Inorg. Chem. **2009**, *48*, 183−192

Inorganic Chemistry Article

Di-, Tri-, Tetra-, and Hexanuclear Copper(II) Mono-organophosphates: Structure and Nuclearity Dependence on the Choice of Phosphorus Substituents and Auxiliary N-Donor Ligands[†]

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Received August 11, 2008

Reactions of 2,6-dimethylphenyl phosphate (dmppH$_2$) and 2,6-diisopropylphenyl phosphate (dippH$_2$) with copper(II) precursors have been investigated in the presence of auxiliary N-donor ligands, and new structural types of copper phosphates have been isolated. Copper acetate reacts with dmppH$_2$ in the presence of either 3,5-di-*tert*-butyl pyrazole (dbpz) or 3,5-dimethyl pyrazole (dmpz), leading to the isolation of tetrameric complex [Cu(dmpp)(dbpz)]$_4$ **1** and hexanuclear cage complex [Cu$_6$(PO$_4$)(dmpp)$_3$(OAc)$_3$(dmpz)$_9$] **2**, respectively. Whereas compound **1** is a cubane-shaped cluster whose Cu$_4$O$_{12}$P$_4$ core resembles the double-4-ring (D4R) zeolite SBU, compound **2** is a novel hexanuclear copper complex with an unprecedented structure in metal phosphate chemistry. Use of bulkier dippH$_2$ in the above reactions, however, yielded metal-free acid−base complexes [(dippH)(dbpz)(dbpzH)] **3** and [(dippH)(dmpz)(dmpzH)] **4**, respectively. The reactions carried out between copper acetate and dmppH$_2$ or dippH$_2$ in the presence of chelating ligand 1,10-phenanthroline produced structurally similar dimeric copper phosphates [Cu(phen)(dmpp)(CH$_3$OH)]$_2$·2CH$_3$OH **5** and [Cu(phen)(dipp)(CH$_3$OH)]$_2$·2CH$_3$OH **6** with a S4R SBU core. Changing the copper source to [Cu$_2$(bpy)$_2$(OAc)(OH)(H$_2$O)]·2ClO$_4$ and carrying out reactions both with dippH$_2$ and with dmppH$_2$ result in the formation of trinuclear copper phosphates [Cu$_3$(bpy)$_3$(dmpp)$_2$(CH$_3$OH)$_3$]·2ClO$_4$·2CH$_3$OH **7** and [Cu$_3$(bpy)$_3$(dipp)$_2$(CH$_3$OH)$_3$]·2ClO$_4$·2CH$_3$OH **8**. The three copper ions in **7** and **8** are held together by two bridging phosphate ligands to produce a tricyclic derivative whose core resembles the 4=1 SBU of zeolites. Compounds **1**−**8** have been characterized by elemental analysis and IR, absorption, emission, and EPR spectroscopic techniques. The crystal structures of compounds **1**, **2**, **4**, **5**, **6**, and **8** have also been established by single-crystal X-ray diffraction studies.

Introduction

Following the discovery of phosphate analogues of zeolites, AlPOs with porous structures,[1] research on extended metal phosphate and similar framework structures gained momentum in the last two decades.[2] The recent realization that larger framework solids can be rationally built from preformed molecular precursors has led to an outburst of activity in the synthesis of smaller metal phosphate (and related phosphonate and siloxane) and similar molecules.[3−6] The research on molecular metal phosph(on)ate chemistry is also propelled by the quest of functional models for phosphate ester hydrolysis and the search of newer single

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[†] Part of this work is described in the M.Sc. dissertation of Amerendra Nath Maity submitted to IIT-Bombay, April 2003.

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10.1021/ic801532y CCC: $40.75

molecular magnets.[6–8] Although phosphoric acid forms extended (often framework) structures because of the presence of three acidic protons, derivatization of one or two hydroxyl groups of the phosphoric acid by ester formation ($(OR)P(O)(OH)_2$ and $(OR)_2P(O)(OH)$) normally results in the formation of metal complexes that are discrete molecules or clusters.[9] The diesters of phosphoric acid, $(RO)_2P(O)(OH)$, are similar to carboxylic acids in some ways and, hence, normally form either mononuclear or dinuclear metal phosphates more readily than larger clusters.[10,11] However, phosphate diesters do not exhibit a chelating mode of coordination, which is very common among metal carboxylates. Although bridging two adjacent metal ions is the most preferred mode of coordination for the phosphate diesters, there are a number of complexes where these molecules are monodentate through the $P-O^-$ group, with dangling $P=O$ groups. Phosphate monoesters, on the other hand, due to the presence of two acidic protons and one phosphoryl oxygen, tend to embrace more metal ions around them and form larger aggregates.[9,10] Hence, the secondary building units (SBUs) of several zeolitic structures can be modeled using these monophosphate esters, as it has been demonstrated in the past decade for the case of phosphonic acids.[12]

Among copper-containing phosphonates and phosphates, layered copper phosphonates $[Cu(RPO_3)(OH_2)]_n$ have been known for a long time.[13] Discrete molecular compounds of copper phosphonates, on the other hand, have been well-investigated in recent years, producing a large number of medium- to large-sized aggregates.[14] In contrary, the majority of the work carried out on copper phosphates has revolved around the synthesis of dinuclear copper complexes with the aim to synthesize functional models for phosphate diester hydrolysis under physiological conditions.[15−17] Much of these studies have focused on the multidentate ligand design to mimic the active sites of hydrolases.

Starting from di-*tert*-butyl phosphate (dtbpH), we have studied copper phosphate chemistry in some detail in recent years.[10c−e] It has been shown that it is possible to assemble one-dimensional polymeric phosphate $[Cu(dtbp)_2]_n$ that

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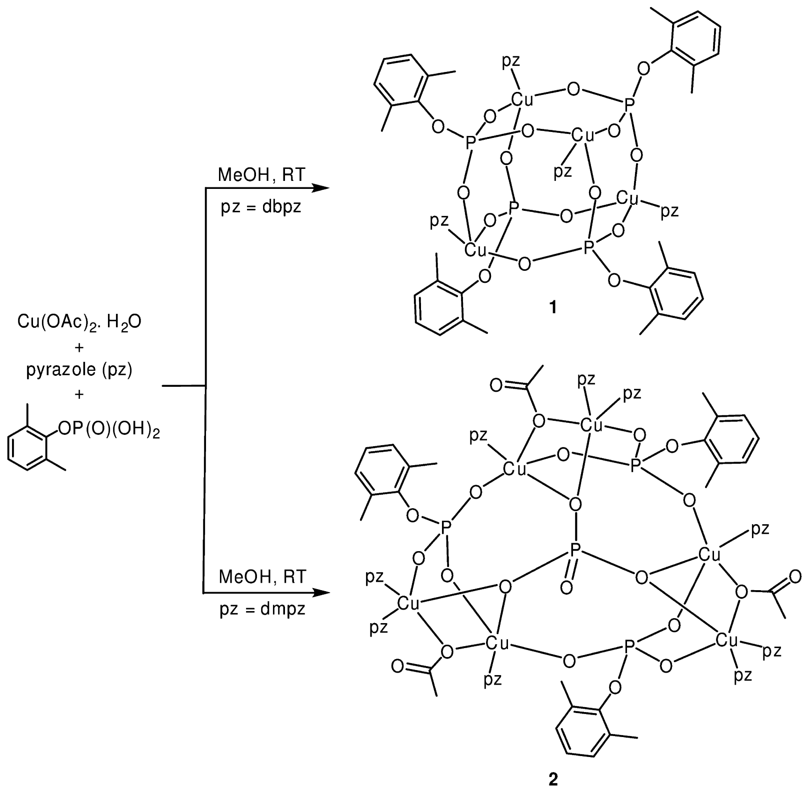
Scheme 1. Synthesis of Tetranuclear and Hexanuclear Copper Phosphates **1** and **2**



serves as a single-source precursor for the preparation of ceramic [$Cu(PO_3)_2$] at low temperatures. The monomeric Cu−dtbp complex, [$Cu(dtbp)_2(phen)(OH_2)$], prepared in the presence of chelating phen (1,10-phenanthroline) ligand, has thrown important mechanistic insights into phosphate diester hydrolysis assisted by H-bonding.[2] An interesting conversion of a water-bridged, one-dimensional polymer to a tetrameric cage phosphate was also unraveled during this study through the synthesis and structural characterization of [$Cu(dtbp)_2(py)_2(\mu\text{-}OH_2)$]$_n$ and [$Cu_4(\mu\text{-}OH)_2(dtbp)_6$].[10c] Inspired by the structural diversity shown by copper di-*tert*-butyl phosphate complexes and the fact that mono-organophosphate esters are better ligands for assembling polynuclear metal phosphate cage complexes,[9] we have now investigated the reactions of Cu^{II}−precursor complexes with two different mono-organophosphates in the presence of a variety of N-donor ligands.

