δ 6.5 (t), 9.7 (d), $^2J_{PP}$ = 50.6 Hz}. The chemical shift of the triplet signal resembles that of $[(dmap)_6P_3N_3]Cl_6$.[22] The dicationic complex appeared in the ESI-MS at 772 Da. We were

Scheme 1[a]



7 **8**

[a] Reagents and conditions: (i) dmap, $CHCl_3$, 24 h reflux; (ii) aq. KOH, dmap, thf, 24 h reflux; (iii) aq. NH_4Cl; Z′ = NHCy.

able to grow crystals of $[\mathbf{6}]Cl_2\cdot 1.5CHCl_3\cdot 2H_2O$ from a solution in chloroform under an atmosphere of thf. The X-ray structure confirmed the existence of the dication. The presence of water indicates that phosphazene-dmap adducts are to some extent stable toward hydrolysis. Although dry thf had been used, moist air might have leaked into the crystallization apparatus during several weeks of storage.

When **4** was refluxed in a mixture of aqueous KOH, thf, and 1 equiv of dmap, a single product formed over the duration of 1 day as indicated by the appearance of an AX_2 signal pattern in the ^{31}P NMR at δ −0.2 (t) and 12.8 (d), which was identified as the potassium salt **7**. Signals of dmap adducts were absent from the spectra, which suggests that the initial reaction of **4** with dmap is slow compared to subsequent hydrolysis.[23] The potassium salt **7** was crystallized from the reaction solution. However, the crystals were highly mosaic giving X-ray data of poor quality. Nonetheless, a crude structure model was obtained that verified the presence of one potassium ion per ligand anion (see Supporting Information). Treatment of the reaction solution with ammonium chloride yielded the neutral zwitterion **8**, which is insoluble in toluene and chloroform, but soluble in methanol and sparingly soluble in thf (Scheme 1). Its ^{31}P NMR displayed an AX_2 signal at δ −3.8 (t) and 9.7 (d) with a $^2J_{PP}$ coupling constant of 13.9 Hz. **8** crystallized from thf in the form of the tetrahydrate $\mathbf{8}\cdot 4H_2O$, which has been confirmed by X-ray structure analysis (see below).

Upon heating, $\mathbf{8}\cdot 4H_2O$ dehydrated to form the pyrophosphate **9** (Scheme 2). The thermogravimetrical analysis of $\mathbf{8}\cdot 4H_2O$ showed a two-step weight loss upon heating to 180 °C, which equates to the removal of 4.5 equiv of water. On a preparative scale heating of $\mathbf{8}\cdot 4H_2O$ to 160 °C under reduced pressure (0.1 Torr) for 2 h yielded a colorless material that is soluble in various organic solvents including thf, chloroform, and toluene. Its ^{31}P NMR spectrum recorded in toluene consisted of two broad multiplets at δ 7.6 and −14.8 displaying an intensity ratio of 2:1.The ESI-MS exhibited a molecular ion peak at 1105 Da, which corresponds to the molecular weight of pyrophosphate **9**. The compound formed glassy

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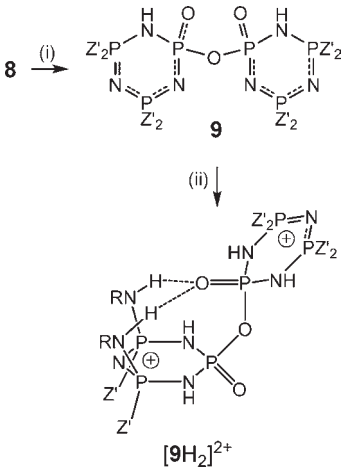
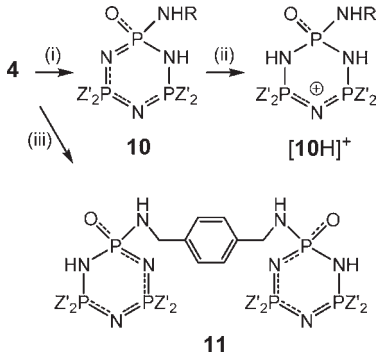
(23) It should be noted that the corresponding *tert*-buytl derivative $(t\text{BuNH})_4Cl_2P_3N_3$ gave only traces of hydrolyzed product after 1 week refluxing in a mixture of aqueous KOH, thf, and dmap.

Scheme 2[a]



[a] Reagents and conditions: (i) 160 °C, 0.1 Torr, 4 h; (ii) aq. HCl; Z′ = NHCy, R = Cy.

Scheme 3[a]



[a] Reagents and conditions: (i) *1*. aq. KOH, RNH_2 (R = benzyl), thf, 24 h reflux, *2*. aq. NH_4Cl; (ii) H_2dhtp, methanol; (iii) *1*. aq. KOH, α,α′-diamino-*p*-xylene (0.5 equiv.), thf, 24h reflux, *2*. aq. NH_4Cl; Z′ = NHCy.

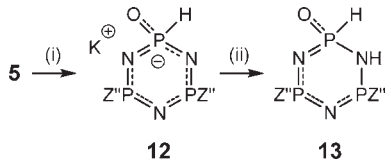
beads from toluene, which were not suitable for X-ray structure determination. However, single crystals of the hydrochloride $[\mathbf{9}H_2]Cl_2 \cdot 3.5H_2O \cdot 0.5HCl$ were obtained by gas-phase diffusion of conc. HCl into a solution of **9** in toluene. The ^{31}P NMR of $[\mathbf{9}H_2]Cl_2$ in chloroform contains four signals, two doublets at δ 8.2 and 6.4, and two triplets at δ 0.0 and −8.5 indicating the presence of two distinct phosphazene rings within the dication $[\mathbf{9}H_2]^{2+}$. The crystal structure showed that the two rings are locked into two different orientations via internal hydrogen bonds.

