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Assembling Discrete D4R Zeolite SBUs through Noncovalent Interactions. 3.[1] Mediation by Butanols and 1,2-Bis(dimethylamino)ethane

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The use of tetrameric zinc phosphate $[Zn(dipp)(CH_3OH)]_4$ (**1**; dipp = diisopropylphenylphosphate dianion) as a suitable building block for realizing new noncovalently linked extended structures, via facile replacement of coordinated methanol molecules by other alcohols, is reported herein. Compounds $[Zn(dipp)(\textit{sec}\text{-butanol})]_4 \cdot 4H_2O$ (**2**) and $[Zn(dipp)(\textit{tert}\text{-butanol})]_4 \cdot 4H_2O$ (**3**) have been synthesized by the addition of *sec*- or *tert*-butanol to **1** at room temperature. The reaction of zinc acetate or zinc sulfate with $dippH_2$ in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) under similar reaction conditions results in the formation of $[H_2tmeda][Zn_4(dipp)_4(MeOH)_2(OAc)_2] \cdot (CH_3OH)$ (**4**) or $[H_2tmeda][Zn_3(dipp)_3(dippH)_2(CH_3OH)] \cdot (CH_3OH)_3$ (**5**), respectively. Analytically pure compounds **2**−**5** have been isolated in the form of single crystals directly from the respective reaction mixtures in very good yields and characterized with the aid of analytical and spectroscopic studies. Single-crystal X-ray diffraction studies reveal that compounds **2** and **3** are neutral tetranuclear zinc phosphates. Compound **4** is also a tetrameric phosphate but is anionic. The core structures of compounds **2**−**4** resemble the double-4-ring secondary building unit (D4R SBU) in zeolites. Compound **5** is a trinuclear ionic zinc phosphate built from three fused S4R SBUs. Compounds **4** and **5** represent the first examples of discrete anionic zinc organophosphates. The presence of coordinated *sec*- or *tert*-butanol molecules and a planar water tetramer cluster in **2** and **3**, and the H_2tmeda cations and methanol solvents in **4** and **5**, leads to the formation of zigzag chainlike supramolecular assemblies in the solid state.

Introduction

The discovery of microporous aluminophosphate materials in 1982 by Flanigen et al. signaled an epoch in the area of porous materials.[2] Efforts to build new microporous and framework metal phosphates have flourished since then. Consequently, the isolation of zinc phosphate based molecular sieves in 1991 fueled research on the synthesis and characterization of newer zinc phosphates and phosphonates.[3−5] Many of these derivatives are microporous materials with well-defined channels and cavities, which allows their utility in a wide range of applications. Compared to metal phosphates and phosphonates possessing extended structures, their discrete molecular analogues, at the oligonuclear scale, are explored only minimally.[6] An exception to this is the isolation of trinuclear zinc clusters, which have been implicated in biological systems such as phospholipase C and P1 nuclease.[7]

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The chemistry of both molecular metal phosphates and extended metal phosphate frameworks has been reviewed by us recently.[8]

Our group has been investigating for some time the means to build discrete main-group or transition-metal phosphate and phosphonate cage complexes that are soluble models for zeolite secondary building units (SBUs).[1,9−11] Metallosiloxanes such as $[RSiO_3Al]_4$ and metallophosphonates $[RPO_3M]_4$ (R = B, Al, Ga, In, and Zn) reported earlier display a core structure that resembles the double-4-ring SBU (D4R SBU) found in zeolites.[12] Several gallium phosphates containing occluded fluoride or oxygen in a D4R cubanelike structure have been reported previously.[13] Monoesters of phosphoric acid $(RO)P(O)(OH)_2$ have served as excellent candidates to assemble D4R SBU look-alike tetrameric zinc phosphates.[1] Modification of the ancillary ligation provides an excellent opportunity to connect these D4R cubanes, thus extending the discrete cage structures into hierarchical supramolecular assemblies of desired dimensions.[1] The synthesis of zeolites with tailored pore volume was earlier achieved using an organic structure-directing agent and the framework isomorphic substitution of germanium for silicon.[14] However, the noncovalent approach, recently described by us, allowed the connection of D4R cubanes rationally, and this can eventually lead to designer zeolitic solids.[1] In the present investigation, we have shown that hydrogen-bonding interactions emanating from the coordinated solvents and lattice water molecules can be used as the glue in connecting $Zn_4O_{12}P_4$ D4R zeolite building blocks to form extended supramolecular motifs. More importantly, it is reported here that the use of alkylamine (instead of arylamine or heterocyclic amine) provides an easy entry to the anionic zinc phosphates, which are discrete and oligomeric. Further investigations revealed that the trinuclear and tetranuclear ionic zinc phosphates synthesized during the course of this study are interrelated and can be considered as viable intermediates in the formation of neutral D4R cubanes, thus providing possible insights into the mechanism.

Results and Discussion

Zinc Phosphate Cubanes with Exocubane Alcohol Ligands: $[Zn(dipp)(butanols)]_4 \cdot 4H_2O$ (2 and 3; dipp = Diisopropylphenylphosphate Dianion). We have very recently shown that the reaction of $Zn(OAc)_2 \cdot 2H_2O$ with $dippH_2$ in methanol results in tetrameric zinc phosphate $[Zn(dipp)(CH_3OH)]_4$ (**1**) in very good yield.[1] Because of the rapid loss of coordinated methanol molecules from **1**, a single-crystal X-ray analysis to elaborate the solid-state structure was not possible. However, the labile methanol molecules can be irreversibly replaced by a wide variety of pyridinic ligands, which paved the way for the synthesis of several tetrameric zinc phosphate complexes $[Zn(dipp)(L)]_4$, having structures identical with the D4R SBU in zeolites. Moreover, by the proper modification of the substituents on the pyridine ancillary ligand, it has been possible to connect these D4R cubanes through noncovalent interactions to obtain extended superstructures. This approach resulted in hierarchical supramolecular assemblies of D4R cubanes.[1]

In order to establish the most likely discrete molecular nature of **1** (through a single-crystal diffraction study), attempts were made to replace CH_3OH with other high boiling alcohols. The addition of a few drops of *sec*- or *tert*-butanol to a solution of **1** leads to the isolation of well-formed single crystals of $[Zn(dipp)(2\text{-}BuOH)]_4 \cdot 4H_2O$ (**2**) or $[Zn(dipp)(t\text{-}BuOH)]_4 \cdot 4H_2O$ (**3**), respectively (Scheme 1). Compounds **2** and **3** can also be prepared from a direct reaction involving zinc acetate and $dippH_2$ in the presence of a methanol−butanol mixture. In both synthetic routes, compounds **2** and **3** have been isolated in quantitative yield and characterized by analytical and spectroscopic studies. The elemental analysis values obtained support the chemical formulation of $[Zn(dipp)(butanol) \cdot H_2O]_x$. IR spectra of both **1** and **2** are quite straightforward, and the strong absorption bands appearing at around 1190, 1020, and 920 cm^{-1} can be assigned to the P═O and M−O−P stretching vibrations, respectively. The absence of any broad absorption at around 2350 cm^{-1} rules out the presence of any undeprotonated P−OH groups of the phosphate ligand. The ^1H NMR spectral intensities confirm the formation of a 1:1:1 zinc−dipp−alcohol complex. The presence of a single resonance in the ^{31}P NMR spectrum (at around δ −4.5 ppm) is indicative of the presence of only one type of phosphate ligand in these compounds. While these studies support the

