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Hierarchical Structures Built from a Molecular Zinc Phosphate Core**

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Dedicated to Professor Herbert W. Roesky

Assembling hierarchical supramolecular structures through a building-block approach is one of the major challenges in chemistry. In the last few decades, several research groups

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have used a modular approach to assemble superstructures through exploitation of the selective recognition of suitably constructed ligands by various metal ions. An elegant example of this approach is the early work of Lehn and coworkers on the use of neutral polypyridine ligands.[1] More recent work on the use of polycarboxylic acids as multianionic spacer ligands has resulted in the realization of framework solids with exceptional surface areas.[2]

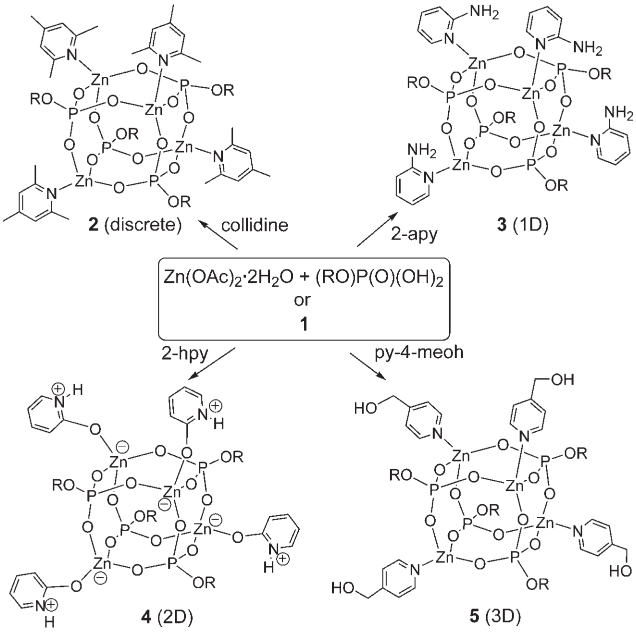
The synthesis of designer silicates and phosphates, on the other hand, is far more difficult. The main reason for this difficulty has been the lack of suitable organic-soluble reactants (or ligands) bearing SiO_4 and PO_4 tetrahedra. This problem was partially overcome in the 1990s with the successful synthesis of kinetically stabilized organosilanetriols containing a Si–N bond, $(R'RN)Si(OH)_3$.[3] These organosilanetriols interact with a variety of main-group and transition-metal ions to produce cages that resemble the secondary building units (SBUs) of zeolites (for example, the double-four-ring (D4R) unit). This approach was later extended to the synthesis of discrete molecular metallophosphonates starting from organophosphonic acids[4] and of metallophosphates starting from organophosphate esters.[5]

Although organosilanetriols and phosphorus acids have served as ideal starting points for the preparation of a number of SBUs, efforts to covalently link the SBUs into larger structures have met with very little success. For example, the activation of a B–C bond of a borophosphonate cube[6] or of a Ti–O bond of a titanosiloxane[7] (both having D4R cores) has proven to be difficult, even in the presence of phenols, alcohols, or acids. Similar difficulties were encountered when Group 13 element phosphonate cubes were treated with diols or diacids.[8] These results suggest that placing covalent linkages between these types of SBUs to build zeolite analogues would be difficult. In an attempt to rationally assemble metallophosphate superstructures, we have succeeded in not only synthesizing hitherto unknown zinc phosphate cubes, but also in linking them through noncovalent interactions.