Phosphamides of type **D** were prepared via a concurrent aminolysis-hydrolysis reaction (Scheme 3). The reaction of the dichloride **4** with benzylamine in a biphasic mixture of thf and aqueous hydroxide solution was followed by ^{31}P NMR. Upon completion it showed two sets of AX_2 signals at δ 15.3 (d)/10.5 (t), and 18.8 (t)/15.9 (d), respectively, with relative intensities of 6.7: 1. The signals of lower intensity were attributed to the mixed amino derivative $(CyNH)_4(BnNH)_2P_3N_3$. Workup of the reaction mixture with aqueous NH_4Cl led to the precipitation of a pure colorless compound, which was identified as the phosphamide **10**. The ^{31}P NMR exhibited an AX_2 signal at δ 12.2 (d) and 5.3 (t). This mirrors the behavior of **7**, which showed a similar upfield shift of the ^{31}P NMR signal upon treatment with NH_4Cl. Attempts to grow single crystals of the neutral phosphamide **10** were unsuccessful. However, addition of 1,4-dihydroxy terephthalic acid (H_2dhtp) to a solution of **10** in methanol yielded crystals of composition [**10**H][Hdhtp]·0.5-H_2dhtp, which were suitable for X-ray structure analysis.

Presumably, the initial step in the aminolysis-hydrolysis reaction is the nucleophilic attack of the amine, which is rapidly followed by hydrolysis. This reaction offers a convenient route toward cyclophosphazene based phosphamides. The analogous reaction with α,α′-diaminoxylenes produced compounds in which two phosphazene rings are connected via a diamino linker. The linked species **11** was obtained by heating a mixture of **4** and α,α′-diamino-*p*-xylene in a 2:1 ratio in the presence of aqueous KOH and a small amount of thf. The ^{31}P NMR of the reaction solution showed the presence of a single product displaying a triplet at δ 15.3 and a doublet at δ 10.8 with a $^2J_{PP}$ coupling constant of 37.4 Hz. Addition of aqueous NH_4Cl solution led to the precipitation of **11**, which showed an AX_2 signal at δ 12.2 (d) and 5.4 (t), ($^2J_{PP}$ = 30.5 Hz). This change in chemical shift is similar to that of the monophosphazene species **10**. The set of four aryl protons and the set of α-CH_2 groups of the xylenene bridge appeared in the ^1H NMR spectrum as single peaks confirming the symmetrical substitution of the xylylene residue. The ESI-MS displayed a signal for the molecular ion at 1224 Da, which corresponds to the molecular weight of **11**.

Cyclophosphazenes of type **E** containing phosphite moieties were prepared via reduction of the PCl_2 group followed by hydrolysis (Scheme 4). The dichloro derivative **5** was reacted with potassium in toluene. Subsequent addition of finely ground KOH to the reaction solution yielded the potassium salt **12**. The P-bonded proton appeared in the ^1H NMR at δ 7.07 displaying a $^1J_{PH}$ coupling constant of 536 Hz, which was also found in the proton-coupled ^{31}P NMR. The $^{31}P\{^1H\}$ NMR showed the characteristic AX_2 signal pattern (δ 24.6 (d), 4.6 (t), $^2J_{PP}$ = 27.7). The P−H stretching frequency was observed at 2331 cm^{-1} in the IR spectrum. Crystals of **12**·3toluene were obtained from a toluene solution. The X-ray structure consists of a hexameric complex (see below). Addition of ammonium chloride to a solution of **12** in toluene yielded the neutral compound **13**, which crystallized from a thf solution. The ^1H NMR of **13** exhibited a chemical shift of δ 7.10 for the P-bound proton with a $^1J_{PH}$ coupling constant of 580 Hz. The proton-coupled ^{31}P NMR recorded at room temperature in thf showed a very broad signal at δ 17.3 and a doublet at δ −5.0. The latter displays the $^1J_{PH}$ coupling; thus it can be assigned to the PHO residue. Variable temperature ^{31}P NMR studies indicated that the signals are broadened

Scheme 4[a]



[a] Reagents and conditions: (i) *1*. K (2 equiv.), toluene, *2*. KOH; (ii) NH_4Cl; Z″ = {EtN(C_3H_6)NEt}.

because of slow proton transfer between the two ring N sites bounding the PHO moiety. Upon lowering the temperature to −40 °C, the signal δ 17.3 split into a doublet of doublets at δ 20.0, and a doublet at δ 13.6, while the signal of the PHO residue gave a doublet at δ −5.0. The dd signal at δ 20.0 can be assigned to the phosphorus atom bonded to two non-protonated ring nitrogen atoms, while the P−P coupling across the protonated N-ring site with its longer P−N bonds (see X-ray structure below) is too small to be observed. The proton transfer between ring N sites in **13** is slow when compared to **7** and **10**, which also contain one NH group per ring, but show sharp AX_2 spectra at room temperature indicating rapid proton transfer. The slow H-transfer in **13** can be attributed to the non-polar character of side chains Z″. In contrast, substituents Z′ contain NH sites, which form stronger interactions with polar solvents and thus enhance the rate of a solvent mediated proton transfer.

