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Molecular and Polymeric Zinc(II) Phosphonates: Isolation of an Octanuclear Ellipsoidal Ensemble

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ABSTRACT

The reaction of zinc(II) perchlorate with trichloromethyl phosphonic acid at room temperature afforded, upon crystallization, a two-dimensional layered coordination polymer, possessing a dinuclear repeat unit, $[\{Zn_2(Cl_3CPO_3)_2(H_2O)_3\} \cdot 1.5H_2O]_n$ (**1**). Modification of the above reaction by involving a co-ligand afforded the tetranuclear complex, $[\{Zn_4(\eta^1\text{-DMPzH})_6(Cl_3C\text{-}PO_3)_2\}(\mu\text{-OH})_2(ClO_4)_2]$ (**2**). The molecular structure of **2** reveals that the tetranuclear core is non-planar and consists of three contiguous inorganic rings which include one 8-membered $Zn_2P_2O_4$ ring and two six-membered Zn_2PO_3 rings. Replacement of $Zn(ClO_4)_2 \cdot 6H_2O$ with $ZnCl_2$ under the same reaction conditions that afforded **2**, allowed the formation of the dinuclear complex $[\{(ZnCl)_2(\eta^2\text{-Pz})_2(Cl_3CPO_3)\}(Et_3NH)_2]$ (**3**). **3** possesses a bicyclic core containing a seven-membered $Zn_2N_2O_2P$ ring. In **3**, the phosphoryl oxygen atom ($P=O$) is involved in a bifurcated hydrogen bonding interaction with the triethylammonium cation. The reaction of $ZnCl_2$ and 2,3,5,6-(Me) $_4C_6HCH_2PO_3H_2$ afforded the octanuclear complex $[Zn_8(Cl)_6\{2,3,5,6\text{-(Me)}_4C_6HCH_2PO_3\}_6(Et_3N)_2](Et_3NH)_2] \cdot 2n\text{-hexane} \cdot 3H_2O$ (**4**). The core of **4** is ellipsoid-shaped with the end-end polar distance (C-C) being ~ 20 Å.

INTRODUCTION

The phosphonate family of ligands, $[\text{RPO}_3]^{2-}$, $[\text{RP}(\text{OH})\text{O}_2]^-$ and related members have been extensively used for the preparation of materials possessing extended structures resulting from the multi-site coordinating behavior of these ligands.¹ Thus, a maximum of up to nine metal centers can be held together by a single $[\text{RPO}_3]^{2-}$ ligand (Chart 1).^{1f} Many of the transition metal phosphonates, thus prepared, have layered or even three-dimensional structures and find applications in diverse areas: NLO materials,² ion sensors,³ catalysis,⁴ catalyst supports,⁵ sorption,⁶ medicinal diagnosis,⁷ treatment of radioactive waste streams⁸ *etc.* In parallel, particularly in the last decade or so, there have been several efforts to prepare molecular transition metal phosphonates.⁹ The synthetic challenges involved are, as mentioned above, the propensity of the phosphonate ligands to afford compounds with polymeric structures.¹⁰ One way to prevent the formation of coordination polymers is to utilize ancillary ligands which would curtail the available coordination sites on a metal ion and hence increase the chances of the formation of a molecular derivative.¹¹ Another method is to use a sterically hindered phosphonic acid which would also make it unfavorable for a proliferation of the structure.¹² Utilizing either of these strategies or a combination of these, several transition metal phosphonates have been prepared and structurally characterized.¹³ Some of these have also been used in plasmid-modification.¹⁴ Among the molecular phosphonate family, compounds containing Zn(II) are relatively sparse: thus far, di-, tri-, tetra-, penta-, hexa- and heptanuclear derivatives have been reported.¹⁵ Representative examples of these compounds are given in the ESI. On the other hand, among molecular Cu(II) phosphonates, a much larger variety is known with the highest nuclearity aggregate being 26.¹⁶ In view of this it was interesting to find out if we can increase the nuclearity of Zn(II) phosphonates, beyond seven, by an appropriate choice of ligand. We