Stirring a solution of $Zn(OAc)_2{\cdot}2H_2O$ (Ac = acetyl) and $(RO)P(O)(OH)_2$ (R = 2,6-di(isopropyl)phenyl) in methanol at room temperature produces a precipitate of $[Zn\{O_3P(OR)\}(MeOH)]_n$ [**1**; Eq. (1)]. Rapid loss of methanol

$$Zn(OAc)_2 \cdot 2\,H_2O + (RO)P(O)(OH)_2 \rightarrow [Zn\{O_3P(OR)\}(MeOH)]_n\ (\mathbf{1}) \qquad (1)$$

from the crystals of **1** precludes a single-crystal X-ray structure determination. The fact that **1** is soluble in methanol, acetonitrile, and dimethyl sulfoxide (DMSO) and the observation that compounds **2**–**5** have tetrameric structures (see below) suggest that **1** is probably composed of discrete molecules, although its powder X-ray diffraction (XRD) pattern resembles that of layered phosphonates such as $[Zn(O_3PPh)(OH_2)]$.[9]



Scheme 1. Syntheses of zinc phosphate cubes **2**–**5** with various substituted pyridine ligands (see the text for details).

The addition of 2,4,6-trimethylpyridine (collidine) to a solution of **1** leads to the isolation of $[Zn\{O_3P(OR)\}(collidine)]_4$ (**2**; Scheme 1), which has been characterized with analytical and spectroscopic techniques. The IR spectrum of **2** shows strong absorption bands at $\nu = 1190$ (P=O) and 1020 and 920 cm^{-1} (M-O-P asymmetric and symmetric stretching). The presence of a single resonance in the ^{31}P NMR spectrum at $\delta = -4.7$ ppm indicates the presence of only one type of phosphorus atom in the molecule. A single crystal XRD study of **2** revealed that the molecule has a tetrameric cube structure (see below). To our knowledge, **2** is the first metallophosphate with a core composed of tetrahedrally coordinated metal and phosphorus centers that resembles the D4R SBU of zeolites and the cores of metallosiloxanes (such as $[RSiO_3Al]_4$; R = 2,6-$i$$Pr_2C_6H_3)N(SiMe_3)$ and metallophosphonates.[10,11]

In anticipation that the use of a bridging bidentate Lewis base would lead to D4R SBUs that are linked to each other through coordinate bonds, the preparation of **1** was carried out in the presence of ligands such as 4,4′-bipyridine or 1,4-diazabicyclo[2.2.2]octane (DABCO). However, a copious amount of insoluble noncrystalline precipitate was formed in each case, precluding single-crystal XRD studies.

Since neither covalent- nor coordinate-linkage approaches to the preparation of zeolite analogues yielded the desired results, a noncovalent approach was tried. In view of the stable cube complex **2** formed by **1** with collidine, a modified Lewis base approach was used. Additional functional groups, namely NH_2, OH, and CH_2OH, were placed in appropriate positions on the pyridine ring to enhance hydrogen bonding between the D4R cubes, thus resulting in noncovalently linked 1D, 2D, and 3D structures.

Thus, treatment of $Zn(OAc)_2{\cdot}2H_2O$ with $(RO)P(O)(OH)_2$ in the presence of 2-aminopyridine (2-apy), 2-hydroxypyridine (2-hpy), or 4-(hydroxymethyl)pyridine (py-4-meoh) produces $[Zn\{O_3P(OR)\}(2\text{-apy})]_4$ (**3**), $[Zn\{O_3P(OR)\}(2\text{-hpy})]_4$ (**4**), or $[Zn\{O_3P(OR)\}(py\text{-}4\text{-}meoh)]_4$ (**5**), respectively, in good yield (Scheme 1).[12] Compounds **3**–**5** were characterized with analytical, spectroscopic, and single-crystal XRD[13] studies. The elemental analyses and ^{1}H NMR spectra suggest the formation of a 1:1:1 zinc/phosphate/pyridine complex in each case. The presence of a single sharp resonance at $\delta \approx -4.5$ ppm in the ^{31}P NMR spectrum of each of the compounds demonstrates the presence of only one type of phosphorus atom. Mass-spectrometric analysis did not provide any useful information about the oligomeric structures of the compounds.