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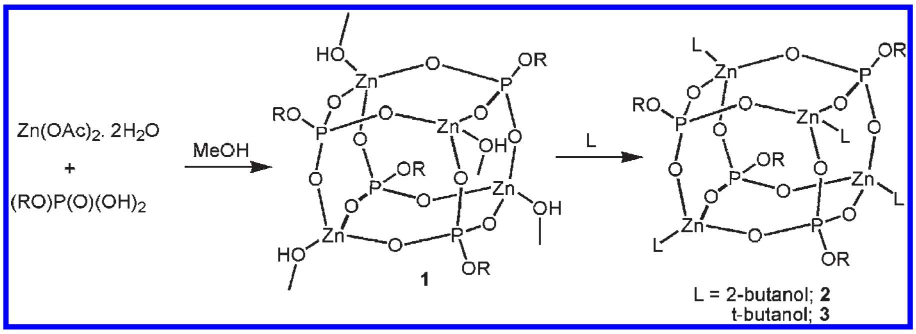
Scheme 1. Synthesis of **2** and **3**



[Zn(dipp)(butanol)]$_x$ formulation of the complexes, the determination of association number x is still elusive. To prove that x is indeed a small number and the products obtained are not polymeric materials (including the case of **1**), the solid-state structures of **2** and **3** have been investigated by a single-crystal X-ray diffraction study.

Structure Description of Cubanes 2 and 3. Poorly diffracting and somewhat mosaic single crystals of compounds **2** and **3** were directly obtained from the reaction mixture. Compounds **2** and **3** are isomorphous and crystallize in orthorhombic space group $P2_12_12$. A perspective view of the final refined molecular structures of both **2** and **3** (Figure 1) reveals that the zinc phosphates are indeed not polymeric solids but tetrameric complexes with a cubanelike core structure that resembles the D4R SBU of zeolites. To the best of our knowledge, compounds **2** and **3** are the only examples of structurally characterized molecular metal phosphates with a D4R SBU like core bearing exo oxygen-donor ligands on tetrahedral zinc centers. It is pertinent to note here that a series of D4R zinc phosphate cubanes with O−N donors have been described by us recently.[1]

Each of these molecules is composed of four zinc atoms, four phosphates, and four alcohol ligands. The molecules are built on a cubic framework, while the zinc and phosphorus atoms occupy the alternate vertices. Each of the Zn···P edges of the cube is bridged by a phosphate oxygen atom in a μ_2 fashion, which results in the formation of six nonplanar, eight-membered $Zn_2O_4P_2$ rings that adopt a distorted pseudo-C_4 crown conformation. The bond parameters found in these complexes are comparable to each other and also to earlier reported zinc phosphates and phosphonates in the literature.[1,5,15] There are no formal P−O and P=O bonds, and the observed average P−O bond distance within the cages of **2** and **3** is 1.496 Å. These distances are significantly shorter than that of the P−O single bond (~1.60 Å) but are considerably longer than that of the P=O double bond (1.45−1.46 Å). The average Zn−O distances in **2** and **3** vary slightly from each other (1.923 and 1.909 Å, respectively). The average Zn−O−P angles along the cubane edges (138.3 and 139.1°) are smaller than 180°, which would be expected for a linear edge, thus providing a spherical finish for the cubane structure. The zinc and phosphorus atoms in all of the complexes remain, by and large, tetrahedral. The dimensions of the cubic core in **2** and **3** can best be understood from the distances of the Zn···P edges (3.173 and 3.168 Å), P···P face diagonals (4.643 and 4.627 Å), Zn···Zn face diagonals (4.319 and 4.322 Å), and Zn···P body diagonals (5.487 and 5.479 Å). The volume of the inorganic core of these molecules is roughly 0.5 nm^3, while the volume of the whole molecule with organic substituents is in the range of 1.6−1.7 nm^3, consistent with the sizes of similar zinc phosphates with nitrigen-donor ligands.[1]

Another interesting structural feature of **2** and **3** is the supramolecular organization of individual S4R cubanes in the lattice. The solvent water molecules in both cases are present close to each other and the crystallographic 2-fold axis, hence forming a loosely hydrogen-bonded water tetramer cluster that is completely planar (Figures 2 and 3). This weak $(OH_2)_4$ cluster (O···O distances 3.135 and 3.294 Å), made up of tetrahedrally coordinated water molecules,[16] is perfectly sandwiched by the adjacent cubanes, as shown in Figures 2 and 3, and is held tightly by a number of strong O−H−O hydrogen bonds on either side. This results in a regular one-dimensional chainlike aggregation of the zinc phosphates in these two compounds.

Case of Aliphatic versus Aromatic Heterocyclic Nitrogen Donors: Synthesis and Characterization of [Zn_4(dipp)$_4$(MeOH)$_2$(OAc)$_2$]·(tmedaH_2)·(CH_3OH) (4) and [Zn_3(dipp)$_3$(dippH)$_2$(CH_3OH)]·(tmedaH_2)·(CH_3OH)$_3$ (5). After recently establishing the formation of noncovalently linked one-, two-, and three-dimensional assemblies based on D4R zinc phosphate cubane building blocks, primarily through the usage of pyridine-based ligands,[1] we investigated the reaction of zinc acetate and dippH_2 in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda). tmeda was chosen because of the flexibility of the N−C−C−N chain as well as the presence of four methyl groups, which would, in turn, be expected to form tmeda-bridged zinc phosphate based superstructures (Scheme 2). Although this attempt did not yield the desired superstructures, it gave easy access to ionic molecular zinc organophosphates for the first time, driven by the facile formation of a (tmedaH_2)$^{2+}$ cation. Thus, the reaction of

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(16) Theoretical ab initio calculations predict different arrangements for the water tetramer. The near-planar water tetramer has also been detected crystallographically as a part of embedded entities in different matrixes. However, the maximum possible tetrahedral coordination of the water molecule in the tetramers has been observed only in one case. See: Zuhayra, M.; Kampen, W. U.; Henze, E.; Soti, Z.; Zsolnai, L.; Huttner, G.; Oberdorfer, F. *J. Am. Chem. Soc.* **2006**, *128*, 424 and references cited therein.