Crystal Structures. The crystal structure of **[6]**$Cl_2 \cdot 1.5CHCl_3 \cdot 2H_2O$ contains a dicationic complex $[\mathbf{6}]^{2+}$, in which two dmap ligands are coordinated to one of the ring phosphorus atoms. The P−N bonds toward the dmap ligands are long (1.737(7) and 1.747(7) Å), which reflects their dative character. The N−P−N angle toward both dmap ligands is sharp (95.8(3)°) compared to the other two exocyclic N−P−N angles, which measure 105.6(3) and 106.0(3)°, respectively. The P_3N_3 ring is very slightly twisted along the P1−N3 axis. The ring angles are significantly wider at P1 (125.4(4)°) and N3 (127.4(4)°) than at the other ring atoms (P2: 114.1(3)°, P3: 114.7(3)°, N1: 118.3(4)°, N2: 118.9(4)°). There is also a marked deviation in the P−N ring bond lengths: The ring bonds at P1 are comparatively short measuring 1.546(6) and 1.558(6) Å, respectively. Similarly short bonds have been observed in the hexacation $[(dmap)_6P_3N_3]^{6+}$.[22] The next two P−N bonds are long (P2−N2: 1.632(7), P3−N1 1.645(7) Å), while the two P−N bonds furthest away from P1 are again short (P2−N3: 1.581(7), P3−N3 1.592(6) Å). This "ripple" effect of alternating P−N ring bond lengths is characteristic of cyclophosphazenes that carry electron withdrawing groups at one P atom and electron donating substituents at the other. The crystal structures of the dichloro derivatives **4** and **5** show a similar bonding pattern (see Supporting Information).

The tetrahydrate **8**$\cdot 4H_2O$ crystallizes in the chiral spacegroup $P2_12_12_1$. The asymmetric unit contains two molecules of **8** with very similar structural parameters. The P_3N_3 rings adopt a twist conformation: The two ring segments N11, P11, N12 and P12, N13, P13 are twisted with respect to each other along the P11−N13 axis by 18.8° (19.7° for the other crystallographically unique molecule). There is a pronounced variation in the bond lengths of the P_3N_3 ring: Long P−N bonds are found adjacent to the protonated N-sites (av. $P(O_2)$-N(H) 1.665 Å, P{$(NHR)_2$}-N(H) 1.645 Å), while the P−N bonds around the non-protonated N site are significantly shorter (av. 1.584 Å). In comparison the P−N bond lengths of hexaamino derivatives $(RNH)_6P_3N_3$ are on average 1.60 Å long,[24] but substantially longer when the ring N sites are protonated or alkylated.[25] The P−O bonds of **8** measure on average 1.498 Å, and the O−P−O bond angles 115.0°. These are similar to values found for $P(=O)_2$ moieties of dihydrogen phosphate ions that are part of organic salts.[26] Also the phosphimate ion **3** shows similar bonding parameters, for example, the P=O bonds in the tris(gunadinium) salt are on average 1.488 Å long.[27] The N−P−N ring angles are more acute at the PO_2 unit (av. N−P(O_2)−N 101.0°) and somewhat wider at the other P atoms (av. 109.1°). The related zwitterion **14** shows a similar (Chart 4), albeit more pronounced, variation of P−N ring bonding parameters.[28]

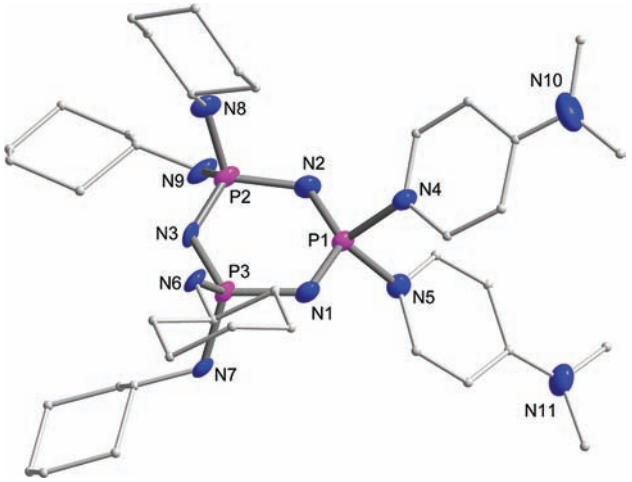
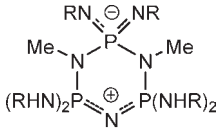


Figure 1. Crystal structure of the dication $[\mathbf{6}]^{2+}$ of **[6]**$Cl_2 \cdot 1.5CHCl_3 \cdot 2H_2O$. H-atoms are omitted for clarity. P and N atoms are drawn as 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg): P1 N1 1.546(6), P1 N2 1.558(6), P1 N5 1.737(7), P1 N4 1.747(7), P2 N3 1.581(7), P2 N2 1.632(7), P3 N3 1.592(6), P3 N1 1.645(7); N1 P1 N2 125.4(4), N5 P1 N4 95.8(3).