As revealed by single-crystal XRD studies, the core structures of **2**–**5** consist of frameworks containing four zinc and four phosphorus atoms at the alternate vertices of a cube (Figure 1). Each of the Zn$\cdots$P edges of the cube is bridged by a μ_2-oxygen atom, thus resulting in six eight-membered $\{Zn_2O_4P_2\}$ rings, which adopt a crown conformation. The central D4R $\{Zn_4O_{12}P_4\}$ core is enclosed by the bulky aryl oxide ligands on the phosphorus atoms and the Lewis base ligands on the zinc atoms, as shown for **2** in Figure 1.

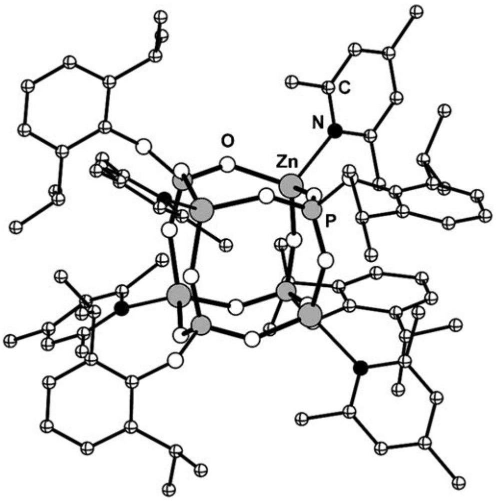


Figure 1. Molecular structure of the zinc phosphate cube **2**; hydrogen atoms are omitted for clarity.

In **3** and **5**, the nitrogen atoms of the pyridine ligands bind to the Zn^{2+} ions, as expected, while the pendant NH$_2$ and CH$_2$OH groups do not interact with the metal centers. On the other hand, the 2-hpy ligand in **4** coordinates to the Zn^{2+} ion through the phenoxide oxygen atom, rather than the pyridine nitrogen atom (Scheme 1); the OH group has undergone a hydrogen-shift during coordination, thus producing a zwitterionic pyridinium phenoxide ligand.

The bond lengths and angles observed for the zinc phosphate cores of **2**–**5** are similar (see the Supporting Information). There are no formal P–O and P=O bonds in **2**–**5**: the average P–O bond lengths are 1.532(3) (**2**), 1.537(2) (**3**), 1.533(2) (**4**), and 1.532(4) Å (**5**). The average Zn–O lengths of 1.916(3) (**2**), 1.923(2) (**3**), 1.919(4) (**4**), and 1.919(2) Å (**5**) are comparable to those observed in several zinc phosphonates and phosphates.[14] The average Zn-O-P angles of 139.9(2) (**2**), 134.3(1) (**3**), 135.4(2) (**4**), and 135.3(1)° (**5**) are smaller than the 180° value expected for a linear edge, thus giving the core a spherical appearance. The bond angles around the zinc and phosphorus atoms do not deviate appreciably from the ideal tetrahedral values. The dimensions of the cores of **2**–**5** can best be understood from the average lengths of the Zn$\cdots$P edges (3.20 (**2**), 3.18 (**3**), 3.17 (**4**), and 3.17 Å (**5**)), the P$\cdots$P face diagonals (4.63 (**2**), 4.60 (**3**), 4.64 (**4**), and 4.62 Å (**5**)), the Zn$\cdots$Zn face diagonals (4.42 (**2**), 4.35 (**3**), 4.32 (**4**), and 4.34 Å (**5**)), and the Zn$\cdots$P body diagonals (5.53 (**2**), 5.48 (**3**), 5.49 (**4**), and 5.48 Å (**5**)). Thus, the volumes of the inorganic cores of the molecules are roughly 85–90 Å^3, whereas the molecular volumes including the organic substituents are 1700–2200 Å^3.