were also interested in experimenting with factors that would allow isolation of compounds possessing extended structures in ambient reaction conditions as well as those that tip the formation of molecular analogues. Experimentation with conditions that allow the modulation of nuclearity in the molecular analogues is an aspect of continued interest. Accordingly, in this paper we report the synthesis and characterization of $[\{\text{Zn}_2(\text{Cl}_3\text{CPO}_3)_2(\text{H}_2\text{O})_3\} \cdot 1.5\text{H}_2\text{O}]_n$ (**1**), $[\{\text{Zn}_4(\eta^1\text{-DMPzH})_6(\text{Cl}_3\text{C-PO}_3)_2\}(\mu\text{-OH})_2(\text{ClO}_4)_2]$ (**2**), $[\{(\text{ZnCl})_2(\eta^2\text{-Pz})_2(\text{Cl}_3\text{CPO}_3)\}(\text{Et}_3\text{NH})_2]$ (**3**) and $[\{\text{Zn}_8(\text{Cl})_6\{2,3,5,6\text{-(Me)}_4\text{C}_6\text{HCH}_2\text{PO}_3\}_6(\text{Et}_3\text{N})_2\}(\text{Et}_3\text{NH})_2] \cdot 2n\text{-hexane} \cdot 3\text{H}_2\text{O}$ (**4**). Of these **1** is a coordination polymer while **2-4** are molecular analogues. To the best of our knowledge, compound **4** represents the largest inorganic Zn(II) phosphonate known so far.

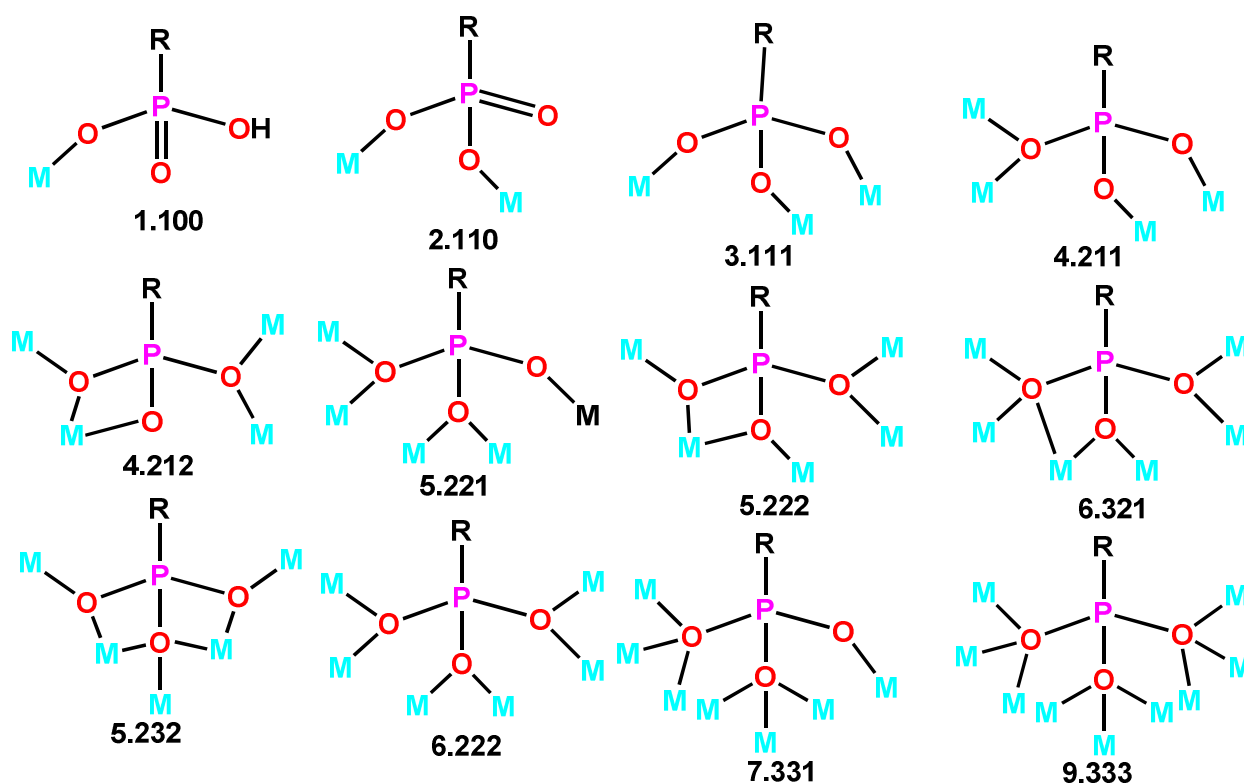


Chart 1. Coordination modes of the phosphonate ligand (See reference 17 for a description of the coordination notation).

EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.¹⁸ The following chemicals were used as obtained: $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, U.S.A.), anhydrous ZnCl_2 (Lancaster, U.K.), 3-(bromomethyl)-1,2,4,5-tetramethylbenzene (Aldrich, U.S.A.), triethyl phosphate (Aldrich, U.S.A.), triethylamine (S.D. fine Chemicals, India), AlCl_3 (S.D. Fine Chemicals, India), PCl_3 (S.D. Fine Chemicals, India), 2,4-pentanedione (S.D. Fine Chemicals, India), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$; S.D. Fine Chemicals, India), acetonitrile (S.D. Fine Chemicals, India) and methanol (S.D. Fine Chemicals, India). 3,5-Dimethyl-1*H*-pyrazole,¹⁹ (trichloromethyl)phosphonic acid ($\text{Cl}_3\text{CPO}_3\text{H}_2$)²⁰ and 2,3,5,6-tetramethylbenzylphosphonic acid ($(2,3,5,6\text{-(Me)}_4\text{C}_6\text{HCH}_2\text{PO}_3\text{H}_2)$)²¹ were prepared according to literature procedures.

Instrumentation. ^1H and ^{31}P NMR were recorded on a JEOL-JNM DELTA model NMR spectrometer operating at 500 MHz, using DMSO-d_6 as the solvent. Chemical shifts were referenced with respect to tetramethylsilane (^1H) and external 85% H_3PO_4 (^{31}P). Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer Spectrum Version FT IR spectrophotometer operating at $400\text{--}4000\text{ cm}^{-1}$. Elemental analyses of the compounds were obtained on a Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. Thermogravimetric analysis (heating rate of $10\text{ }^\circ\text{C min}^{-1}$) was carried out on a Perkin-Elmer Pyris 6 machine.

Synthesis

$[\{\text{Zn}_2(\text{Cl}_3\text{CPO}_3)_2(\text{H}_2\text{O})_3\} \cdot 1.5\text{H}_2\text{O}]_n$ (1). (Scheme 1). $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0501 g, 0.134 mmol)

was taken in acetonitrile (25 mL). To this a solution of (trichloromethyl)phosphonic acid (0.0268 g, 0.134 mmol) in acetonitrile (25 mL) was added and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.0273 g, 0.268 mmol) was added to the reaction mixture. The resulting, clear, colorless solution was stirred for an additional 24 h. The solution was evaporated and the residue obtained was re-dissolved in dichloromethane/toluene and kept for crystallization at room temperature. After 5-6 days colorless block-shaped crystals of **1** were obtained. Yield: 0.021 g, ~25% (based on zinc). Mp: 170 °C (d). Anal. Calcd for $C_2H_9O_{11}Cl_6P_2Zn_2$ (**1**): C, 3.91; H, 1.48 Found: C, 3.86; H, 1.57. IR (KBr, ν/cm^{-1}): 3436 (br, s), 2976 (m), 2939(m), 2739(m), 2678(s), 2491(m), 1466(s), 1398(w), 1351(w), 1246(s), 1090(s), 1005(s), 804(s), 758(m), 627(s), 554(m), 458(w). ESI-MS {negative ionisation mode} (m/z): Theoretical mass peak: 596.62, Experimental mass peak: 596.60 [$\{Zn_2(Cl_3CPO_3)_2(H_2O)_3\}_1 + H_2O - H^+\}^-$ (Figure 1). ^{31}P NMR (500 MHz, DMSO- d_6): δ 3.93 (s) (ESI).