Chart 4



14

The supramolecular structure of **8**$\cdot 4H_2O$ displays a double helix (Figure 3). It consists of a tubular assembly of zwitterions that are arranged in a helical chain, which is intertwined with a helical chain of water molecules The zwitterions are connected to each other via pairs of hydrogen bonds between N(ring)H and PO functions with N···O distances ranging from 2.79 to 2.84 Å. The good quality of the X-ray data facilitated the location of all hydrogen atoms including those of the water molecules. The hydrogen bonding within the helical chain of water molecules follows the sequence [···HOH··· OH···O···HO···]. The water chain interacts as both H-donor as well as H-acceptor with N(exo)H functions

(24) Bickley, J. F.; Bonar-Law, R.; Lawson, G. T.; Richards, P. I.; Rivals, F.; Steiner, A.; Zacchini, S. *Dalton Trans.* **2003**, 1235–1244.

(25) (a) Richards, P. I.; Benson, M. A.; Steiner, A. *Chem. Commun.* **2003**, 1392–1393. (b) Benson, M. A.; Zacchini, S.; Boomishankar, R.; Chan, Y.; Steiner, A. *Inorg. Chem.* **2007**, *46*, 7097–7108.

(26) The mean P=O distance is 1.505 Å, and the mean O=P=O angle 114.7° (sample taken from 171 non-disordered crystal structures deposited in the Cambridge Structural Database with $R < 5\%$).

(27) Stock, N.; Jürgens, B.; Schnick, W. *Z. Naturforsch.* **1998**, *B53*, 1115–1118.

(28) Benson, M. A.; Ledger, J.; Steiner, A. *Chem .Commun.* **2007**, 3823–3825.

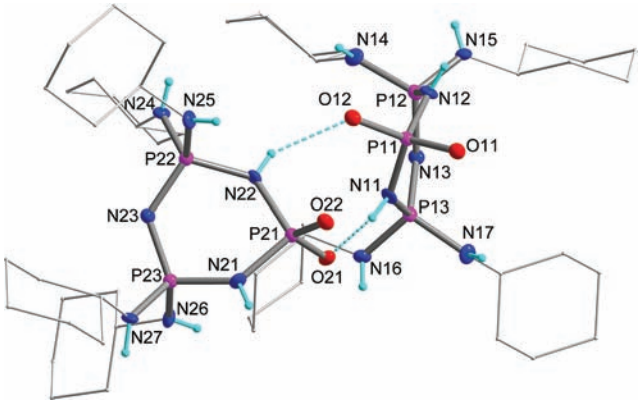


Figure 2. Crystal structure of the two crystallographically unique zwitterions **8** of the tetrahydrate **8**·4H_2O. P, N, and O atoms are drawn as 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg): P11 O11 1.497(2), P11 O12 1.500(2), P11 N11 1.667(3), P11 N12 1.665(3), P12 N12 1.641(3), P12 N13 1.586(3), P13 N11 1.642(3), P13 N13 1.584(3), P21 O21 1.500(2), P21 O22 1.497(2), P21 N21 1.668(3), P21 N22 1.660(3), P22 N22 1.658(3), P22 N23 1.580(3), *P*23 N21 1.639(3), *P*23 N23 1.585(3); O11 P11 O12 114.99(11), N12 P11 N11 100.95(13), O22 P21 O21 114.98(11), N22 P21 N21 101.10(13).

and PO_2 moieties of zwitterions. The double helix exhibits pseudo 4_1 symmetry and contains 4 zwitterions and 16 water molecules per turn. The result is a tightly knit network of hydrogen bonds which explains the low solubility of the tetrahydrate in aprotic solvents. The polar core of the double helix is surrounded by a hydrophobic layer of cyclohexyl groups. In the crystal the helical chains are homochiral and are packed alongside each other via hydrophobic interactions. Tubular supramolecular structures that host water chains are of great interest as models for biological membranes and proton conductors.[29] The few examples that have been described are tubular assemblies of short peptides[30] or organic macrocycles.[31]

The X-ray structure of [**9**H_2]Cl_2·3.5H_2O·0.5HCl contains the dication [**9**H_2]$^{2+}$ featuring a pyrophosphate residue, which fuses the two phosphazene rings via a bridging oxygen atom (Figure 4). All four ring nitrogen sites bounding the pyrophosphate group are protonated. The P_2O_3 chain is nearly planar with dihedral angles of 174° for O2−P1−O1−P4 and 8° for O3−P4−O1−P1. The chain shows a *cis*−*trans* arrangement and as a result the terminal oxygen atom O3 is situated directly above the phosphazene ring bound to the other end of the P_2O_3 chain. This arrangement is held in place by hydrogen bonds between two exocyclic NH groups and O3 displaying N···O distances of 2.936(9) and 2.969(10) Å, respectively. There is a slight difference in the terminal P−O bond lengths of the pyrophosphate group. The P2−O3 bond, which is locked into position by the intramolecular NH···O interactions, is slightly shorter (1.444(6) Å) than P1−O2 (1.474(6) Å). The bridging P−O bonds vary by a smaller margin (P1−O1 1.608(6), P4−O1 1.629(6) Å). The P−O−P angle amounts to 131.6(4)°. The bonding