The most interesting aspect of the zinc phosphate cubes is their ability to assemble through noncovalent interactions, when the appropriate surface functionalities are present, as in **3**–**5**. In the absence of surface functionalities, the tetrameric zinc phosphate clusters in **2** remain discrete. The presence of NH$_2$ groups in *ortho* positions on the pyridine rings in **3** is the source of intra- and intermolecular N–H$\cdots$O hydrogen bonds. While each of the four NH$_2$ groups in **3** forms an intramolecular N–H$\cdots$O interaction with one of the framework oxygen atoms, two of the NH$_2$ groups are also involved intermolecular N–H$\cdots$O interactions with adjacent cubes, thus resulting in a 1D assembly (Figure 2). The intercube distance of 6.812 Å is largely dictated by the strong intermolecular hydrogen bonding.

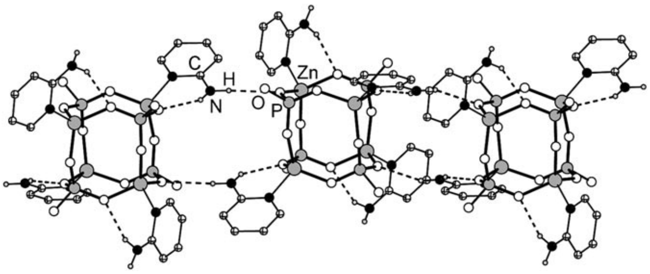


Figure 2. 1D assembly of zinc phosphate cubes in the crystal structure of **3**; dashed lines indicate hydrogen bonds; 2,6-di(isopropyl)phenyl groups and carbon-bound hydrogen atoms are omitted for clarity.

The crystal structure of **4** presents a different type of supramolecular aggregation. As the Zn^{2+} ion is bound to the phenoxide oxygen atom, rather than the pyridine nitrogen atom of the 2-hpy ligand, the NH group is farther away from the framework oxygen centers and hence, prefers intermolecular over intramolecular N–H$\cdots$O hydrogen bonds. Thus, three of the four NH groups form intermolecular hydrogen bonds with the oxygen atoms of the 2-hpy ligands of three adjacent cubes (Figure 3a). The fourth NH group is content with an intramolecular N–H$\cdots$O interaction with a framework oxygen atom, as in the case of **3**. The propagation of hydrogen bonds between the cubes occurs through only three terminals, which are oriented approximately 120° from one another in the same plane. Thus, an extended 2D sheet of D4R cubes, which contains hexagonal channels, is formed (Figure 3b). Additional C–H$\cdots$O hydrogen bonds between pyridine CH groups and framework oxygen centers stabilize the hexagonal arrangement. The average distance of 6.801 Å between the cubes is comparable to that observed for **3**.

It is clear from the crystal structure of **4** that the formation of a 3D structure is hampered by the presence of the single