Results and Discussion

To synthesize the new copper phosphates, two monoaryl esters of phosphoric acid, viz. 2,6-dimethylphenyl phosphate ($dmppH_2$) and 2,6-diisopropylphenyl phosphate ($dippH_2$), have been used. $Cu(OAc)_2 \cdot 2H_2O$ and dimeric precursor [$Cu_2(bpy)_2(OAc)(OH)(H_2O)$]$\cdot 2ClO_4$ have been used as the source of copper ions. To avoid the formation of insoluble, extended polymeric structures, monodentate N-donor ligands (substituted pyrazoles) and chelating N-donor ligands, 1,10-phenanthroline and 2,2′-bipyridine, have been used as the auxiliary ligands to block one or more coordination sites on the metal.

Synthesis of Copper Phosphate with Pyrazole Ligands. The reaction of $dmppH_2$ with copper acetate in the presence of a pyrazole coligand is highly sensitive to the substituents on the 3,5-positions of the pyrazole ring. The reaction in the presence of bulkier 3,5-di-*tert*-butyl pyrazole (dbpz) proceeds smoothly to yield the tetrameric copper phosphate [$Cu(dmpp)(dbpz)$]$_4$ **1** as the only product (Scheme 1). On the other hand, the use of less bulky 3,5-dimethylpyrazole (dmpz) leads to the exclusive formation of the novel hexanuclear copper phosphate [$Cu_6(PO_4)(dmpp)_3(OAc)_3(dmpz)_9$] **2**. Despite the fact that the syntheses of both **1** and **2** have been carried out under almost identical reaction conditions (in methanol at room temperature under aerobic conditions), the products isolated in the two reactions are quite different. Whereas in the case of **1** a 1:1:1 M/phosphate/pyrazole complex is formed, an interesting phosphate monoester hydrolysis is observed to produce hexanuclear complex **2**. Although the formation of a monomer was not anticipated in either case due to the ability of the phosphate ligand to embrace more metal centers, the selectivity of hexanuclear and tetranuclear structures for the two pyrazole ligands used is somewhat puzzling. It could, however, be argued that, although the presence of less bulky

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substituents on the pyrazole ligand (dmpz) can result in accommodating more than one pyrazole ligand per metal as in **2**, there is very little room around the metal ion to accommodate more than one bulky dbpz ligand. To overcome this coordinative unsaturation, the P═O group on dmpp acts as a bridge between the dimeric eight-membered rings, and, hence, a tetrameric aggregate is formed in the case of **1**. An additional difference between the formation of **1** and **2** is the Cu^{2+} ion-promoted hydrolysis of $dmppH_2$ to produce PO_4^{3-} anion during the synthesis.

Compounds **1** and **2** have been characterized by the aid of elemental analysis; IR, UV−visible, and EPR spectroscopy; room temperature magnetic measurements; thermal analysis; and single-crystal X-ray diffraction studies. The single crystals obtained for **1** and **2** were found to be analytically pure. The infrared spectra of both **1** and **2** are devoid of any absorption in the region of 2300 cm^{-1}, indicating the complete deprotonation (neutralization) of $dmppH_2$ during the reaction, leaving no P−OH groups in the product. The UV−visible spectrum of the hexanuclear **2** shows a weak absorption at 742 nm (ϵ = 67 $L\cdot mol^{-1}\cdot cm^{-1}$) due to the spin-forbidden d−d transitions, whereas the absorptions at 214 and 254 nm are assignable to ligand-based transitions.

Molecular Structure of 1. The central core of this tetrameric copper phosphate is made up of a $Cu_4O_{12}P_4$ unit that is somewhat similar to a number of metal phosphonates with a $M_4O_{12}P_4$ cubane core and metallosiloxanes with a $M_4O_{12}Si_4$ core (Figure 1).[5b,9b,14a] Compounds with this core have assumed particular importance due to their resemblance to the commonly observed D4R (double-four-ring) SBU of zeolites and other framework solids. Among the molecular metal phosphates, so far only zinc[9b] has been incorporated in the D4R core; hence, **1** represents the first metal phosphate cubane cluster involving a nontetrahedral metal in the alternate vertices of the cubane cluster.[14d]

The coordination geometry of copper ions in **1** can be best described as distorted square-planar. Because of the presence of four tetrahedral phosphorus centers and four square-planar copper centers in the eight vertices of the cluster, the D4R unit in **1** is distorted to a large extent (as compared to such units in octasilsequioxanes $(RSi)_8O_{12}$ or borophosphonate $[RPO_3BR']_4$, where the corners are occupied by tetrahedral main group elements such as B, Si, and P).[4c,5b,18] The irregularity of the cubic structure of **1** could be easily understood by viewing the core structure down *a*-, *b*-, and *c*-axes, as shown in Figure 2. For comparison, the core structure of $[(RO)PO_3Zn\cdot collidine]_4$ **A**,[9b] which is made up of a regular cubic core, is also shown in Figure 2.

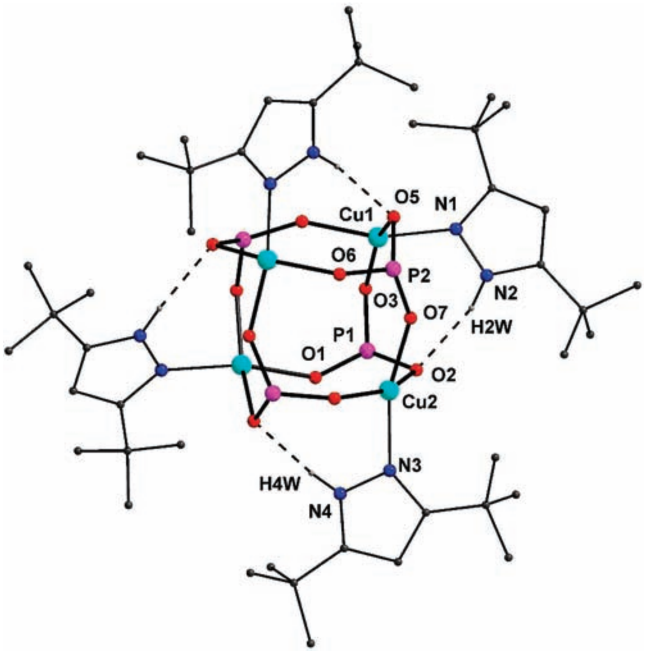

Figure 1. Molecular structure of **1** (lattice 1,4-dioxane molecules, phenoxide groups on phosphorus atoms, and hydrogen atoms have been omitted for clarity). Selected bond distances [Å]: Cu(1)−N(1) 1.970(3), Cu(1)−O(1) 1.919(3), Cu(1)−O(3) 1.930(3), Cu(1)−O(5) 1.978(3), Cu(2)−N(3) 1.984(3), Cu(2)−O(2) 1.980(3), Cu(2)−O(6) 1.919(3), Cu(2)−O(7) 1.923(3), P(1)−O(1) 1.516(3), P(1)−O(2) 1.533(3), P(1)−O(3)#1 1.518(3), P(1)−O(4) 1.609(3), P(2)−O(5) 1.545(3), P(2)−O(6) 1.514(3), P(2)−O(7)#1 1.515(3), P(2)−O(8) 1.600(3). Bond angles [°]: N(1)−Cu(1)−O(5) 91.4(1), O(1)−Cu(1)−N(1) 162.2(1), O(1)−Cu(1)−O(3) 96.0(1), O(1)−Cu(1)−O(5) 88.5(1), O(3)−Cu(1)−N(1) 91.9(1), O(3)−Cu(1)−O(5) 153.6(1), O(2)−Cu(2)−N(3) 95.8(1), O(6)−Cu(2)−N(3) 90.8(1), O(6)−Cu(2)−O(2) 155.1(1), O(6)−Cu(2)−O(7) 94.2(1), O(7)−Cu(2)−N(3) 161.6(1), O(7)−Cu(2)−O(2) 87.2(1), P(1)−O(1)−Cu(1) 145.3(2), P(1)−O(2)−Cu(2) 108.4(2), P(1)#1−O(3)−Cu(1) 125.0(2), P(2)−O(5)−Cu(1) 109.8(2), P(2)−O(6)−Cu(2) 126.3(2), P(2)#1−O(7)−Cu(2) 143.9(2). Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, $-y + 1$, z. Hydrogen bond parameters: N2···O2 = 2.873(4) Å, H2W···O2 = 2.030(3) Å, N2−H2W = 0.890(3) Å, N2−H2W···O2 = 157.6(2)°; N4···O5 = 2.792(4) Å, H4W···O5 = 1.970(3) Å, N4−H4W = 0.865(3) Å, N4−H4W···O5 = 158.1(2)°. Equivalent positions: (a) $-x + 1$, $-y + 1$, $+z$; (b) x, y, z.