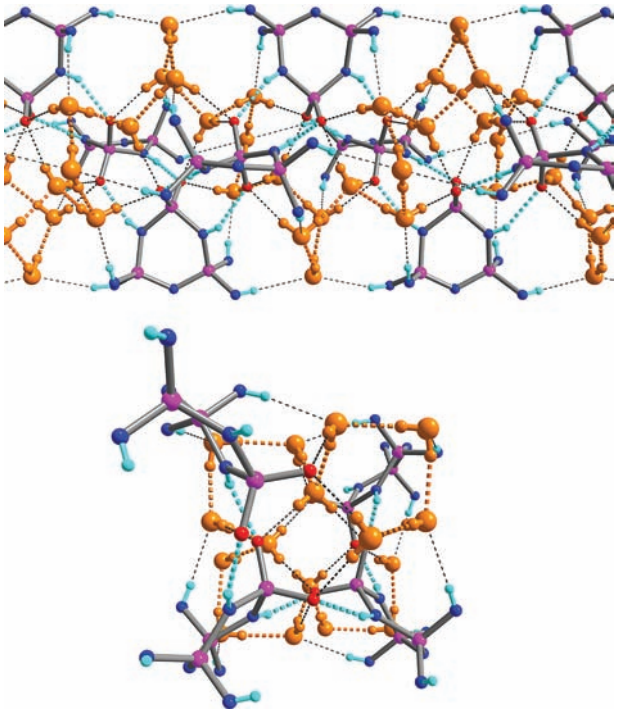


Figure 3. Double helical arrangement of **8**·4H_2O (water molecules drawn in orange, hydrogen bonds as dashed lines (orange: H-bonds between water molecules, turquoise: H-bonds between phosphazene molecules: gray, H-bonds between phosphazene and water molecules), cyclohexyl groups are omitted). The bottom diagram shows a view along the helical axis of one repeat unit (**8**·4H_2O)$_4$.

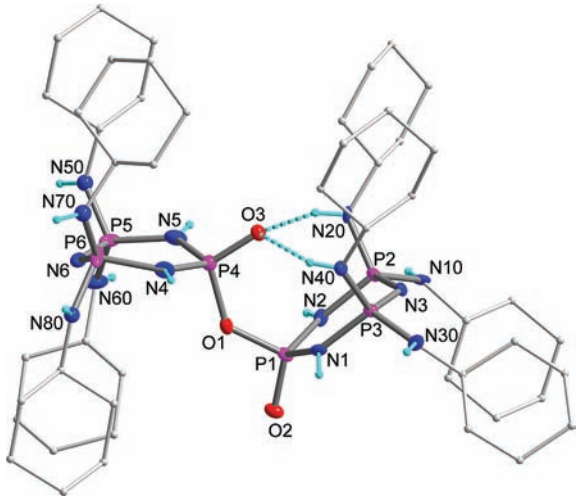


Figure 4. Crystal structure of the dication [**9**H_2]$^{2+}$ of [**9**H_2]Cl_2·3.5H_2O·0.5HCl. C-bound H-atoms are omitted for clarity. P, N, and O atoms are drawn as 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg): P1 O2 1.474(6), P1 O1 1.608(6), P4 O3 1.444(6), P4 O1 1.629(6); O2 P1 O1 106.0(3), O3 P4 O1 109.0(3), P1 O1 P4 131.6(4); N20···O3 2.936(9), N40···O3 2.969(10).

parameters of the pyrophosphate residue of the ion [**9**H_2]$^{2+}$ compare well with those observed in organic esters of pyrophosphates.[32] Analogous to the bonding pattern in the zwitterion **8**, the P−N ring bonds in [**9**H_2]$^{2+}$

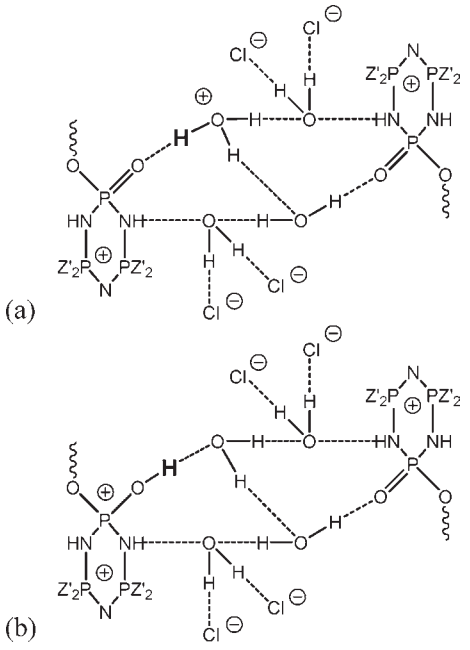
(29) (a) Agre, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4278–4290. (b) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808–1827.

(30) Guha, S.; Drew, M. G. B.; Banerjee, A. *Tetrahedron Lett.* **2006**, *47*, 7951–7955.

(31) Ono, K.; Tsukamoto, K.; Hosokawa, R.; Kato, M.; Suganuma, M.; Tomura, M.; Sako, K.; Taga, K.; Saito, K. *Nano Lett.* **2009**, *9*, 122–125.

(32) (a) Jones, P. G.; Sheldrick, G. M.; Kirby, A. J.; Briggs, A. J. *Acta Crystallogr.* **1985**, *C41*, 1374–1377. (b) Cullis, P. M.; Fawcett, J.; Griffith, G. A.; Harger, M. J. P.; Lee, M. *J. Am. Chem. Soc.* **2001**, *123*, 4147–4154.