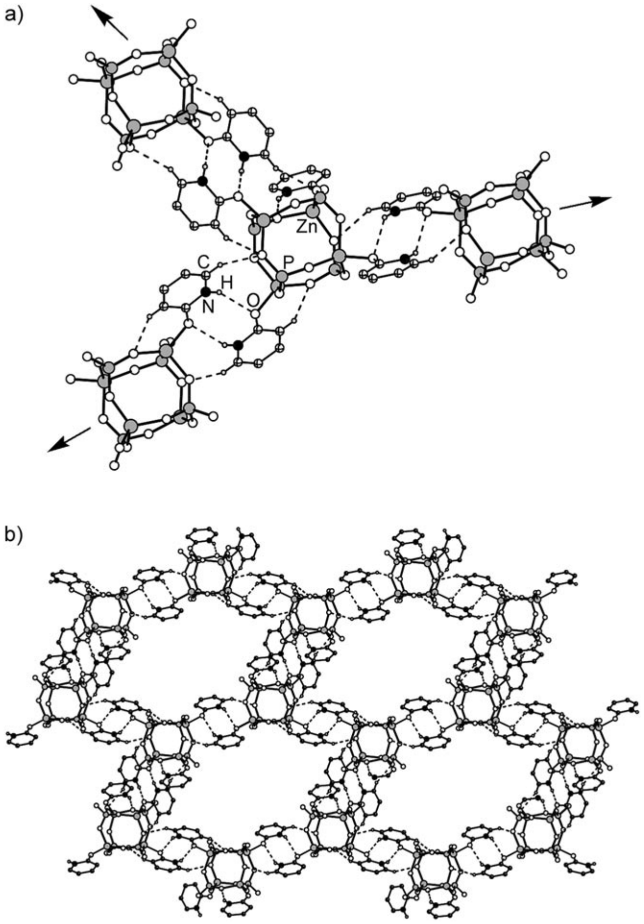


Figure 3. In the crystal structure of **4**, a) each zinc phosphate cube is linked to three others through hydrogen bonding, thus leading to b) a hexagonal 2D assembly; dashed lines indicate hydrogen bonds; 2,6-di(isopropyl)phenyl groups and hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

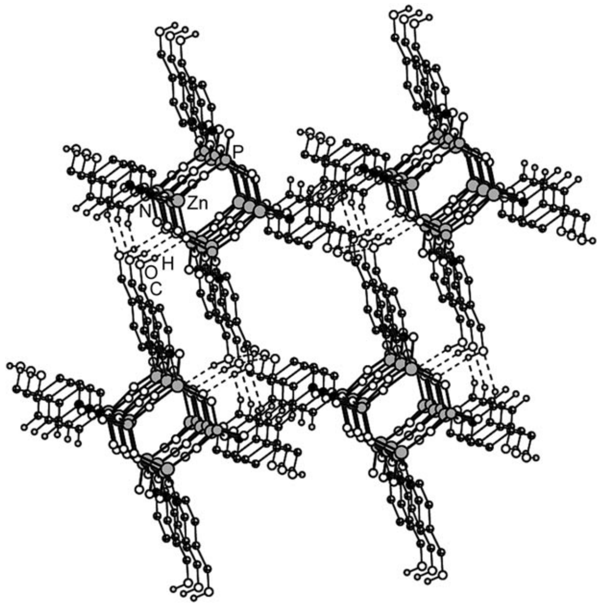


Figure 4. 3D assembly of zinc phosphate cubes in the crystal structure of **5**; dashed lines indicate hydrogen bonds; 2,6-di(isopropyl)phenyl groups and hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

intramolecular N–H···O interaction in each cube. This problem is overcome by introducing a spacer between the functional groups and the pyridine ring. Thus, the OH groups of all four of the py-4-meoh ligands in **5** form exclusively intermolecular hydrogen bonds. As the four OH groups are pointed roughly towards the four corners of a tetrahedron, a 3D supramolecular aggregation results (Figure 4). Two of the four OH groups, which are opposite to one another, form three intermolecular hydrogen bonds each: one with a framework oxygen atom, one with a CH group of a pyridine ring, and one with another OH group. The two remaining OH groups of the cube each form an intermolecular hydrogen bond to an OH group (not shown in Figure 4). Owing to the presence of only intermolecular interactions involving the para CH_2OH groups, the average distance between the cubes in **5** is 10.471 Å, which is much larger than that observed for **2**–**4**.

In conclusion, we have synthesized the first examples of organic-soluble transition-metal phosphates with cores that resemble the D4R SBUs of zeolites. Strategies for arranging these SBUs into either 1D, 2D, or 3D supramolecular structures through noncovalent interactions have also been presented. These studies suggest that it is not only important to have a hydrogen-bond donor on the pyridine ligand, but also to place it in an appropriate position. Furthermore, to build superstructures with higher dimensionalities, it is important to decrease or eliminate intramolecular hydrogen bonds. Note that the reaction of aryl phosphonic acids with metal ions normally leads to the isolation of insoluble layered metal phosphonates. However, when an aryl phosphoric acid (in which an oxygen atom is located between the aryl ring and the phosphorus atom) is used as a reagent herein, discrete organic-soluble clusters are isolated. Finally, the presence of NH, NH_2, or OH groups on the surfaces of clusters **3**–**5** opens up new possibilities for further reactions with metal alkyl reagents (for example, AlR_3) to build dendritic heterometallic superstructures. We are currently investigating these aspects.