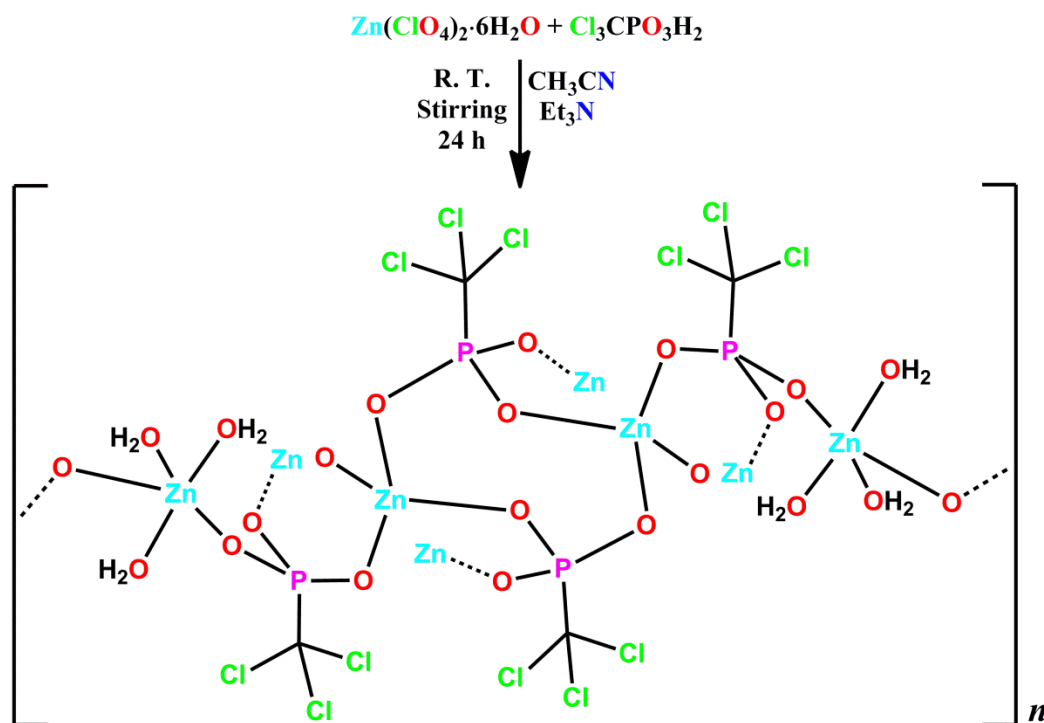
[{Zn₄(η^1 -DMPzH)₆(Cl₃C-PO₃)₂}(μ -OH)₂(ClO₄)₂] (**2**). (Scheme 2). Zn(ClO₄)₂·6H₂O (0.0601 g, 0.161 mmol) was taken in acetonitrile (25 mL). To this, a solution of 3,5-dimethyl-1*H*-pyrazole (0.0155 g, 0.161 mmol) and (trichloromethyl)phosphonic acid (0.0160 g, 0.0805 mmol) in acetonitrile (25 mL) was added and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.0328 g, 0.322 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated and the residue obtained was re-dissolved in dichloromethane and kept for crystallization by vapor diffusion with Et₂O at room temperature. After 7-8 days colorless block-shaped crystals of **2** were obtained. Yield: 0.032 g, 54% (based on zinc). Mp: 154 °C (d). Anal. Calcd for $C_{32}H_{50}Cl_8N_{12}O_{16}P_2Zn_4$ (**2**; 1465.94): C, 26.22; H, 3.44; N, 11.47; Found: C, 26.14; H, 3.37; N, 11.41. IR (KBr, ν/cm^{-1}): 3555 (m), 3230 (br), 3048 (m), 2679 (w), 1582 (m), 1478 (m), 1420

(m), 1296 (m), 1137 (s), 1056 (s), 917 (w), 825 (m), 798 (m), 765 (m), 627 (m), 574 (m), 526 (m), 425 (w). ESI-MS (m/z): Theoretical mass peak: 1268.89, Experimental mass peak: 1268.78 $[\{Zn_4(\eta^1\text{-DMPzH})_6(\text{Cl}_3\text{C-PO}_3)_2\}(\text{ClO}_4)_2 + 3\text{H}^+]^+$ (ESI). ^1H NMR (500 MHz, DMSO-d_6): δ 2.08 $[(\text{CH}_3, \text{DMPz}), \text{s}]$, δ 5.70 $[(\text{CH}, \text{DMPz}), \text{s}]$; ^{31}P NMR (500 MHz, DMSO-d_6): δ 4.30 (s).