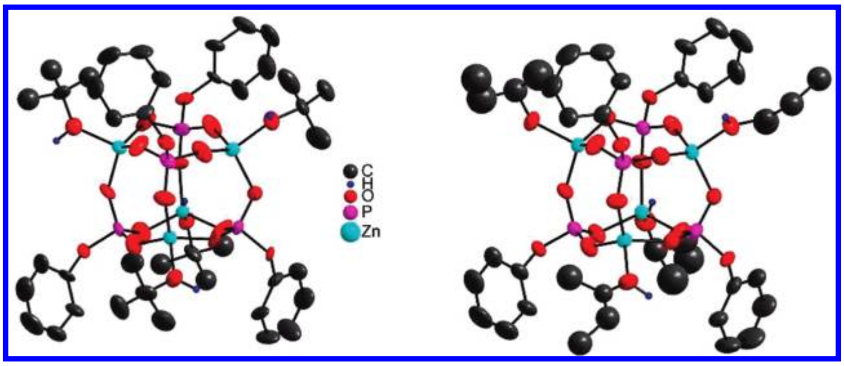


Figure 1. ORTEP diagrams (ellipsoids at the 50% probability level) of **2** (left) and **3** (right) drawn at the 50% probability level (C−H hydrogen atoms and the aryl substituents have been omitted for clarity).

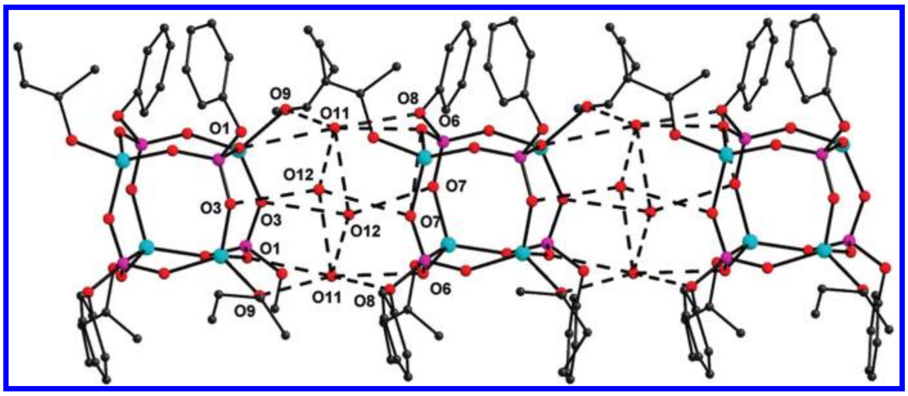


Figure 2. Planar tetrameric water-cluster-assisted, one-dimensional polymeric supramolecular assembly formation in the lattice of **2**.

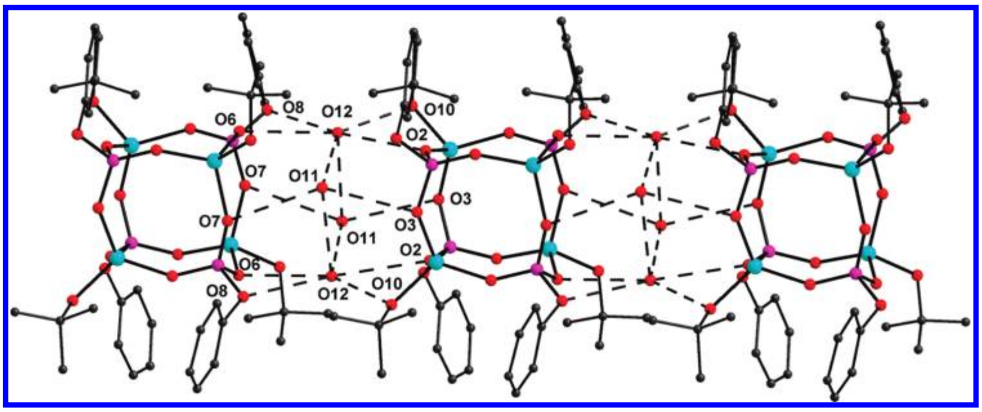
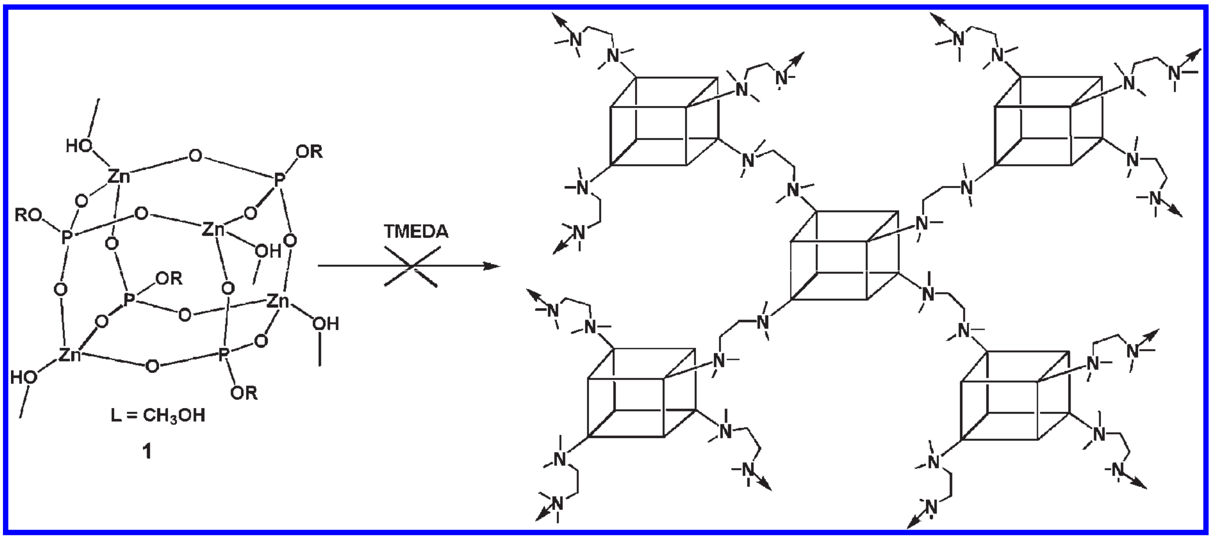


Figure 3. One-dimensional polymeric chain formation through the trapped tetrameric water clusters between the D4R zinc phosphate cubanes of **3**.