It is of interest to compare a few key structural parameters in **1** to those of **A**.[9b] Whereas all three Zn−O(P) distances around each zinc ion in **A** are almost equal, two types of Cu−O(P) distances are found in **1** (Figure 1). Similarly, whereas all the Zn−O−P angles within **A** are similar (average 139.9(2)°), very acute to wide-open Cu−O−P angles are found in **1** (108.4(2)−145.3(2)°). These variations explain the asymmetrical nature of the cubane core in **1** (Figure 2). Despite these distortions, the angles around both Cu1 and Cu2 indicate a near square-planar geometry around the metal ions. Similarly, the angles at phosphorus suggest a slightly distorted tetrahedral geometry. The Cu−N (pyrazole) distances are considerably shorter (1.970(3) and 1.984(3) Å) than the Zn−N (collidine) distances in **A** (2.087(4) Å). Finally, although the square-planar geometry around Cu^{II} ions in **1** could be attributed to the asymmetric nature of the cubane, an additional obvious reason for this distortion appears to be the intramolecular hydrogen bonding involving exocubane dbpz N−H protons and the cubane oxygen atoms, which draws the O2 and O5 oxygen atoms out of the ideal cubane geometry, resulting in enormously decreased Cu−O−P angles around these two atoms. The only example of a tetranuclear D4R cluster with a distorted cubane structure similar to **1** has been recently reported for $[Cu(tBuPO_3)(dbpz)]_4$ by Chandrasekhar and co-workers.[14d]

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[18] (a) Bassindale, A. R.; Pourny, M.; Taylor, P. G.; Hursthouse, M. B.; Light, M. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3488. (b) Bassindale, A. R.; Liu, Z.; MacKinnon, I. A.; Taylor, P. G.; Yang, Y.; Light, M. E.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, 2945.

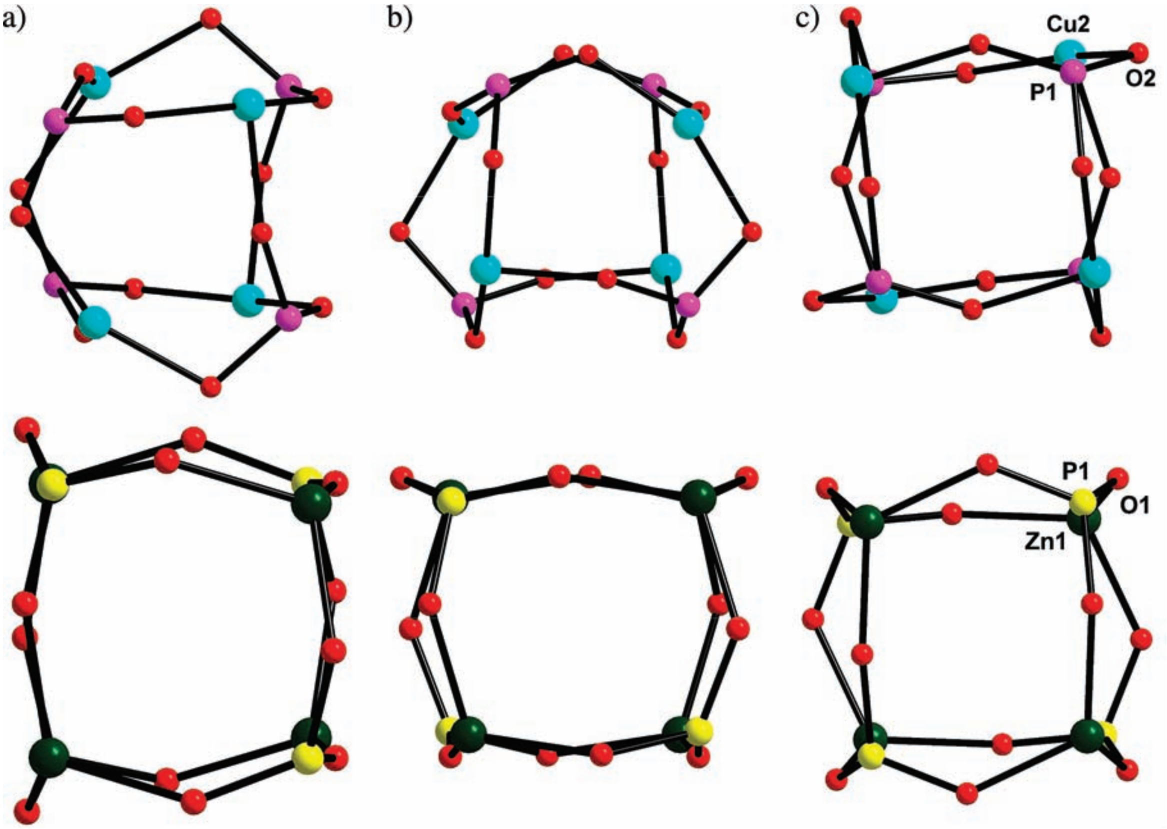

Figure 2. Comparison between the $M_4O_{12}P_4$ core **1** (above) and $[(RO)PO_3Zn{\cdot}collidine]_4$ **A**[9b] (below), viewed along *a*- (left), *b*- (middle), and *c*- (right) axes.

Molecular Structure of $[Cu_6(PO_4)(dmpp)_3(OAc)_3(dmpz)_9]$ (2). As described above, the change of the auxiliary ligand to less bulky 3,5-dimethyl pyrazole in the reaction between $Cu(OAc)_2{\cdot}H_2O$ and dmppH$_2$ leads to the isolation of the hexanuclear copper phosphate **2**. The single crystals of **2** were found to be unsuitable for single-crystal X-ray diffraction experiments due to persistent twinning problems. The skeletal molecular structure of the compound, however, could be derived from poor diffraction data obtained from one such crystal (Figure 3).[19] Due to the poor quality of the structure, a detailed description of the metric parameters is not warranted at the present time. Apart from the fact that compound **2** is a hexanuclear complex with an unprecedented cluster architecture in metal phosph(on)ate chemistry, it boasts a PO_4^{3-} ligand that has been produced in the course of the reaction. Whereas the hydrolysis of activated esters of phosphoric acid (e.g., bis(nitrophenyl)phosphate) by Cu(II) or other transition-metal ions is fairly well-established under favorable conditions,[20] it is interesting to note that an unactivated phosphate monoester (bearing a bulky aryl group) has undergone facile hydrolysis to produce phosphoric acid. This PO_4^{3-} anion acts a template for the formation of the hexanuclear complex by coordinating to all six metal ions in a [6.2220] mode of coordination (Harris notation).[21] In other words, each of the O^- of the phosphate ion acts as a bridging ligand to hold two copper ions while the phosphoryl group (P=O) remains uncoordinated. Apart from the central

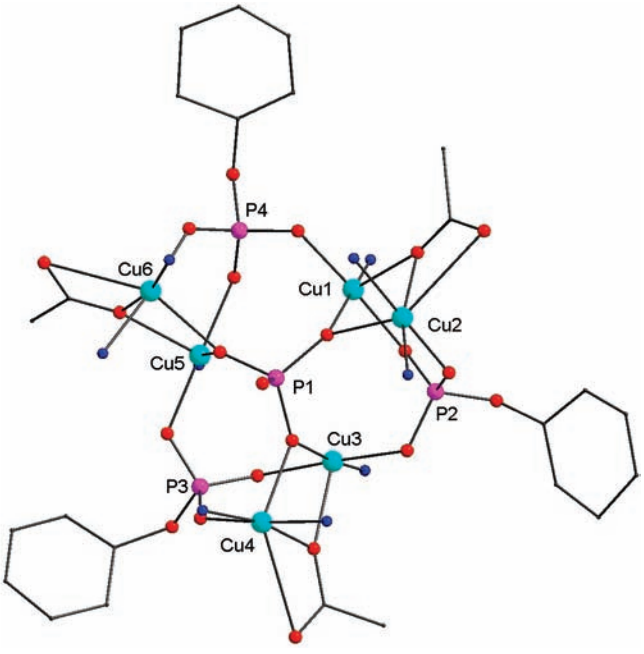

Figure 3. The core structure of **2**.