Experimental Section

$Zn(OAc)_2\cdot 2H_2O$ (219 mg, 1 mmol) and 2,6-di(isopropyl)phenylphosphoric acid (258 mg, 1 mmol) were mixed in methanol (30 mL) and warmed to produce a clear solution. The reaction mixture was filtered, concentrated, and left overnight to yield a precipitate of **1**. Compounds **2**–**5** were synthesized in a similar manner, by adding the appropriate substituted pyridine ligand to the reaction mixture.

1: M.p. >275 °C; yield: 0.3 g (85 %); elemental analysis (%) calcd for $C_{13}H_{21}O_5PZn$ ($M_r = 353.7$): C 44.15, H 5.98; found: C 44.88, H 5.87; ^1H NMR ($[D_6]$acetone, 300 MHz): $\delta = 7.02$ (s, 12 H, aryl), 3.77 (sept, 8 H, CH; $^3J_{HH} = 6.9$ Hz), 3.65 (br, 4 H, OH), 3.30 (s, 12 H, CH_3), 1.11 ppm (d, 48 H, CH_3); ^{31}P NMR ($[D_6]$acetone, 121 MHz): $\delta = -4.5$ ppm. **2**: M.p. >275 °C; yield: 0.3 g (68 %); elemental analysis (%) calcd for $C_{80}H_{112}N_4O_{16}P_4Zn_4$ ($M_r = 1771.1$): C 54.24, H 6.37, N 3.16; found: C 52.80, H 6.21, N 2.95; ^1H NMR ($[D_6]$DMSO, 300 MHz): $\delta = 7.02$–6.95 (m, 12 H, aryl), 6.85 (s, 8 H, aryl), 3.69 (sept, 8 H, CH; $^3J_{HH} = 6.6$ Hz), 2.34 (s, 24 H, CH_3), 2.20 (s, 12 H, CH_3), 1.08 ppm (d, 48 H, CH_3); ^{31}P NMR ($[D_6]$DMSO, 121 MHz): $\delta =$

−4.7 ppm. **3**: M.p. >275 °C; yield: 0.3 g (77 %); elemental analysis (%) calcd for $C_{68}H_{92}N_8O_{16}P_4Zn_4$ ($M_r = 1663.0$): C 49.11, H 5.57, N 6.73; found: C 48.99, H 5.54, N 6.73; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.37–7.51 (m, 8H, aryl), 6.94–7.10 (m, 12H, aryl), 6.37–6.41 (m, 8H, aryl), 5.41 (S, 8H, NH), 3.65 (sept, 8H, CH; $^3J_{HH} = 6.9$ Hz), 0.98 ppm (d, 48H, CH_3); ^{31}P NMR ([D$_6$]acetone, 121 MHz): $\delta = -4.9$ ppm. **4**: M.p. 257–258 °C, yield: 0. 28 g (68 %), elemental analysis (%) calcd for $C_{68}H_{88}N_4O_{20}P_4Zn_4$ ($M_r = 1666.8$): C 48.99, H 5.32, N 3.36; found: C 49.39, H 5.62, N 3.44; ^{1}H NMR ([D$_6$]DMSO, 400 MHz): $\delta = 11.58$ (S, 4H, NH), 7.39–7.43 (m, 4H, aryl), 7.35 (dd, 4H, aryl; $^3J_{HH} = 5.2$ Hz), 6.94–7.02 (m, 12H, aryl), 6.31 (d, 4H, aryl; $^3J_{HH} = 9.2$ Hz), 6.16 (t, 4H, aryl; $^3J_{HH} = 6.4$ Hz), 3.68 (sept, 8H, CH; $^3J_{HH} = 6.8$ Hz), 1.09 ppm (d, 48H, CH_3); ^{31}P NMR ([D$_6$]DMSO, 121 MHz): $\delta = -4.7$ ppm. **5**: M.p. >275 °C; yield: 0.4 g (93 %); elemental analysis (%) calcd for $C_{72}H_{96}P_4O_{20}N_4Zn_4$ ($M_r = 1723.0$): C 50.18, H 5.61, N 3.25; found: C 50.21, H 5.75, N 3.39; ^{1}H NMR ([D$_6$]DMSO, 400 MHz): $\delta = 8.22$ (s, 8H, aryl), 7.38 (d, 8H, aryl; $^3J_{HH} = 4.8$ Hz), 6.99 (s, 12H, aryl), 5.55 (t, 4H, OH; $^3J_{HH} = 5.2$ Hz), 4.58 (d, 8H, CH_2; $^3J_{HH} = 5.6$ Hz), 3.64 (sept, 8H, CH; $^3J_{HH} = 6.4$ Hz), 0.98 ppm (d, 48H, CH_3); ^{31}P NMR ([D$_6$]DMSO, 121 MHz): $\delta = -4.4$ ppm.