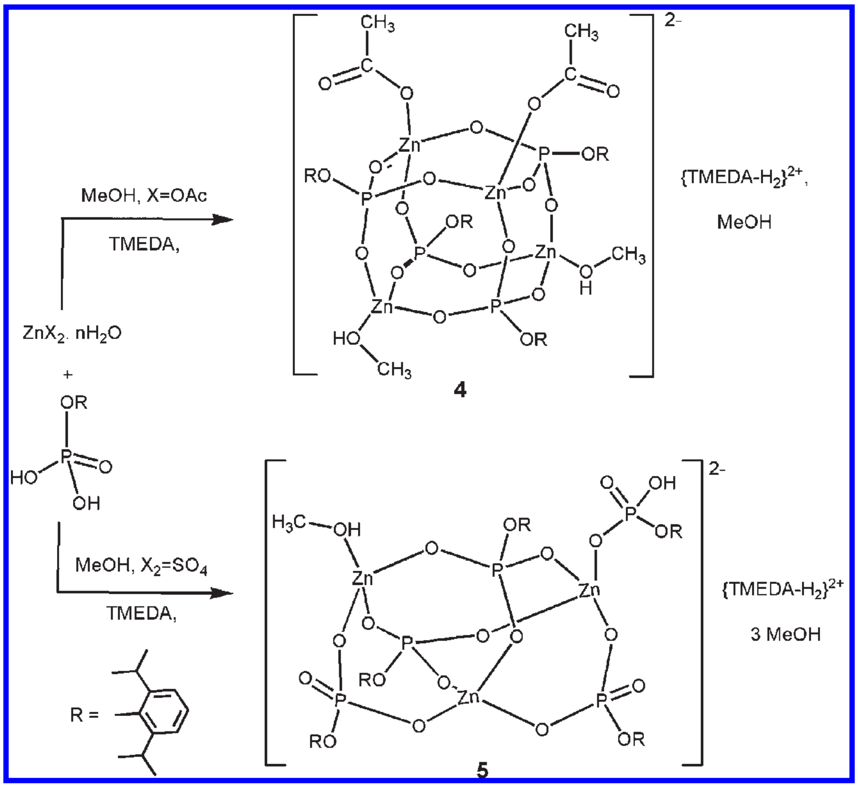
$Zn(OAc)_2 \cdot 2H_2O$, dippH_2, and tmeda yielded $[Zn_2(dipp)_2(MeOH)(OAc)]_2 \cdot (tmedaH_2) \cdot (CH_3OH)$ (**4**) as analytically pure single crystals. When the same reaction was repeated in the presence of zinc sulfate (instead of zinc acetate) under otherwise identical reaction conditions, $[Zn_3(dipp)_3(dippH)_2(CH_3OH)] \cdot (tmedaH_2) \cdot (CH_3OH)_3$ (**5**) was isolated (Schemes 2 and 3). Compounds **4** and **5** have been characterized by analytical and spectroscopic studies. The absence of any absorption at around 2350 cm^{-1} in the IR spectrum shows the complete reaction of dippH_2 with Zn^{2+}. The strong bands observed at around 1144 and 1010 cm^{-1} for **4** are readily assignable to P═O and M−O−P vibrations, respectively. In addition, hydroxyl or N−H and carbonyl stretching vibrations appear at around 3435 and 1582 cm^{-1}. Compound **4** shows a broad resonance in the ^{31}P NMR spectrum in an acetone-d_6 solution (δ −0.4 ppm). It is possible that the two expected signals appear as a broad signal in solution because of the dynamic exchange of −OAc and CH_3OH ligands on zinc centers.

The IR spectrum of **5** shows a broad signal at 2345 cm^{-1}, which can readily account for the presence of the P−OH group. The P═O and M−O−P stretching vibrations appear as very strong signals at 1178 and 1090 cm^{-1}. The ^{31}P NMR spectrum of **5** shows two single resonances at δ −3.0 and −4.7 ppm. While the resonance at δ −3.0 ppm could be attributed to the monodeprotonated phosphate ligands, the resonance appearing at δ −4.7 ppm is due to the fully deprotonated phosphate ligands. The observed ^1H NMR spectral pattern and the ratio of integrated intensities are consistent with the formulation of compounds **4** and **5**.

Scheme 2. Attempted Synthesis of tmeda-Bridged D4R Cubane Frameworks



Scheme 3. Synthesis of **4** and **5**



The solid-state diffuse-reflectance (DR)UV−vis spectrum of **4** shows absorption with a maximum at 314 nm, presumably originating from aromatic substitutions and the quaternary N−H protons of tmeda. It emits on the longer wavelength side at 430 nm, while excitation was at 272 and 376 nm. Unlike **4**, compound **5** absorbs at around 220, 267, and 308 nm. In spite of having multiple absorption maxima, compound **5** shows a single sharp emission at around 436 nm, while excitation is at 374 nm.

Molecular Structures of 4 and 5. X-ray-quality single crystals of **4** were obtained from a methanol solution by slow evaporation of the solvent over a period of 24 h at room temperature. A perspective view of the molecular structure of **4** is shown in Figure 4. The cubanelike core structure of **4** resembles the D4R SBU and is similar to the above-described zinc phosphates **2** and **3**. The molecule is built on a cubic framework containing four zinc and four phosphorus atoms at the alternate vertices. The major difference between cubic zinc phosphate **1** and the structure of **4** is the presence of two acetate ligands in the latter complex on two of the four zinc atoms. This unreacted acetate ligation leaves two of the four metal centers in the anionic zincate form. To balance this charge, one $[tmedaH_2]^{2+}$ cation is present per cubane.

The bond parameters observed for **4** are comparable to those found for the neutral cubic zinc phosphates

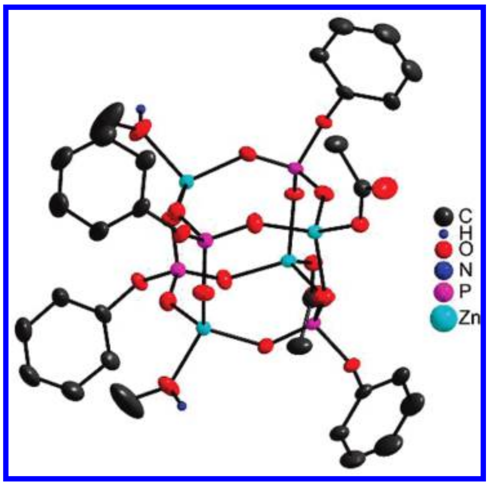


Figure 4. ORTEP diagram of the anionic part of molecular structure **4** (tmedaH_2 cation, methanol molecules, and some of the carbon and hydrogen atoms are omitted for clarity; ellipsoids are at the 50% probability level). Selected bond distances [Å]: Zn−O(P) 1.9063(2)−1.9515(2), Zn−O(CH_3OH) 1.978(2), Zn−O(OAc) 1.9421(2), P−O-(Zn) 1.497(2)−1.528(2), P−O(Ar) 1.610(2)−1.614(2). Bond angles [deg]: ∠Zn 101.10(8)−116.04(8) (ave 109.3), ∠P 104.00(1)−114.45(1) (ave 109.3), ∠Zn−O−P 130.02(1)−139.21(1) (ave 135.2).

described above. The observed average P−O distance inside the cage is 1.507 Å, while the average Zn−O distance is 1.919 Å. The Zn−O−P angles vary over a wide range [130.0(2)−139.2(1)°] and are considerably smaller than 180°, which would be expected for a linear edge. The zinc and phosphorus atoms display tetrahedral geometry. The dimensions of the cubic core can be best understood from the distances of the Zn···P edges (ave 3.170 Å), P···P face diagonals (ave 4.591 Å), Zn···Zn face diagonals (ave 4.371 Å), and Zn···P body diagonals (ave 5.423 Å). In addition, the D4R cages are connected through triple intermolecular hydrogen-bonding interactions via tmeda N−H protons and lattice methanol molecules, as shown in Figure 5 and Table 1.