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[19] The twinning in the crystal could not be modeled.

[20] (a) Rossi, L. M.; Neves, A.; Bortoluzzi, A. J.; Hoerner, R.; Szpoganicz, B.; Terenzi, H.; Mangrich, A. S.; Pereira-Maia, E.; Castellano, E. E.; Haase, W. *Inorg. Chim. Acta* **2005**, *358*, 1807. (b) Jurek, P. E.; Martell, A. E. *Inorg. Chem.* **1999**, *38*, 6003. (c) Young, M. J.; Wahnon, D.; Hynes, R. C.; Chin, J. *J. Am. Chem. Soc.* **1995**, *117*, 9441. (d) Wall, M.; Hynes, R. C.; Chin, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1633. (e) Maldonado Calvo, J. A.; Vahrenkamp, H. *Inorg. Chim. Acta* **2006**, *359*, 4079.

[21] 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.

PO_4^{3-} ligand, there are three dmpp ($ROPO_3^{2-}$) ligands that hold the complex together. Each of these dmpp ligands bridges three copper ions in a [3.111] fashion. Each of the three acetate ligands in the molecule bridges two copper ions. The coordinative unsaturation at the metal ions is overcome by the complexation of auxiliary pyrazole ligands. In the final structure, the copper ions attain a pentacoordination, although they fall distinctly into two different types. In the first type, the copper ions are surrounded by two dmpp oxygen centers, one PO_4^{3-} oxygen, one acetate oxygen, and a dmpz ligand. In the second set, the three Cu^{2+} ions are surrounded by one dmpp oxygen, one PO_4^{3-} oxygen, one acetate oxygen, and two dmpz ligands.

Synthesis of Pyrazole−Diisopropylphenyl Phosphates [(dippH)(dbpz)(dbpzH)] (3) and [(dippH)(dmpz)(dmpzH)] (4). Following the synthesis of compounds **1** and **2** and the demonstration of the role played by auxiliary pyrazole (dbpz or dmpz) ligands in determining the nuclearity of the complex produced, the role played by the phosphate ligand has been evaluated by changing the substituent on phosphorus to a bulkier diisopropylphenyl group. Thus, the reactions leading to compounds **1** and **2** were repeated with dippH$_2$. Because of the more bulky dipp group, there was no reaction between Cu(OAc)$_2$·H$_2$O and dippH$_2$, and only acid−base complexes [(dippH)(dbpz)(dbpzH)] **3** and [(dippH)(dmpz)(dmpzH)] **4** were obtained (see Supporting Information for details).

Synthesis of Dimeric Copper Phosphates [Cu(phen)(dmpp)(CH$_3$OH)]$_2$·2CH$_3$OH (5) and [Cu(phen)(dipp)(CH$_3$OH)]$_2$·2CH$_3$OH (6). After evaluating the role of monodentate pyridinic ligands (dmpz and dbpz) in copper phosphate chemistry, the use of a bidentate ligand such as 1,10-phenanthroline has been investigated. It is well-known that, in the reactions of polydentate ligands with metal ions, the nuclearity of the complex can be considerably reduced by the use of chelating ligands such as 2,2′-bipyridine and 1,10-phenanthroline, which occupy two cis-coordination sites on the metal ion and, thus, impede the aggregation of metal ions. Thus, the reaction of copper acetate with both dmppH$_2$ and dippH$_2$ in the presence of phen in methanol at room temperature yields dinuclear copper phosphates [Cu(phen)(dmpp)(CH$_3$OH)]$_2$·2CH$_3$OH **5** and [Cu(phen)(dipp)(CH$_3$OH)]$_2$·2CH$_3$OH **6** in good yield. Compounds **5** and **6** (Scheme 2) yielded satisfactory analytical data. The absence of any absorption in the IR spectra of both compounds in the range 2350−2400 cm^{-1} is indicative of the fact that there are no unreacted P−OH groups left on the phosphate ligands.

The UV−vis spectrum of **5** recorded in methanol shows absorptions at 214, 271, and 673 nm. Whereas the strong absorptions at 214 and 271 nm are ligand-centered transitions, the very weak absorption at 673 nm ($\epsilon = 92$ L·mol^{-1}·cm^{-1}) is due to the d−d transition of d^9 Cu^{2+} ion. A similar spectral pattern with absorption maxima at 262, 304, 351, and 639 nm was observed in the solid-state diffuse reflectance UV spectrum of **5**. The EPR spectra of polycrystalline samples of **5** and **6** yield a g_{av} value of 2.08 and 2.07 at room temperature, respectively.

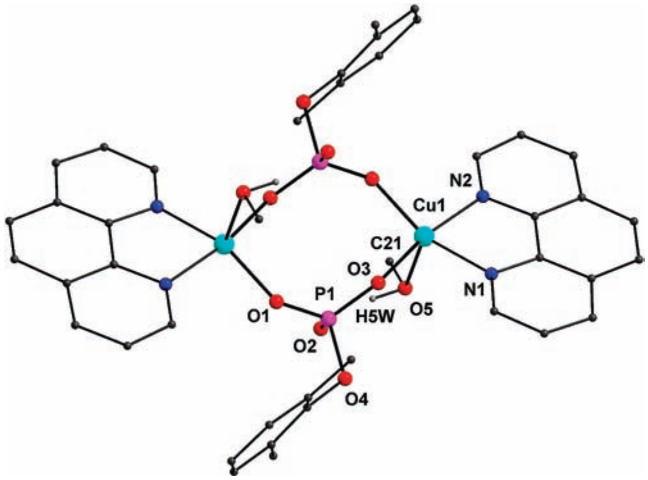
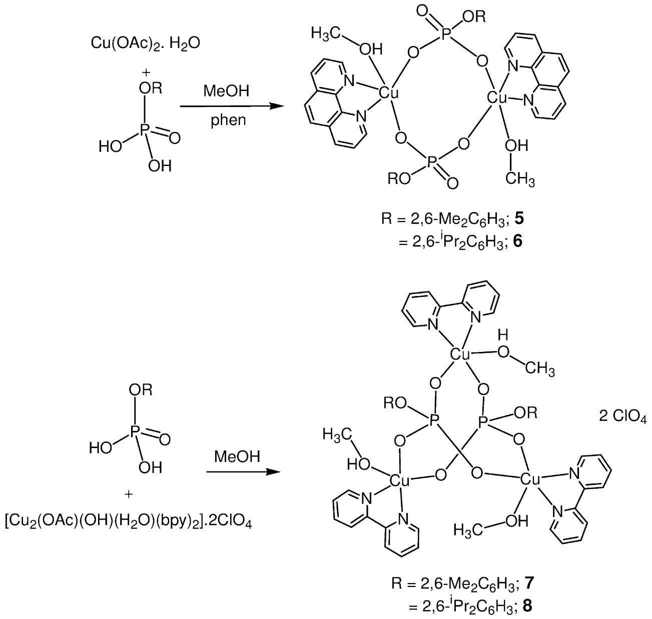


Figure 4. Molecular structure of **5** (lattice methanol molecules and hydrogen atoms have been omitted for clarity). Selected bond distances [Å]: Cu(1)−N(1) 2.012(2), Cu(1)−N(2) 2.012(2), Cu(1)−O(1) 1.913(2), Cu(1)−O(3) 1.918(2), Cu(1)−O(5) 2.383(2), P(1)−O(1) 1.514(2), P(1)−O(2) 1.505(2), P(1)−O(3) 1.516(2), P(1)−O(4) 1.635(2). Bond angles [°]: N(1)−Cu(1)−N(2) 81.42(8), N(1)−Cu(1)−O(5) 103.65(7), N(2)−Cu(1)−O(5) 87.38(7), O(1)−Cu(1)−N(1) 158.85(8), O(1)−Cu(1)−N(2) 91.01(8), O(1)−Cu(1)−O(3) 98.40(7), O(1)−Cu(1)−O(5) 95.65(8), O(3)−Cu(1)−N(1) 89.38(7), O(3)−Cu(1)−N(2) 170.53(8), O(3)−Cu(1)−O(5) 92.68(7), P(1)−O(1)−Cu(1) 131.1(1), P(1)#1−O(3)−Cu(1) 133.1(1).