Scheme 5. Part of the Supramolecular Structure of $[\mathbf{9}H_2]Cl_2 \cdot 3.5H_2O \cdot 0.5HCl$ Showing the Possible Sites of the Extra Proton (Shown in Bold): (a) As Part of an H_3O^+ ion; (b) Bonded to the Terminal Oxygen Atom O2 As Part of the Trication $[\mathbf{9}H_3]^{3+}$ [a]



[a] Note that there is a crystallographic inversion center between the two centrally arranged water molecules, which projects the disorder onto the other dication.

are long around the protonated ring nitrogen atoms and short at the non-protonated N atom. There are no previous reports of pyrophosphates derived from cyclophosphazenes. However, two polymorphs of the oxo-bridged species $(Cl_5P_3N_3)_2O$ have been structurally characterized.[33] Their X-ray structures show that the central P−O−P angle is somewhat flexible measuring 123 and 136°, respectively. A copper complex of a pyrophosphate compound derived from cyclocarbaphosphazene has been structurally described. The P_2O_3 chains in this complex adopt both *cis*−*cis* and *trans*−*trans* arrangements.[34]

We were able to deduce a reasonable model for the supramolecular structure of $[\mathbf{9}H_2]Cl_2 \cdot 3.5H_2O \cdot 0.5HCl$, which is governed by NH···O, NH···Cl, OH···O, and OH···Cl bonds (for further details see Supporting Information). It shows that the crystal contains half an equivalent of HCl per formula unit. The proton, formally derived from HCl, is disordered across a chain of water molecules connecting the terminal PO moieties of two dications. Scheme 5 shows the two arrangements: in (a) the proton is part of a H_3O^+ ion, while in (b) the proton is bonded to the terminal oxygen atom O2 as part of the trication $[\mathbf{9}H_3]^{3+}$. The partial protonation of O2 could explain the difference of terminal P−O bond lengths of P1−O2 and P2−O3 mentioned above. The PO bonds of triphenyl phosphine oxide[35] and tris(*tert*-butylamino) phosphine oxide[36] exhibit similar elongations upon protonation.

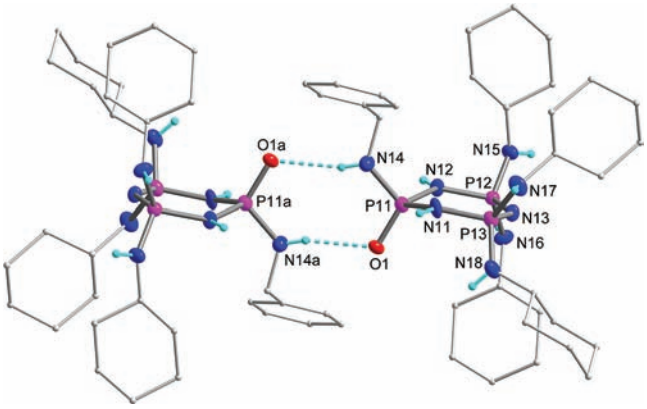


Figure 5. Crystal structure of $[\mathbf{10}H]^+$ of $[\mathbf{10}H][Hdhtp] \cdot 0.5H_2dhtp$ showing the hydrogen bonded dimer. P, N, and O atoms are drawn as 50% probability displacement ellipsoids. C bound H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P11 O1 1.489(3), P11 N14 1.599(4), P11 N11 1.654(4), P11 N12 1.660(3), O1 P11 N14 109.7(2), N11 P11 N12 102.3(2).

The neutral phosphamide **10** crystallizes upon addition of H_2dhtp to a solution of **10** in methanol yielding crystals of composition $[\mathbf{10}H][Hdhtp] \cdot 0.5H_2dhtp$. The crystals contain two cations $[\mathbf{10}H]^+$ in the asymmetric unit. It shows that both ring N atoms adjacent to the phosphamide residue are protonated. The P−O bonds measure on average 1.487 Å resembling the P−O bond lengths of the zwitterion **8**. The exocylic P−N bond length of the phosphamide residue (av. 1.607 Å) is similar to the exocyclic P−N bonds of the $(CyNH)_2P$ moieties (av. 1.615 Å). The P−N ring bonds of $[\mathbf{10}H]^+$ show a pattern that corresponds to that observed in **8** and $[\mathbf{9}H_2]^{2+}$ displaying long bonds around the protonated ring N sites and short bonds at the non-protonated site located opposite the oxo-P center. The cations $[\mathbf{10}H]^+$ form centrosymmetric hydrogen bonded dimers via pairs of NH···O bonds between the phosphamide residues (Figure 5). The N···O distances of NH···O interactions are 2.92 Å on average. The dimers are embedded in a hydrogen bonded network of $[Hdhtp]^-$ ions and H_2dhtp molecules. The $[Hdhtp]^-$ ions form H-bonded chains that interact with the dimers via NH···O bonds. The resulting two-dimensional sheets are interlinked by neutral H_2dhtp molecules that again are connected to the dimers via NH···O bonds (Figure 6).

Crystals of the potassium salt **12** were obtained from toluene in the form of the solvate **12**·3toluene. The crystal structure consists of a hexameric potassium complex (Figure 7). The potassium ions and the O atoms of the monoanionic phosphite ligands form a K_6O_6 core structure that can be described as an arrangement of two face-sharing cubes. Alternatively, the structure can be portrayed as a stack of three K_2O_2 squares. Similar K_6O_6 arrangements are exhibited by some hexameric potassium aryloxide and amino oxide complexes, which contain additional donor

(33) (a) Brinek, J.; Alberti, M.; Marek, J.; Zak, Z.; Touzin, J. *Polyhedron* **1998**, *17*, 3235–3241. (b) Brandt, K.; van de Grampel, J. C.; Meetsma, A.; Jekel, A. P. *Rec. Trac. Chim. Pays-Bas* **1991**, *110*, 27–28.

(34) Chandrasekhar, V.; Azhakar, R.; Krishnan, V.; Athimoolam, A.; Pandian, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 6802–6803.