Colorless block-shaped crystals of **5** obtained directly from the reaction mixture were found to be poorly diffracting but suitable for X-ray diffraction studies. Compound **5** crystallizes in the monoclinic space group $P2_1/n$. A close look at the structure reveals that the core is made up of four fused $Zn_2O_4P_2$, eight-membered ring systems in a *constrained* trinuclear arrangement (Figures 6 and 7). It is interesting to note that the trinuclear core found in **5** is unique among zinc phosphate clusters.[5c] Five phosphate ligands found in **5** exist in four different forms. The doubly deprotonated (P2 and P4) phosphate ligands are bridging three Zn^{II} ions in a bicapping tridentate [3.111] fashion, as per Harris notation.[17] Two bridging phosphate anions bind the metal centers in either a doubly deprotonated (P5) and monodeprotonated (P3) form. The monodeprotonated phosphate (P1) anion acts as a terminal ligand. The electroneutrality of the compound is retained by the doubly protonated tmedaH_2 dication. The periphery of the cluster core is enveloped by bulkier organic phenoxide substituents.

As expected, the (Zn)O−P bonds (ave 1.507 Å) are shorter than the (C)O−P bonds (ave 1.597 Å) and the average Zn−O distance is 1.932 Å. The average Zn−O−P angle (135.1°) is significantly shorter than that known for cubic zinc phosphates described above, owing to the highly strained nature of the cluster unit in **5**. The phosphorus and zinc centers adopt nearly tetrahedral geometry, and the average angles around them are 109.3 and 109.3°, respectively. The three zinc atoms occupy three corners of triangles whose sides are not equal. The observed distance of Zn1···Zn3 is significantly longer (4.705 Å) than those of Zn1···Zn2 and Zn2···Zn3 (3.711 and 3.648 Å, respectively). Similarly, the P···P distances are not equal (3.986, 4.563, 4.663, 4.664, and 4.723 Å).

The free P=O, P−OH, lattice methanol, and N−H (tmedaH_2) protons on either side of the molecule are the sources of interionic hydrogen-bonding interaction to yield a tmedaH_2-sandwiched polymeric network. The adjacent zinc phosphate anions sandwich the tmedaH_2 cations, as shown in Figure 8, through the strong N2−H−O19 and N1−H−O13 hydrogen bonds on either side (Table 1). In addition to this, the methanol molecules present in the lattice make additional bridges between the adjacent anions. Interestingly, on one side of the anion, a strongly bound methanol dimer formed by a solitary hydrogen bond between them (O24···O22 2.63 Å) connects the neighboring P−OH (O11) and P−O (O19) groups, as shown in Figure 8. On the other side of the anion, the third methanol molecule (O23) forms additional linkages.

Conversion of 4 and 5 to Neutral Cubanes. Although compounds **4** and **5** represent the ionic forms of molecular zinc phosphates and they have been synthesized from different starting materials, there are common structural features. It is likely that both compounds have essentially followed a similar reaction pathway. The cluster growth, however, terminated at different stages in different cases, yielding different nuclearity. A way to verify this hypothesis would be to react both **4** and **5** with the same reagent and expect to isolate the same products, preferably a D4R cubane. This is best done by investigating the reactivity of **4** or **5** with pyridine or 2-aminopyridine. Interestingly, in both cases, we isolated the corresponding neutral tetrameric zinc phosphate with a D4R cubanelike structure (Scheme 4). These reactions provide valuable insight into the formation of D4R cubic structures, and the ionic zinc phosphates **4** and **5** can thus be regarded as possible intermediates. A plausible pathway to the formation of neutral D4R cubanes via trinuclear and tetranuclear ionic structures is shown in Scheme 5.

Thermal Decomposition Studies. In addition to the remarkable aggregation properties described above, compounds **2**−**4** also show very interesting thermal properties. For example, thermogravimetric analysis (TGA) of **2** under dinitrogen reveals a weight loss (~60%) in the range of 50−700 °C corresponding to the loss of all organic substituents and water molecules in two distinct steps, leading to the formation of zinc pyrophosphate $[Zn_2P_2O_7]_{0.5}$. Compounds **3** and **4** show similar thermal behavior, and the ceramic yield obtained in each case

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[17] Harris notation describes the binding mode as [*X.Y*1*Y*2*Y*3...*Yn*], where *X* is the overall number of metals bound by the whole ligand and each value of *Y* refers to the number of metal atoms attached to the different donor atoms. See: Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349.

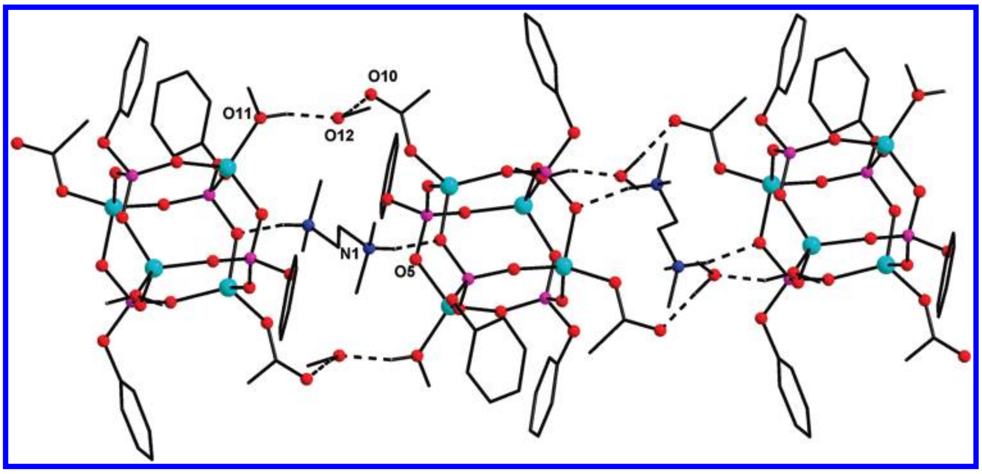


Figure 5. Formation of a one-dimensional polymeric chain through intermolecular hydrogen-bonding interactions (N−H···O and O−H···O) of **4**.

Table 1. Hydrogen-Bonding Parameters for **4** and **5**[a]

compound	hydrogen bonds	D−H [Å]	D···A [Å]	H···A [Å]	∠D−H···A [deg]
4	N1−H1···O5(a)	0.929	2.712	1.798	167.1
	O11−H11···O12(b)	0.951	2.574	1.672	157.0
	O12−H12···O10(c)	0.917	2.613	1.705	170.0
5	N1−H1···O13(a)	0.930	2.790	1.878	166.4
	N2−H2···O19(b)	0.930	2.567	1.654	166.2
	O2−H2A···O23(c)	0.917	2.623	1.713	170.8
	O21−H21···O3(d)	0.950	2.531	1.660	150.7
	O23−H23···O15(e)	0.840	2.767	1.932	172.7
	O24−H24···O22	0.840	2.631	1.793	176. 7
	O11−H11···O24	0.840	2.552	1.766	155.0

[a] Equivalent positions for **4**: (a) x, y, z; (b) $x, +y, +z-1$; (c) $x, +y, +z+1$. Equivalent positions for **5**: (a) x, y, z; (b) $-x+1, -y, -z+1$; (c) $-x+1, -y+1, -z+1$.