Scheme 2. Synthesis of **5**−**8**



Molecular Structure of [Cu(phen)(dmpp)(CH$_3$OH)]$_2$·2CH$_3$OH (5). Compound **5** is a dimeric copper phosphate where each copper ion is bound to two bridging phosphate oxygen atoms, one chelating phen ligand, and a solvent methanol molecule (Figure 4). Whereas the central unit **1** is a distorted cubane resembling D4R building units of zeolites, the nonplanar eight-membered ring in compound **5** resembles the S4R (single-four-ring) SBU of zeolites. Thus, the syntheses of both **1** and **5** demonstrate that either a D4R or S4R building block can be obtained by choosing either a monodentate ligand of appropriate size or a chelating bidentate ligand, respectively.

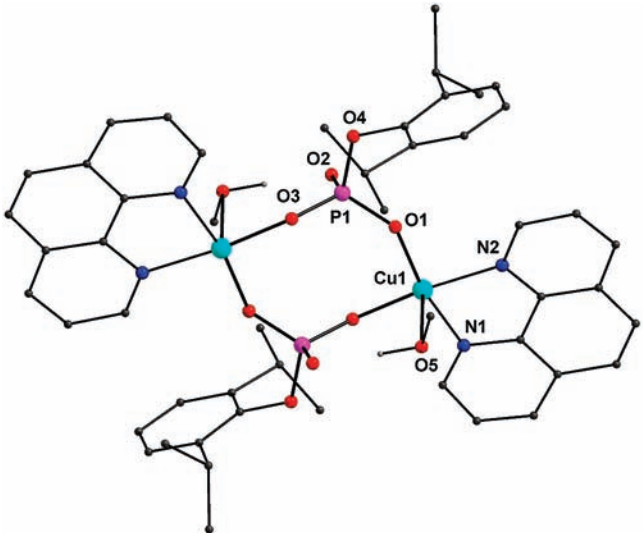


Figure 5. Molecular structure of **6** (lattice methanol molecules and hydrogen atoms have been omitted for clarity). Selected bond distances [Å]: Cu(1)−N(1) 2.024(2), Cu(1)−N(2) 2.028(2), Cu(1)−O(1) 1.924(2), Cu(1)−O(3)#1 1.921(2), Cu(1)−O(5) 2.409(2), P(1)−O(1) 1.520(2), P(1)−O(2) 1.506(2), P(1)−O(3) 1.516(2), P(1)−O(4) 1.636(2). Bond angles [°]: N(1)−Cu(1)−N(2) 81.35(8), O(1)−Cu(1)−N(1) 168.89(8), O(3)#1−Cu(1)−N(1) 90.09(7), N(1)−Cu(1)−O(5) 96.01(7), O(3)#1−Cu(1)−O(1) 98.65(6), O(3)#1−Cu(1)−N(2) 171.16(7), O(1)−Cu(1)−N(2) 89.60(7), O(3)#1−Cu(1)−O(5) 92.22(6), O(1)−Cu(1)−O(5) 90.54(6), N(2)−Cu(1)−O(5) 90.87(7), P(1)−O(1)−Cu(1) 130.35(9), P(1)−O(3)−Cu(1)#1 135.40(10).

In the molecular structure of **5**, because of the presence of a bidentate phen ligand occupying two of the coordination sites around the metal, the phosphoryl oxygen P═O (O2) remains uncoordinated, and, hence, the ligand exhibits a [2.110] mode of coordination. The five-coordinated copper centers adopt square-pyramidal geometry, in which the equatorial plane is occupied by the two nitrogen atoms of phen (Cu−N = 2.012(2) Å) and two phosphate oxygen atoms (Cu−O distances 1.913(2) and 1.918(2) Å), while the axial position is occupied by a coordinated methanol molecule (Cu−O distance 2.383(2) Å). The metric parameters are comparable with those of known copper phosphate compounds. The separation between the metal centers is 4.977 Å, whereas the corresponding P···P distance is 3.828 Å. The observed average Cu···P distance within the eight-membered ring (3.140 Å) is slightly longer than that observed in the eight-membered rings of **1** (3.073 Å). The lattice methanol molecules play a vital role in intermolecular interactions through extensive hydrogen-bonding interactions (see Supporting Information).

Molecular Structure of [Cu(phen)(dipp)(CH$_3$OH)]$_2$·2CH$_3$OH (6). Compound **6** is isostructural to **5**, although they do not belong to the same space group (Figure 5). Since the overall structure, ring conformation, and the bond distances and angles of **6** are similar to those of **5**, a detailed description of the structure of **6** is not presented here. The separation between metal centers in **6** is 5.006 Å, whereas the corresponding P···P distance is 3.848 Å. The average distance between Cu···P is 3.157 Å. The intermolecular hydrogen-bonding interactions involved in **6** are described in the Supporting Information.

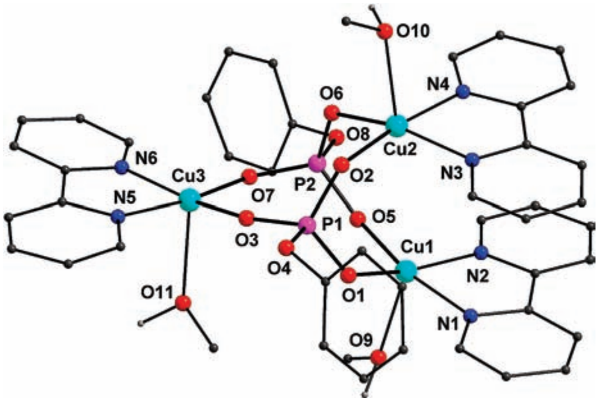


Figure 6. Molecular structure (cationic part) of **8** (lattice methanol and perchlorate ions and hydrogen atoms have been omitted for clarity). Selected bond distances [Å]: Cu(1)−N(1) 2.006(3), Cu(1)−N(2) 2.022(3), Cu(1)−O(1) 1.930(2), Cu(1)−O(5) 1.922(2), Cu(1)−O(9) 2.230(2), Cu(2)−N(3) 2.020(3), Cu(2)−N(4) 2.006(3), Cu(2)−O(2) 1.920(2), Cu(2)−O(6) 1.957(2), Cu(2)−O(10) 2.264(2), Cu(3)−O(3) 1.935(2), Cu(3)−O(7) 1.913(2), Cu(3)−O(11) 2.364(3), Cu(3)···O(12) 2.845(2). Bond angles [°]: N(1)−Cu(1)−N(2) 80.0(1), N(1)−Cu(1)−O(9) 91.3(1), N(2)−Cu(1)−O(9) 97.4(1), O(1)−Cu(1)−N(1) 92.1(1), O(1)−Cu(1)−N(2) 162.9(1), O(1)−Cu(1)−O(9) 97.90(9), O(5)−Cu(1)−N(1) 168.8(1), O(5)−Cu(1)−N(2) 89.8(1), O(5)−Cu(1)−O(1) 96.57(9), O(5)−Cu(1)−O(9) 94.47(9), N(3)−Cu(2)−O(10) 104.4(1), N(4)−Cu(2)−N(3) 79.8(1), N(4)−Cu(2)−O(10) 88.9(1), O(2)−Cu(2)−N(3) 93.3(1), O(2)−Cu(2)−N(4) 172.9(1), O(2)−Cu(2)−O(6) 92.46(9), O(2)−Cu(2)−O(10) 94.36(9), O(6)−Cu(2)−N(3) 161.1(1), O(6)−Cu(2)−N(4) 93.7(1), O(6)−Cu(2)−O(10) 93.06(9), N(5)−Cu(3)−N(6) 80.5(1), N(5)−Cu(3)−O(11) 88.3(1), N(6)−Cu(3)−O(11) 96.0(1), O(3)−Cu(3)−N(5) 91.5(1), O(3)−Cu(3)−N(6) 166.4(1), O(3)−Cu(3)−O(11) 94.7(1), O(7)−Cu(3)−N(5) 170.6(1), O(7)−Cu(3)−N(6) 90.3(1), O(7)−Cu(3)−O(3) 97.26(9), O(7)−Cu(3)−O(11) 94.36(9), P(1)−O(1)−Cu(1) 129.2(1), P(1)−O(2)−Cu(2) 127.0(1), P(1)−O(3)−Cu(3) 158.0(2) P(2)−O(5)−Cu(1) 150.5(2), P(2)−O(6)−Cu(2) 119.5(1), P(2)−O(7)−Cu(3) 132.3(1).