(35) (a) Haupt, H. J.; Huber, F.; Krüger, C.; Preut, H.; Thierbach, D. *Z. Anorg. Allg. Chem.* **1977**, *436*, 229–236. (b) Ruthe, F.; Jones, P. G.; du Mont, W.-W.; Deplanoa, P.; Mercuria, M. L. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1105–1111. (c) Brock, C. P.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 6964–6970.

(36) (a) Chivers, T.; Fu, Z.; Thompson, L. K. *Chem. Commun.* **2005**, 2339–2341. (b) Chivers, T.; Krahn, M.; Schatte, G.; Parvez, M. *Inorg. Chem.* **2003**, *42*, 3994–4005.

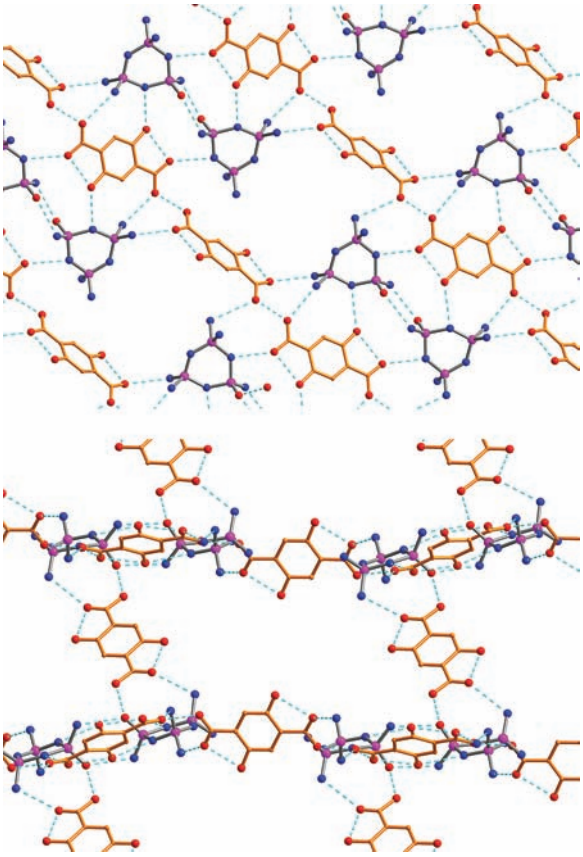


Figure 6. Supramolecular structure of [**10**H][Hdhtp]·0.5H_2dhtp. *top:* Layer assembly of [**10**H]$^+$ and [Hdhtp]$^-$ ions. *bottom:* Layers containing [**10**H]$^+$ and [Hdhtp]$^-$ ions are connected via H_2dhtp molecules. H-atoms and cyclohexyl groups are omitted for clarity.

ligands in the coordination sphere of the potassium ions.[37] To our knowledge, **12** is the only homoleptic complex of a molecular K_nO_n aggregate with $n > 4$. The K−O distances range from 2.585(4) to 3.056(4) Å. The long contacts involve the O atoms of the central K_2O_2 square, which coordinate to four potassium ions, while shorter bonds are observed around the three coordinate O-atoms of the base squares. The centrosymmetric complex contains three crystallographically independent ligands (labeled *L1*, *L2* and *L3* in Figure 7). The ligands coordinate to the metal centers via the O-atoms and both ring N-sites that are adjacent to the PHO moiety. This unique arrangement of donor sites yields two bidentate N/O chelates. Each of the three independent ligands is chelating a pair of potassium ions, albeit at distinct sites of the central K_6O_6 core: *L1* chelates a pair located at opposite base squares, *L2* a pair occupying the same base square, and *L3* a pair of potassium ions, one of which is part of a base and the other of the central square. The K−N bond lengths vary from 2.720(5) to 2.949(6) Å. In addition, *L2* forms a long K−N contact of 3.091(6) Å with an exocyclic nitrogen atom. The P−O bonds of the ligands are on