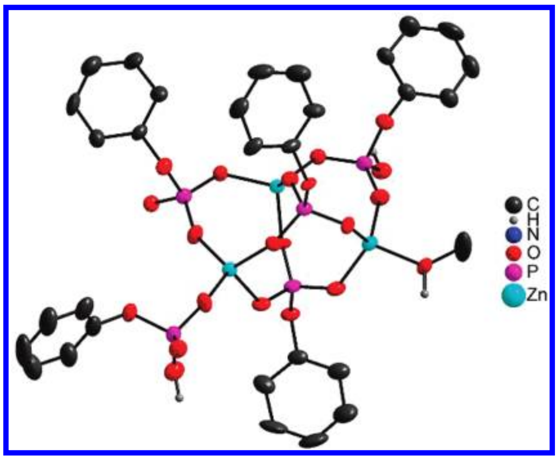


Figure 6. ORTEP diagram of the anion of **5** (the tmedaH_2 cation, methanol molecules, and some of carbon and hydrogen atoms are omitted for clarity; ellipsoids are at the 50% probability level). Selected bond distances [Å]: Zn−O(P) 1.878(3)−1.982(4), Zn−O(CH_3OH) 1.965(4), P−O(Zn) 1.488(4)−1.521(4), P−O(H) 1.547(4) and 1.547(5), P−O(Ar) 1.584(4)−1.607(4). Bond angles [deg]: ∠Zn 97.34(2)−119.76(2) (ave 109.3), ∠P 102.1(2)−116.2(2) (ave 109.4), ∠Zn−O−P 122.4(2)−155.7(3) (ave 134.1).

corresponds to the theoretical yield for zinc pyrophosphate. Thus, compounds **2**−**4** also prove to be useful precursors for the preparation of ceramic phosphates.[5] Thermal degradation of trimeric derivative **5**, however, produced a complex mixture of phosphates because of the Zn/P ratio of 3:5 in the precursor complex.

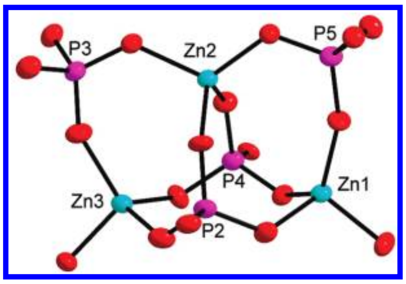


Figure 7. Molecular core structure of **5**. Ellipsoids are drawn at the 50% probability level.

Conclusion

We have shown in this contribution that it is possible to assemble the D4R cubanes by solvent-mediated supramolecular interactions. By using an alkylamine, ionic zinc phosphates with the nuclearities **3** and **4** have been isolated. Compound **5**, the trinuclear zinc phosphate open structure, is stabilized by tmeda interactions and is possibly a key intermediate in the formation of D4R cages. Although compounds **4** and **5** represent the first examples of molecular ionic zinc organophosphates, it appears that these complexes could serve as ideal multinuclear systems to isolate mixed metallic zinc phosphate assemblies.

Experimental Section

Apparatus. All operations were carried out under aerobic conditions in a beaker. IR spectra were obtained on a Perkin-Elmer FT-IR Spectrum One spectrometer as KBr-diluted disks.

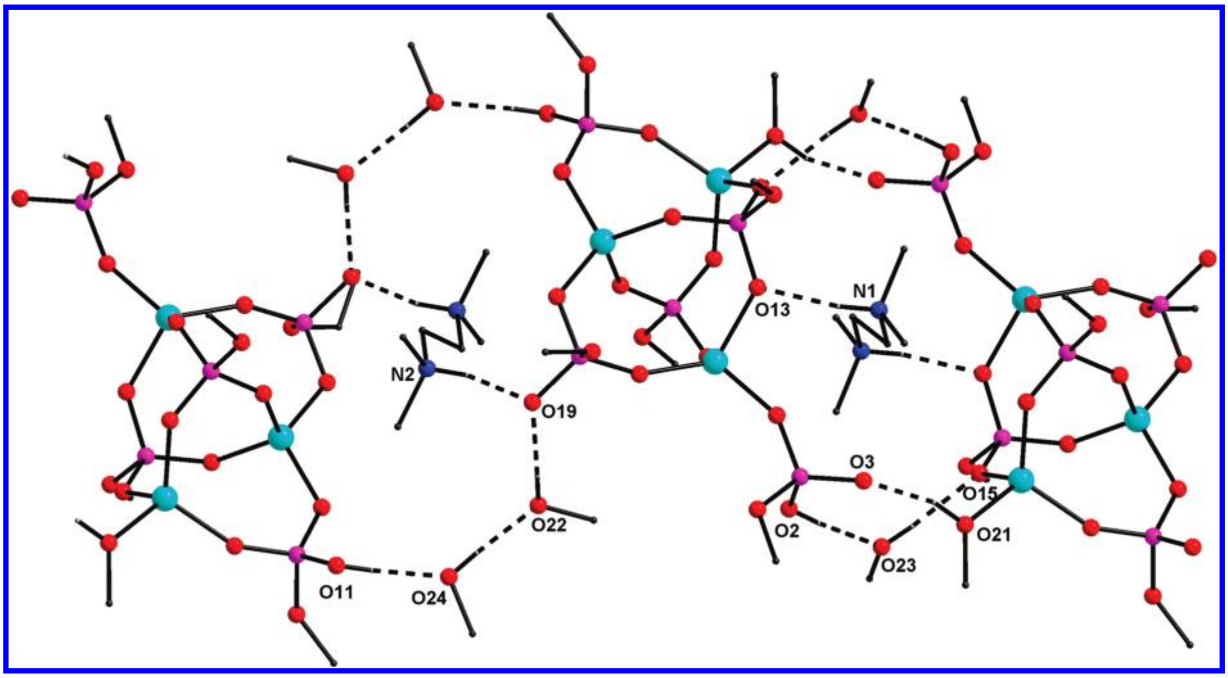
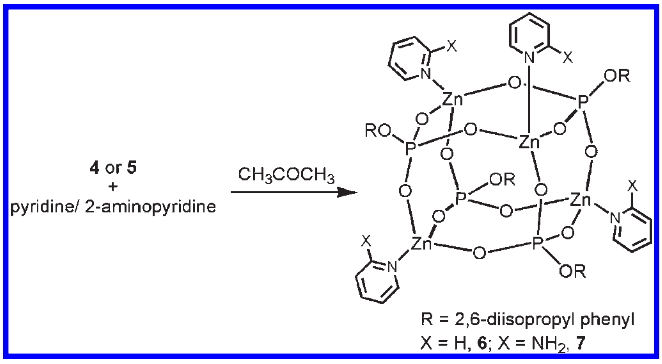


Figure 8. Formation of a one-dimensional chain in the lattice of **8** through extensive hydrogen bonding involving phosphate oxygen atoms, tmeda cations, and methanol molecules (coordinated and lattice) including a methanol dimer. See the text for a full description.