Synthesis and Characterization of [Cu$_3$(bpy)$_3$(dmpp)$_2$(CH$_3$OH)$_3$]·2ClO$_4$·2CH$_3$OH (7) and [Cu$_3$(bpy)$_3$(dipp)$_2$(CH$_3$OH)$_3$]·2ClO$_4$·2CH$_3$OH (8). After varying the substituents on phosphate esters and pyrazole ligands and also after studying the role of monodentate versus bidentate N-donor auxiliary ligand in the synthesis of molecular copper phosphates, the possibility of synthesizing complexes of other nuclearity has been investigated by changing the copper(II) ion source. The precursor complex [Cu$_2$(bpy)$_2$(OAc)(H$_2$O)]·2ClO$_4$ that already incorporates a chelating N-donor bidentate ligand has been chosen as the starting material. Stirring a methanol solution of this precursor complex and dmppH$_2$/dippH$_2$ at room temperature, followed by slow evaporation of the solvent, leads to the isolation of trinuclear copper complexes [Cu$_3$(bpy)$_3$(dmpp)$_2$(CH$_3$OH)$_3$]·2ClO$_4$·2CH$_3$OH **7** and [Cu$_3$(bpy)$_3$(dipp)$_2$(CH$_3$OH)$_3$]·2ClO$_4$·2CH$_3$OH **8**, respectively. The crystalline products obtained were found to be analytically pure. The IR spectra of both **7** and **8** contain strong absorptions due to both M−O−P and ClO$_4^-$ moieties in the region of 1000−1100 cm^{-1}. The UV−vis spectrum of **7** in methanol exhibits three strong absorptions in the UV region (211, 244, and 302 nm) due to the ligand-centered transitions. The broad, weak absorption appearing at 672 nm (ϵ = 80 L·mol^{-1}·cm^{-1}) is due to the spin-forbidden d−d transition of the d^9 Cu^{2+} ion. Compound **8** also displays similar absorption spectral characteristics. The EPR spectra of both compounds recorded for polycrystalline samples at 298 and 77 K yield a g_{av} value of 2.08 and 2.09, respectively.

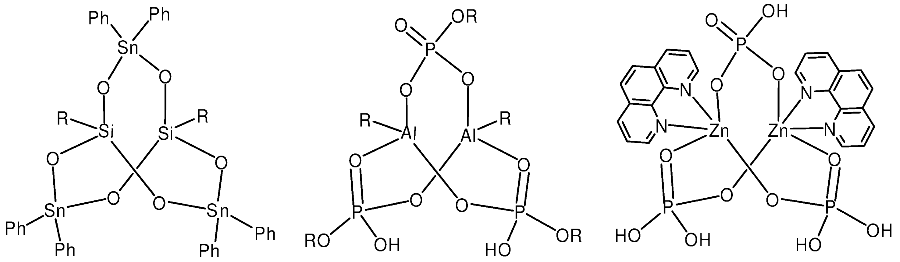


Figure 7. Molecular siloxanes and phosphates exhibiting 4=1 SBU of zeolites.

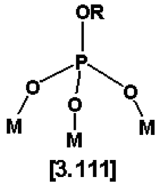
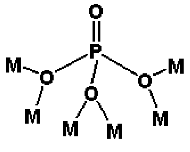
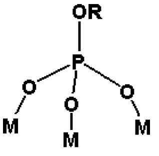
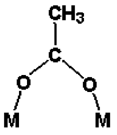
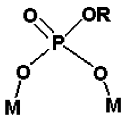
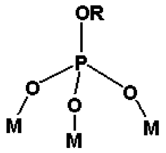
1	 [3.111]
2	 [6.2220]  [3.111]  [2.11]
5, 6	 [2.110]
7, 8	 [3.111]

Figure 8. Denticity and Harris notation[21] of ligands in complexes **1**, **2**, and **5**−**8**.

Molecular Structure of $[Cu_3(bpy)_3(dipp)_2(CH_3OH)_3]\cdot 2ClO_4\cdot 2CH_3OH$ (8). The molecular structure of **8** consists of a trimeric core of $[Cu_3(bpy)_3(dipp)_2(CH_3OH)_3]^{2+}$ cationic part, uncoordinated ClO_4^- anions, and lattice methanol molecules (Figure 6). The three copper ions in the cationic part of complex **8** are held together by the two dipp ligands, each of which acts as a triply bridging ligand, displaying a [3.111] mode of Harris notation (Figure 8). The $Cu_3O_6P_2$ core is similar to bicyclic, eight-membered-ring systems that have been recently unravelled in tin(IV) siloxane and main group metal (Al and Zn) phosphate chemistries (Figure 7).[9c,22,23] The most interesting aspect of this arrangement is that the structural unit has been identified as an important secondary building unit of zeolites, namely 4=1, which has been found in zeolites such as thomsonite and edingtonite.[24]

This SBU is essentially made up of a S4R $A_2O_4B_2$ SBU that has been capped by another AO_2 or BO_2 fragment. The five-coordinated (Cu(1)) copper centers in the molecule adopt a square-pyramidal geometry. The equatorial coordination sites are occupied by two nitrogen atoms of bpy (Cu−N = 2.006(3) and 2.022(3) Å) and two oxygen atoms of the phosphate ligand (Cu−O = 1.922(2) and 1.930(2) Å). Oxygen of a coordinated methanol molecule (Cu−O = 2.230(2) Å) fills up the fifth axial site on each Cu^{2+} ion. Interestingly, around the Cu(3) ion, a second methanol shows a very weak interaction to the metal (Cu(3)−O12 = 2.845(2) Å) diagonally opposite to the other methanol oxygen (O(11)) that is firmly bound to the metal.

Conclusion

It has been shown in this contribution that a number of structurally diverse oligomeric copper arylphosphate complexes, whose core resembles the secondary building units of zeolites, can be synthesized by varying (a) the aryl substituent on the phosphate ester, (b) the ancillary ligand, (c) the organic substituents on the auxiliary ligands, and (d) the source of the metal ion. The change of substituent on the auxiliary pyrazole ligand from *tert*-butyl to methyl group changes the nuclearity of the cluster from four to six (complexes **1** and **2**), whereas the change of substituent from dmpp to dipp leads to large differences in the reactivity and the isolation of only organic acid−base phosphate complexes (**3** and **4**). Changing monodentate to chelating bidentate 1,10-phenanthroline results in the blocking of coordination sites on the metal, which impedes the oligomeric growth and leads to the eventual isolation of the dimeric phosphates **5** and **6**. Use of a precursor complex in place of simple copper acetate resulted in the isolation of trinuclear complexes **7** and **8**. The dimeric, tetrameric, and trimeric copper phosphates reported in this study serve as useful, suitable model compounds for the S4R, D4R, and 4=1 SBUs of zeolites, respectively, that incorporate transition metals. The presence of square-planar copper corners in complex **1** reveals the extent of distortion a D4R cubane would undergo when tetrahedral atoms are substituted with metal ions in other coordination environments. Isolation of the hexanuclear copper phosphate **2** unravels a new structural form for copper clusters and is also significant in terms of the hydrolysis of an unactivated phosphate ester during its formation. Clearly, there is further scope for the isolation of newer structural types of copper phosphates through attendant changes in the phosphate ligand and by changing the auxiliary N-donor ligand. We are currently investigating these possibilities.