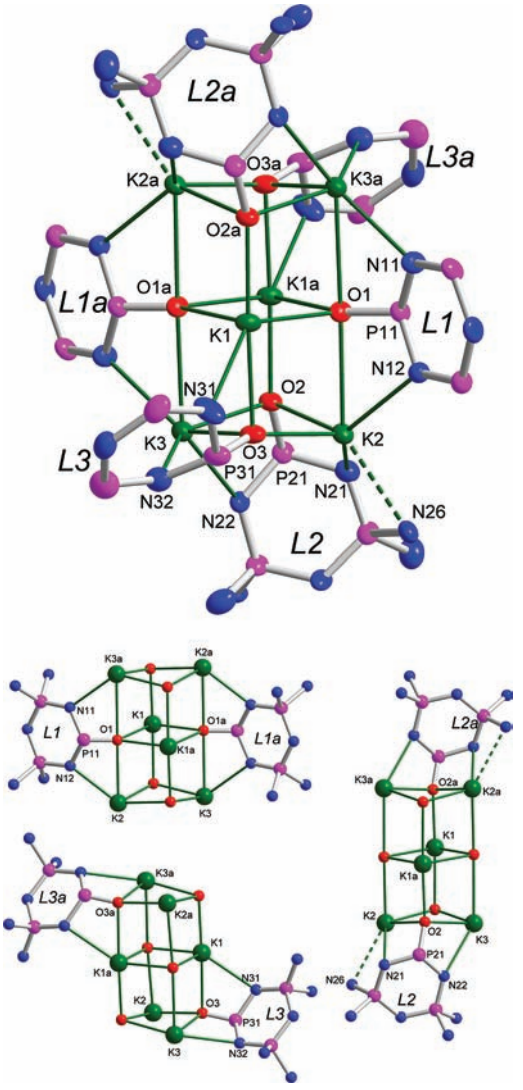


Figure 7. *top:* Crystal structure of the hexameric complex **12**. N(exo) atoms of phosphite ligands *L1* and *L3*; C and H atoms of all ligands are omitted for clarity. P, N, O, and K atoms are drawn as 50% probability displacement ellipsoids. Selected bond lengths (Å): K1 O2a 2.585(4), K1 O1a 2.692(4), K1 O3 2.747(4), K1 O1 2.752(5), K1 N31 2.895(7), K2 O3 2.602(5), K2 N12 2.720(5), K2 O2 2.839(5), K2 N21 2.944(5), K2 O1 2.967(4), K2 N26 3.091(6), K3 O3 2.682(5), K3 O2 2.683(5), K3a N11 2.761(6), K3 N22 2.898(5), K3 N32 2.949(6), K3 O1a 3.056(4), P11 O1 1.507(5), P21 O2 1.495(4), P31 O3 1.501(5). *bottom:* coordination of the three independent ligands toward the K_6O_6 core.

average 1.501 Å long, while the P−N(ring) bonds around the PHO residue measure on average 1.612 Å. The P−N(ring) bonds between the PZ″ center and the coordinated ring N site are on average 1.585 Å long, while the P−N bonds involving the non-coordinated ring N atoms amount to an average value of 1.589 Å.

The crystal structure of **13** shows a centrosymmetric hydrogen bonded dimer held together by two NH···O bridges with a N···O distance of 2.772(5) Å (Figure 8). The P−O bond measures 1.474(3) Å, which is slightly shorter than the P−O bond in the monoanionic ligand of **12**. The hydrogen atom at P1 was located in the Fourier difference map. It was freely refined and shows a P−H distance of 1.39(5) Å. The P−N bonds at N2, the protonated N atom, (P1−N2 1.672(4),

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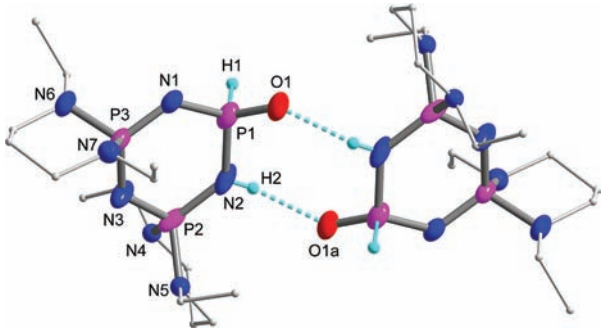

Figure 8. Crystal structure of **13** showing the H-bonded dimer. H bound C atoms are omitted for clarity. P, N, and O atoms are drawn as 50% probability displacement ellipsoids. P1 O1 1.474(3), P1 N1 1.589(3), P1 N2 1.672(4), N1 P3 1.568(4), N2 P2 1.659(5), N3 P2 1.565(4), N3 P3 1.602(4).

P2−N2 1.659(5) Å) are significantly longer than those of N1 and N3, which range between 1.565(4) and 1.602(4) Å and are comparable to the P−N ring bonds found in the anionic ligands of **12**. Both diamino susbtituents are affected by disorder indicating some conformational flexibility of the spirocyclic arrangement in the solid state.

Conclusion

A range of oxo-derivatives of cyclophosphazenes, including phosphate, pyrophosphate, phosphamide, and phosphite, were prepared from geminal dichlorophosphazenes using straightforward synthetic routes. The products are chemically highly inert and stable toward aqueous acids and bases. Similar to common phosphates the compounds show amphiprotic behavior: In neutral conditions they exist as neutral species, while in the presence of bases (e.g., hydroxide ions) anions are generated via deprotonation of ring NH sites. Upon addition of acids (e.g. carboxylic acids, aq. HCl) protonation occurs at vacant ring N sites giving cations. The crystal structures exhibit extensive networks of hydrogen bonding. In particular systems that carry exocyclic NH functions offer a multitude of H-bonding sites. Furthermore the compounds show amphiphilic properties: One section of the phosphazene ring is headed by the polar P-oxo group and its two adjacent N (or NH) sites, while the other section carries four hydrophobic alkyl groups. In some cases the unique electronic structure of the ring systems facilitates the existence of zwitterions, such as **8**, which contains a highly polar anionic end group and a cationic hydrophobic backbone. Hence, these systems offer a variety of applications, for example, as surfactants, supramolecular building blocks, and ligands for metal coordination and anion binding. In addition, larger aggregates can be generated via covalent connections joining the oxo-moieties of two phosphazene rings, such as **9** and **11**. This complements previously reported strategies for the generation of polyionic systems.[38]

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Supporting Information Available: Synthetic procedures and spectroscopic data for compounds **4**, **4**·HCl, **5**, **6**, **7**, **8**·4H_2O, **9**, [**9**H_2]Cl_2·3H_2O·0.5HCl, **10**, [**10**H][Hdhtp]·0.5H_2dhtp, **11**, **12**, and **13**; variable temperature NMR spectra of **13** in thf; thermogravimetric analysis of **8**·4H_2O; crystallographic data including information on the refinement of disorder. This material is available free of charge via the Internet at http://pubs.acs.org.

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