Scheme 4. Neutral D4R Zinc Phosphate Cubane Formation through the Ionic Zinc Phosphates **4** and **5**

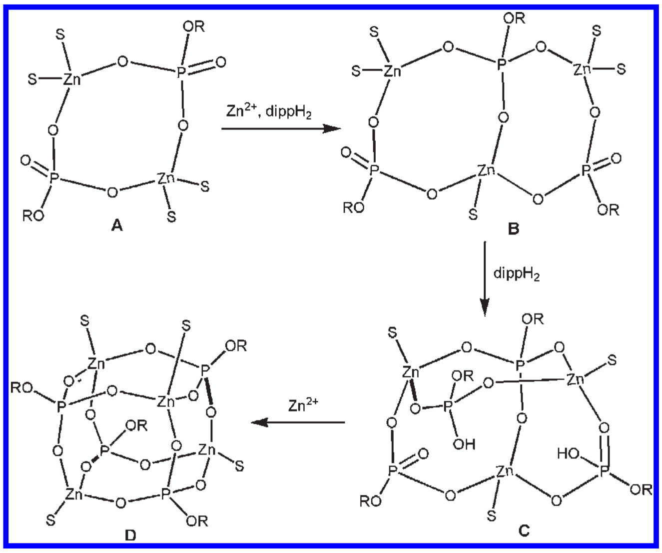


Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. The ^{1}H (Me$_4$Si internal standard) and ^{31}P (85% H$_3$PO$_4$ external standard) NMR spectra were recorded on a Varian VXR 300S spectrometer. TGA was carried out on a Perkin-Elmer Pyris thermal analysis system, under a stream of nitrogen gas at a heating rate of 10 °C/min. UV–vis spectra were obtained on a Shimdzu UV-260 spectrophotometer, and fluorescence spectra were obtained on a Perkin-Elmer LS-55 luminescence spectrometer.

Materials. Solvents were purified according to standard procedures prior to use.[18] Commercially available starting materials such as Zn(OAc)$_2$·2H$_2$O (s.d. Fine-Chem), ZnSO$_4$·7H$_2$O (s.d. Fine-Chem), pyridine (s.d. Fine-Chem), 2-aminopyridine (Lancaster), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda; Lancaster) were used as procured. 2,6-Diisopropylphenyl dihydrogen phosphate was synthesized as described previously in the literature.[19]

Synthesis of 2 and 3. [Zn(OAc)$_2$·2H$_2$O] (219 mg, 1 mmol) and diisopropylphenyl phosphate (258 mg, 1 mmol) were mixed in methanol (30 mL) and warmed to get a clear solution. The reaction mixture was filtered, concentrated, and left overnight to yield a precipitate of **1**. The addition of few drops of *sec*- or *tert*-butanol to **1** (0.354 g, 0.25 mmol) in a methanolic solution and subsequent crystallization at room temperature yielded block-shaped single crystals of **2** or **3** after 24–48 h (Table 2).

Scheme 5. Plausible Pathway to the Formation of Neutral D4R Zinc Cubane



Characterization Data of 2. Mp: >275 °C. Yield: 0.32 g (79%). Anal. Calcd for C$_{64}$H$_{116}$P$_4$O$_{24}$Zn$_4$ (M_r = 1655.1): C, 46.45; H, 7.06. Found: C, 45.81; H, 7.04. IR (KBr, cm^{-1}): 3436(br), 3066(w), 2968(s), 2929(w), 2869(w), 1627(br), 1466(m), 1441(m), 1383(w), 1337(w), 1257(m), 1178(vs), 1094(w), 1047(m), 1018(vs), 928(s), 769(s). ^{1}H NMR (acetone-d_6, 300 MHz): δ 7.02 (s, 12H, Ar), 3.79 (septet, 8H, ^{i}PrCH; $^3J_{HH}$ = 6.9 Hz), 3.56–3.60 (m, 8H, CH$_2$), 3.44 (br, 4H, CH), 1.08–1.13 (m, 24H, CH$_3$), 0.87 (d, 48H, ^{i}PrCH$_3$). ^{31}P NMR (acetone-d_6, 121 MHz): δ −4.4. TGA [temp range °C (% weight loss)]: 50–295 (22.4); 295–700 (38.2). DSC (°C): 89 (endo).

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[18] *Vogel's Text Book of Practical Organic Chemistry*, 5th ed.; Langman Group: Essex, Harlow, U.K., 1989.

[19] Kosolapoff, G. M.; Arpke, C. K.; Lamb, R. W.; Reich, H. *J. Chem. Soc. C* **1968**, *7*, 815.

Table 2. Crystal Data and Structure Refinement for **2**−**5**

	2	**3**	**4**	**5**
identification code	SK582	SK511	newrm156	newrm165
formula	$C_{64}H_{124}O_{24}P_4Zn_4$	$C_{64}H_{124}O_{24}P_4Zn_4$	$C_{62}H_{108}N_2O_{24}P_4Zn_4$	$C_{70}H_{121}N_2O_{24}P_5Zn_3$
fw	1662.99	1662.99	1650.86	1725.65
temp [K]	213(2)	213(2)	150(2)	150(2)
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12$	$P2_12_12$	$I2/a$	$P2_1/n$
a [Å]	14.675(2)	14.675(2)	21.5514(1)	18.0119(1)
b [Å]	28.204(4)	27.914(4)	14.9202(7)	25.1888(2)
c [Å]	9.7815(12)	10.006(1)	27.3888(1)	19.3179(7)
α [deg]	90	90	90	90
β [deg]	90	90	110.599(4)	98.724(6)
γ [deg]	90	90	90	90
V [Å^3]	4048.6(10)	4098.5(10)	8243.5(7)	8663.1(9)
Z	2	2	4	4
D(calcd) [g/cm^3]	1.364	1.348	1.330	1.323
μ [mm^{-1}]	1.318	1.302	1.295	0.985
cryst size [mm^3]	0.30 × 0.30 × 0.20	0.20 × 0.20 × 0.10	0.36 × 0.32 × 0.30	0.34 × 0.27 × 0.22
θ range [deg]	2.00−24.16	4.08−22.48	2.98−25.00	4.08−22.49
no. of reflns collcd	25 927	21 803	21 331	36 256
no. of obsd reflns [$I_0 > 2\sigma(I_0)$]	6217	5303	7201	11 175
GOF	0.991	0.980	0.966	1.049
R1 [$I_0 > 2\sigma(I_0)$]	0.0347	0.0653	0.0325	0.0590
wR2 (all data)	0.0834	0.1440	0.0932	0.1088
largest hole and peak [e/Å^3]	−0.288, 0.392	−0.664, 1.777	−0.443, 0.592	−0.448, 0.505