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Experimental Section

Instruments and Methods. Solvents were purified by employing conventional procedures and were distilled prior to their use.[26] Commercially available starting materials such as 2,2′-bipyridine (Aldrich), 1,10-phenanthroline (Aldrich), and $Cu(OAc)_2\cdot H_2O$ (Fluka) were used as received. Compounds $[Cu_2(bpy)_2(OAc)(OH)(H_2O)]\cdot 2ClO_4$,[25] 3,5-dimethylpyrazole (dmpz),[26] 3,5-di-*tert*-butylpyrazole (dbpz),[26] 2,6-diisopropylphenyl phosphate (dippH$_2$),[27] and 2,6-dimethylphenyl phosphate (dmppH$_2$)[27] were synthesized according to previously described literature methods. Infrared spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer using KBr diluted discs. The melting points were measured in glass capillaries and are reported uncorrected. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. Thermogravimetric analysis was carried out on a PerkinElmer Pyris thermal analysis system under a stream of nitrogen gas with the heating rate of 10 °C/min. Magnetic susceptibility was measured on a PAR vibrating sample magnetometer. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer, and the spectra were calibrated using tetracyanoethylene. UV−vis spectra were obtained on a Shimadzu UV-260 spectrophotometer, and the fluorescence measurements were carried out on a PerkinElmer LS-55 luminescence spectrometer. X-ray powder diffraction data were obtained on a Philips X'Pert Pro X-ray diffraction system using monochromated Cu Kα1 radiation ($\lambda = 1.5406$ Å).

Synthesis of $[Cu(dmpp)(dbpz)]_4$ (1). A solution of 3,5-di-*tert*-butyl pyrazole (180 mg, 1 mmol) in methanol (10 mL) was added to a hot solution of $Cu(OAc)_2\cdot H_2O$ (198 mg, 1 mmol) in MeOH (30 mL). The resulting mixture was stirred to obtain a clear solution, and then solid dmppH$_2$ (202 mg, 1 mmol) was added. The reaction mixture was stirred for 4 h at room temperature, and 1,4-dioxane (5 mL) was added. The reaction mixture was subsequently filtered, and the filtrate was kept for crystallization at room temperature. Blue single crystals of **1** were obtained from this solution after one week. Mp: 202−204 °C. Yield: 340 mg (77%, based on dmppH$_2$). Anal. Calcd for $C_{76}H_{116}N_8O_{16}P_4Cu_4$ ($M_r = 1775.88$): C, 51.40; H, 6.58; N, 6.30. Found: C, 51.65; H, 6.99; N, 6.08. IR (KBr, cm^{-1}): 3188(br), 3110(w), 3018(w), 2963(s), 2869(w), 1583(m), 1472(s), 1364(m), 1303(w), 1253(m), 1201(m), 1170(w), 1150(vs), 1122(w), 1055(m), 1033(m), 1003(w), 980(vs), 925(s), 875(w), 778(m). UV−vis (CH$_3$OH, nm): 211 (ϵ = 17632 L·mol^{-1}·cm^{-1}), 252 (ϵ = 5141 L·mol^{-1}·cm^{-1}), 766 (ϵ = 53 L·mol^{-1}·cm^{-1}). Diffuse reflectance UV−vis (nm): 210, 261, 355, 770. TGA: temp range °C (% weight loss): 87−163 (7.1), 163−296 (30.8), 296−480 (25). DSC (°C): 129 (endo), 221 (endo). EPR (polycrystalline sample): $g_{av} = 2.134$ (RT), 2.196 (LNT). $\chi_M T_{obs}$ (cm^3·K·M^{-1}) = 1.16, $\chi_M T_{calcd}$ (cm^3·K·M^{-1}) = 1.51.

Synthesis of $[Cu_6(PO_4)(dmpp)_3(OAc)_3(dmpz)_9]$ (2). A solution of 3,5-dimethyl pyrazole (dmpz) (192 mg, 2 mmol) in methanol (10 mL) was added to $Cu(OAc)_2\cdot H_2O$ (198 mg, 1 mmol) in methanol (30 mL). Immediately, the solution color changed from sky blue to dark blue. A solution of dmppH$_2$ (202 mg, 1 mmol) in methanol (10 mL) was added to the above solution, and the mixture was stirred for 1 h, filtered, and the clear solution was kept at room temperature for crystallization. Blue color single crystals of **2** were obtained from the reaction mixture after 3 to 4 days. Mp: 205−210 °C. Yield: 350 mg (66%, based on dmppH$_2$). Anal. Calcd for $C_{75}H_{108}N_{18}O_{22}Cu_6P_4$ ($M_r = 2118.97$): C, 42.51; H, 5.14; N, 11.90. Found: C, 42.28; H, 5.24; N, 11.50. IR (KBr, cm^{-1}): 3434(br), 3196(w), 3136(w), 3032(w), 2928(w), 2868(w), 1580(s), 1474(m), 1423(m), 1380(w), 1314(m), 1266(w), 1198(m), 1146(s), 1092(vs), 1042(m), 986(vs), 901(s), 778(s). UV−vis (CH$_3$OH, nm): 214 (ϵ = 19 795 L·mol^{-1}·cm^{-1}), 254 (ϵ = 5039 L·mol^{-1}·cm^{-1}), 742 (ϵ = 67 L·mol^{-1}·cm^{-1}). DRUV−vis (nm): 217, 354, 612. EPR (polycrystalline sample): $g_{av} = 2.052$ (RT), 2.054 (LNT). $\chi_M T_{obs}$ (cm^3·K·M^{-1}) = 2.60, $\chi_M T_{calcd}$ (cm^3·K·M^{-1}) = 2.25.

Synthesis of $[Cu(phen)(dmpp)(CH_3OH)]_2\cdot 2CH_3OH$ (5). [Cu(OAc)$_2$·H$_2$O] (198 mg, 1 mmol), 1,10-phenanthroline (199 mg, 1 mmol), and dmppH$_2$ (202 mg, 1 mmol) were mixed in methanol (30 mL) and stirred to obtain a clear solution. The solvent was subsequently removed under reduced pressure, and the residue was dissolved in methanol (10 mL). The insoluble components were filtered, and the filtrate was kept at 5 °C for crystallization. Blue crystals of **5** were obtained after 7 days. Mp: >275 °C. Yield: 320 mg (63%, based on dmppH$_2$). Anal. Calcd for $C_{44}H_{50}N_4O_{12}P_2Cu_2$ ($M_r = 1015.94$): C, 52.02; H, 4.96; N, 5.52. Found: C, 50.40; H, 4.32; N, 5.90. IR (KBr, cm^{-1}): 3451(br), 3076(m), 3006(m), 2922(m), 2854(w), 1690(m), 1627(w), 1585(m), 1512(m), 1470(m), 1215(s), 1168(vs), 1095(vs), 980(s), 856(s), 781(s), 761(m), 725(s). UV−vis (CH$_3$OH, nm): 214 (ϵ = 17 970 L·mol^{-1}·cm^{-1}), 271 (ϵ = 14 003 L·mol^{-1}·cm^{-1}), 673 (ϵ = 92 L·mol^{-1}·cm^{-1}). DRUV−vis (nm): 311, 404, 646. EPR (polycrystalline sample): $g_{av} = 2.08$ (RT). $\chi_M T_{obs}$ (cm^3·K·M^{-1}) = 0.96, $\chi_M T_{calcd}$ (cm^3·K·M^{-1}) = 0.75.