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[12] Alternatively, compounds **2**–**5** can also be prepared by the addition of the respective substituted pyridine ligand to a methanol solution of **1**. By this route, better yields and good-quality crystals are obtained.

[13] Crystal data for **2**: $C_{80}H_{112}N_4O_{16}P_4Zn_4$, $M_r = 1771.1$, size $= 0.15 \times 0.05 \times 0.05$ mm^3, tetragonal, space group $I4_1/a$, $Z = 4$, $a = 23.722(2)$, $c = 14.608(2)$ Å, $V = 8220(1)$ Å^3, $\rho_{calcd} = 1.431$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.298$ mm^{-1}, $F(000) = 3712$, $R_1(I > 2\sigma(I)) = 0.0378$, wR_2(all data) $= 0.0640$, GOF $= 0.824$. **3**: $C_{68}H_{92}N_8O_{16}P_4Zn_4$, $M_r = 1663.0$, size $= 0.2 \times 0.2 \times 0.2$ mm^3, monoclinic, space group $C2/c$, $Z = 4$, $a = 29.3099(17)$, $b = 14.4890(7)$, $c = 19.9454(14)$ Å, $\beta = 111.282(5)°$, $V = 7893(1)$ Å^3, $\rho_{calcd} = 1.399$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.348$ mm^{-1}, $F(000) = 3456$, $R_1(I > 2\sigma(I)) = 0.0311$, $wR_2 = 0.0649$, GOF $= 0.932$. **4**: $C_{68}H_{88}N_4O_{20}P_4Zn_4$, $M_r = 1666.8$, size $= 0.3 \times 0.3 \times 0.2$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 15.384(3)$, $b = 15.421(3)$, $c = 19.551(3)$ Å, $\alpha = 86.45(2)$, $\beta = 67.62(2)$, $\gamma = 66.42(2)°$, $V = 3909(1)$ Å, $\rho_{calcd} = 1.416$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.363$ mm^{-1}, $F(000) = 1728$, $R_1(I > 2\sigma(I)) = 0.0529$, $wR_2 = 0.1241$, GOF $= 0.934$. **5**: $C_{72}H_{96}N_4O_{20}P_4Zn_4$, $M_r = 1723.0$, size $= 0.3 \times 0.2 \times 0.2$ mm^3, monoclinic, space group $C2/c$, $Z = 4$, $a = 24.466(3)$, $b = 14.663(2)$, $c = 23.074(3)$ Å, $\beta = 104.77(1)°$, $V = 8004(2)$ Å, $\rho_{calcd} = 1.430$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.334$ mm^{-1}, $F(000) = 3584$, $R_1(I > 2\sigma(I)) = 0.0316$, $wR_2 = 0.0705$, GOF $= 0.907$. CCDC-289557 (**3**), -289558 (**4**), -289559 (**2**), and -289560 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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