Characterization Data of 3. Mp: >275 °C. Yield: 0.36 g (89%). Anal. Calcd for $C_{64}H_{116}P_4O_{24}Zn_4$ (M_r = 1655.1): C, 46.45; H, 7.06. Found: C, 45.12; H, 7.02. IR (KBr, cm^{-1}): 3444(br), 3066(w), 2971(s), 2929(w), 2869(w), 1631(br), 1466(m), 1440(m), 1372(w), 1337(w), 1257(m), 1174(vs), 1112(w), 1047(m), 1020(vs), 925(s), 887(w), 768(s). ^{1}H NMR (acetone-d_6, 300 MHz): δ 7.02 (s, 12H, Ar), 3.79 (septet, 8H, CH; $^3J_{HH}$ = 6.9 Hz), 1.19 (s, 36H, CH$_3$), 1.11 (d, 48H, CH$_3$). ^{31}P NMR (acetone-d_6, 121 MHz): δ −4.6. TGA [temp range °C (% weight loss)]: 50−205 (13.8); 205−305 (11.8); 305−650 (34.4); 660−1000 (1.7). DSC (°C): 97 (endo); 197 (endo).

Synthesis and Characterization Data of 4. A solution of dippH$_2$ (258 mg, 1 mmol) in methanol (10 mL) was added to the solution (MeOH, 30 mL) of Zn(OAc)$_2$·2H$_2$O (219 mg, 1 mmol). To the clear solution obtained by stirring was added tmeda (116 mg, 1 mmol). The resulting mixture was refluxed for 45 min and filtered. The filtrate was allowed to evaporate slowly at room temperature, and this yielded colorless single crystals of **4** after 36−48 h. Mp: >275 °C. Yield: 0.35 g (88%, based on Zn^{2+}). Anal. Calcd for $C_{60}H_{100}N_2O_{22}P_4Zn_4$ (M_r = 1586.9): C, 45.41; H, 6.35; N, 1.77. Found: C, 44.78; H, 6.30; N, 2.63. IR (KBr, cm^{-1}): 3435(sharp), 3064(w), 2966(s), 2869(w), 1582(br), 1519(w), 1442(s), 1336(m), 1257(m), 1144(vs), 1110(vs), 1046(w), 1010(vs), 922(s), 801(w), 770(s). DRUV−vis (nm): 314. Fluorescence (λ_{ex} = 272, 376 nm): 430 nm. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.37−7.51 (m, 8H, Ar), 7.02 (br, 12H, Ar), 3.77 (br, 8H, CH), 2.63 (br, 2H, CH$_2$), 2.27 (br, 2H, CH$_2$), 2.03 (br, 6H, CH$_3$), 1.92 (br, 6H, CH$_3$), 1.15 (br, 48H, CH$_3$). ^{31}P NMR (acetone-d_6, 121 MHz): δ −0.4. TGA [temp range °C (% weight loss)]: 62−200 (9.3); 200−480 (48.5); 480−700 (3.1).

Synthesis and Characterization Data of 5. A solution of dippH$_2$ (438.6 mg, 1.7 mmol) in methanol (10 mL) was added to the solution (MeOH, 30 mL) of ZnSO$_4$·7H$_2$O (288 mg, 1 mmol). To the resulting reaction mixture was added tmeda (116 mg, 1 mmol), and the mixture was refluxed for 45 min. The reaction mixture was subsequently filtered, and the filtrate was allowed to evaporate slowly at room temperature. Colorless single crystals of **22** were obtained from the mother liquor after 2−3 days. Mp: >275 °C. Yield: 0.4 g (70%, based on Zn^{2+}). Anal. Calcd for $C_{70}H_{121}N_2O_{24}P_5Zn_3$ (M_r = 1725.8): C, 48.72; H, 7.07; N, 1.62. Found: C, 48.30; H, 6.89; N, 2.47. IR (KBr, cm^{-1}): 3427(br), 3065(w), 2966(s), 2870(w), 2345(br), 1633(br), 1466(m), 1442(m), 1383(w), 1336(w), 1256(m), 1178(vs), 1107(w), 1090(vs), 1047(w), 1003(s), 923(m), 771(s). DRUV−vis (nm): 220, 267, 308. Fluorescence (λ_{ex} = 374 nm): 436 nm. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.97−7.03 (m, Ar), 4.86 (br, N−H), 3.64−3.71 (septet, CH), 2.94 (s, CH$_2$), 2.45 (s, CH$_3$), 1.10−1.12 (d, CH$_3$). ^{31}P NMR (DMSO-d_6, 121 MHz): δ −3.0, −4.7. TGA [temp range °C (% weight loss)]: 50−180 (3.6); 180−440 (53.8); 440−540 (6.0).

Single-Crystal X-ray Structures. The single crystals suitable for X-ray diffraction studies have been obtained directly from the reaction mixture as described above. Intensity data were collected on a Stoe IPDS (**2** and **3**) and on an Oxford Xcalibur CCD diffractometer (**4** and **5**) using monochromatic Mo Kα radiation. The structures were solved by direct methods using *SHELX*[20] and *SIR-92*,[21] respectively. The structures were refined with full-matrix least squares against F^2 using all data (*SHELX*).[20] The crystals of **3** and **5** suffered from mosaicity and diffracted weakly. In both cases, the data were truncated at 45° in 2θ. All non-hydrogen atoms were refined anisotropically with the exception of atoms from disordered groups, which were split over two positions and refined isotropically using *similar bond* and *similar U* restraints as well as occupancy factors. Hydrogen atoms were constrained geometrically to their parent atoms, while one parameter was refined for the torsion angle of an OH group. **2** contains two disordered isobutyl groups; these were refined with restraints over two positions. The hydrogen positions of the two independent water molecules of **2** could not be located reliably. **3** contains one disordered *tert*-butyl group, which was split over two positions and refined using restraints. One of the two independent water molecules is disordered over two positions; again hydrogen atoms of the water molecules could not be located reliably. One of the dipp ligands in **4** shows disorder at one isopropyl group. The group was split over two positions and refined with restraints. **5** features three dipp ligands that have disordered isopropyl groups, which were split and refined with restraints. The Flack parameters[22] of the crystal structures of **2** and **3** refined to 0.26(1) and

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(20) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(21) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(22) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

0.14(3), respectively, which indicates some degree of racemic twinning.

Acknowledgment. This work was supported by DST, New Delhi, India. We thank the DST-funded National Single Crystal Diffraction Facility at Indian Institute of Technology—Bombay (IIT—Bombay) for the diffraction data and SAIF, IIT—Bombay, for the spectral data.

Supporting Information Available: Details of X-ray structure investigations (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.