Synthesis of $[Cu(phen)(dipp)(CH_3OH)]_2\cdot 2CH_3OH$ (6). This compound has been synthesized by essentially following the procedure used for the preparation of **5**. Mp: >275 °C. Yield: 300 mg (53%, based on dippH$_2$). Anal. Calcd for $C_{52}H_{66}N_4O_{12}P_{22}Cu_2$ ($M_r = 1128.2$): C, 55.36; H, 5.90; N, 4.97. Found: C, 56.70; H, 5.72; N, 3.77. IR (KBr, cm^{-1}): 3436(br), 3063(w), 2966(s), 2929(w), 2867(w), 2382(br), 1630(w), 1589(w), 1519(m), 1441(m), 1330(w), 1291(w), 1211(w), 1201(m), 1175(vs), 1142(w), 1105(w), 1073(s), 978(m), 935(s), 910(vs), 848(w), 769(s). DRUV−vis (nm): 262, 304, 351, 639. EPR (polycrystalline sample): $g_{av} = 2.07$ (RT). $\chi_M T_{obs}$ (cm^3·K·M^{-1}) = 0.58, $\chi_M T_{calcd}$ (cm^3·K·M^{-1}) = 0.75.

Synthesis of $[Cu_3(bpy)_3(dmpp)_2(CH_3OH)_3]\cdot 2ClO_4\cdot 2CH_3OH$ (7). Solid dmppH$_2$ (101 mg, 0.5 mmol) was added to a methanolic solution (35 mL) of $[Cu_2(bpy)_2(OAc)(OH)(H_2O)]\cdot 2ClO_4$ (366 mg, 0.5 mmol) and stirred for 1 h, then filtered. The filtrate was kept at room temperature. Blue crystals of **7** were obtained from the reaction mixture after 3 to 4 days. Mp: >275 °C. Yield: 230 mg (65%, based on dmppH$_2$). Anal. Calcd for $C_{51}H_{62}P_2O_{21}N_6Cl_2Cu_3$ ($M_r = 1418.6$): C, 43.18; H, 4.41; N, 5.92. Found: C, 42.12; H, 3.75; N, 6.27. IR (KBr, cm^{-1}): 3439(br), 3115(w), 3068(w), 2957(w), 2923(w), 1603(s), 1569(w), 1474(s), 1447(s), 1314(m), 1253(w), 1180(s), 1120(w), 1096(vs), 1060(w), 1031(m), 1021(m), 1001(w), 897(s), 768(s). UV−vis (CH$_3$OH, nm): 211 (ϵ = 13 612 L·mol^{-1}·cm^{-1}), 244 (ϵ = 5232 L·mol^{-1}·cm^{-1}), 302 (ϵ = 11 061 L·mol^{-1}·cm^{-1}), 672 (ϵ = 80 L·mol^{-1}·cm^{-1}). DRUV−vis (nm): 215, 360, 605. EPR (polycrystalline sample): $g_{av} = 2.08$ (RT, LNT). $\chi_M T_{obs}$ (cm^3·K·M^{-1}) = 1.02, $\chi_M T_{calcd}$ (cm^3·K·M^{-1}) = 1.12.

Synthesis of $[Cu_3(bpy)_3(dipp)_2(CH_3OH)_3]\cdot 2ClO_4\cdot 2CH_3OH$ (8). This compound has been synthesized by essentially following the procedure used for the preparation of **7**. Mp: >275 °C. Yield: 310 mg (81%, based on dippH$_2$). Anal. Calcd for $C_{59}H_{78}P_2O_{21}N_6Cl_2Cu_3$ ($M_r = 1530.8$): C, 46.29; H, 5.14; N, 5.49. Found: C, 44.86; H, 4.55; N, 5.96. IR (KBr, cm^{-1}): 3420(br), 3115(w), 3082(w), 2964(m), 2868(w), 1603(s), 1575(w), 1496(w), 1472(m),

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Table 1. Crystal Data and Structure Refinement Details for Compounds **1**, **4**, **5**, **6**, and **8**

compound	**1**	**4**	**5**	**6**	**8**
identification code	mur111	rm166a	newrm137	newrm136	newrm119
formula	$C_{84}H_{132}Cu_4N_8O_{20}P_4$	$C_{22}H_{35}N_4O_4P$	$C_{46}H_{58}Cu_2N_4O_{14}P_2$	$C_{54}H_{74}Cu_2N_4O_{14}P_2$	$C_{59}H_{78}Cl_2Cu_3N_6O_{21}P_2$
fw	1952.02	450.51	1079.98	1192.19	1530.73
temp [K]	100(2)	293(2)	150(2)	150(2)	150(2)
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
space group	*Aba*2	*P*1	*C*2/*c*	$P2_1/n$	$P2_1/n$
a [Å]	17.8321(21)	9.5984(19)	22.0352(13)	12.1723(5)	13.4608(3)
b [Å]	26.9021(18)	11.7585(11)	10.5235(6)	18.5865(5)	13.8104(4)
c [Å]	19.4751(13)	12.3069(10)	22.1141(13)	13.3937(6)	35.7174(9)
α [°]	90	68.357(7)	90	90	90
β [°]	90	84.115(10)	108.522(5)	108.113(4)	92.906(3)
γ [°]	90	75.241(10)	90	90	90
V [Å^3]	9342.6(11)	1248.4(3)	4862.4(5)	2880.04(19)	6631.3(3)
Z	4	2	4	2	4
D_{calcd} [g/cm^3]	1.388	1.198	1.475	1.375	1.533
μ [mm^{-1}]	1.037	0.143	1.010	0.860	1.161
cryst size [mm^3]	0.27 × 0.23 × 0.22	0.30 × 0.25 × 0.25	0.34 × 0.28 × 0.22	0.22 × 0.17 × 0.13	0.38 × 0.34 × 0.26
θ range [°]	2.74 to 25.00	1.78 to 24.97	3.11 to 25.00	2.93 to 25.00	3.03 to 25.00
no. of reflns collected	4236	4674	15873	15618	39764
no. of obsd reflns ($I_0 > 2\sigma(I_0)$)	4236	4387	4285	5045	11643
GOF	1.065	1.013	1.084	1.045	1.036
R1($I_0 > 2\sigma(I_0)$)	0.0291	0.0499	0.0321	0.0317	0.0420
wR2 (all data)	0.0782	0.1397	0.0860	0.0909	0.0894
largest hole and peak [e·Å^{-3}]	−0.542, 1.117	−0.302, 0.196	−0.473, 0.526	−0.262, 0.875	−0.476, 0.411

1446(s), 1383(w), 1336(w), 1313(w), 1254(m), 1165(s), 1119(vs), 1107(vs), 1059(s), 1031(m), 1021(m), 1000(m), 911(m), 881(w), 808(w), 770(s). UV−vis (CH_3OH, nm): 302 (ϵ = 9973 L·mol^{-1}·cm^{-1}), 667 (ϵ = 310 L·mol^{-1}·cm^{-1}). DRUV−vis (nm): 216, 262, 317, 635. EPR (polycrystalline sample): $g_{av} = 2.09$ (RT, LNT). $\chi_M T_{obs}$ (cm^3·K·M^{-1}) = 1.10, $\chi_M T_{calcd}$ (cm^3·K·M^{-1}) = 1.12.

Single-Crystal X-ray Diffraction Studies. Intensity data were collected for **1** on a Siemens STOE AED2 four-circle diffractrometer, for **4** on a Bruker AXS, and for **2**, **5**, **6**, and **8** on an Oxford Xcalibur CCD diffractometer. All calculations were carried out using the programs in WinGX module.[28] The structure was solved in each case by direct methods (SIR-92).[29] The final refinement of the structure was carried out using full least-squares methods on F^2 using SHELXL-97.[30] Several crystals of **2** were examined for the diffraction experiments. The crystals were, however, found to suffer from persistent twinning problems. The data obtained with one such crystal yielded the molecular structure of **2**, with a twin component that could not be resolved or modeled. Hence, only the gross structural features are described herein. If successful, the fully refined structure will be reported in a crystallographic journal in the future. The crystal data for **1**, **4**−**6**, and **8** are presented in Table 1.

Acknowledgment. This work was supported by DST, New Delhi. M.P.S. thanks UGC, New Delhi, for a research fellowship. We thank the DST funded National Single Crystal Diffraction Facility at IIT-Bombay for the diffraction data, and SAIF, IIT-Bombay, for the spectral data.

Supporting Information Available: Details of X-ray structure investigations and the details of synthesis, spectral characterization, solution studies, and crystal structure details of **3** and **4**, and packing diagrams for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801532Y

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