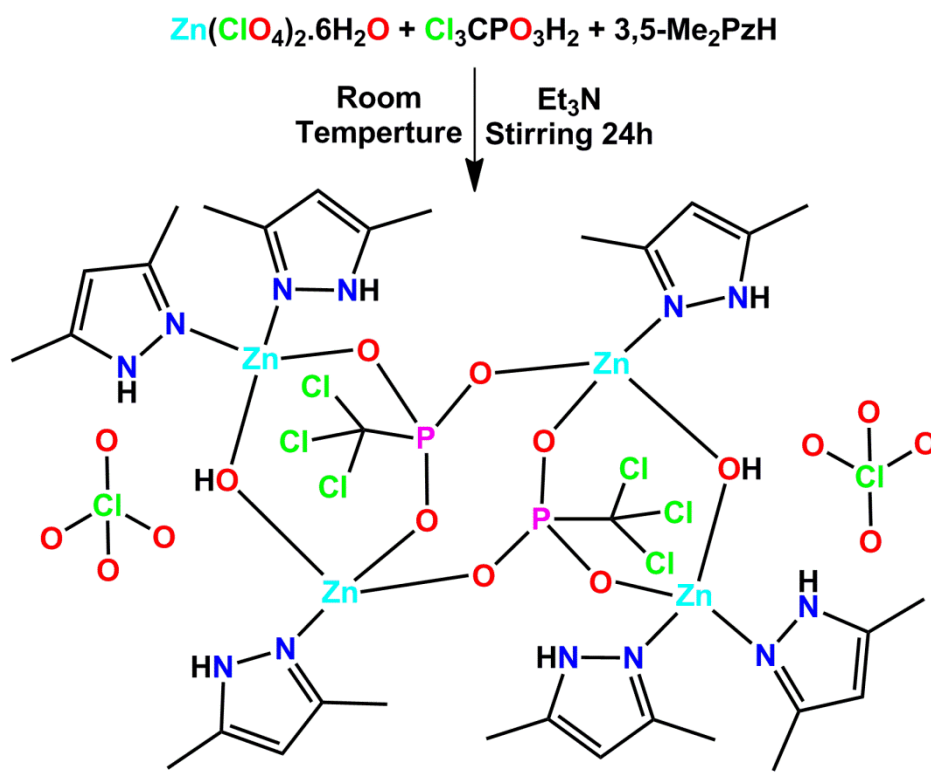
$[\{(ZnCl)_2(\eta^2\text{-Pz})_2(\text{Cl}_3\text{CPO}_3)\}(\text{Et}_3\text{NH})_2]$ (3). (Scheme 3). Anhydrous ZnCl_2 (0.0366 g, 0.268 mmol) was taken in methanol (15 mL). To this, a solution of pyrazole (0.0182 g, 0.268 mmol) and (trichloromethyl)phosphonic acid (0.0267 g, 0.134 mmol) in methanol (15 mL) was added and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.054 g, 0.536 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated and the residue obtained was re-dissolved in toluene and kept for crystallization by allowing *n*-hexane vapor to diffuse slowly at room temperature. After 5-6 days colorless block shaped crystals of **3** were obtained. Yield: 0.0045 g, 46% (based on zinc). Mp: 136 °C (d) Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{Cl}_5\text{N}_6\text{O}_3\text{PZn}_2$ (**3**; 737.55): C, 30.94; H, 5.19; N, 11.39. Found: C, 30.86; H, 5.25; N, 11.28. IR (KBr, ν/cm^{-1}): 3492 (b), 2925 (s), 2854 (m), 2487 (m), 1479 (s), 1381 (s), 1275 (m), 1178 (m), 1119 (s), 1048 (s), 1007 (s), 893 (w), 837 (m), 757 (s), 632 (m), 552 (s), 499 (m). ESI-MS (m/z): Theoretical mass peak: 743.90, Experimental mass peak: 743.28 $[\{(ZnCl)_2(\eta^2\text{-Pz})_2(\text{Cl}_3\text{CPO}_3)\} + 6\text{CH}_3\text{OH} + \text{H}_2\text{O} + 3\text{H}^+]^+$ (ESI). ^1H NMR (500 MHz, DMSO-d_6): δ 6.16-7.54 $[(\text{CH}, \text{Pz})]$, δ 1.04 $[\text{N}(\text{CH}_2\text{CH}_3)_3]$, δ 2.47 $[\text{N}(\text{CH}_2\text{CH}_3)_3]$; ^{31}P NMR (500 MHz, DMSO-d_6): δ 7.56 (s) (ESI).

$[\{Zn_8(\text{Cl})_6\{2,3,5,6\text{-(Me)}_4\text{C}_6\text{HCH}_2\text{PO}_3\}_6(\text{Et}_3\text{N})_2][(\text{Et}_3\text{NH})_2] \cdot 2\text{-}n\text{-hexane} \cdot 3\text{H}_2\text{O}$ (4). (Scheme 4). A solution of 2,3,5,6-(Me)₄C₆HCH₂PO₃H₂ (0.0742 g, 0.325 mmol) and Et₃N (0.0663 g, 0.651 mmol) in acetonitrile (10 mL) was added drop wise to a solution of anhydrous ZnCl_2 (0.0887 g, 0.651 mmol) in acetonitrile (40 mL). The reaction mixture was then heated under reflux for 24 h.

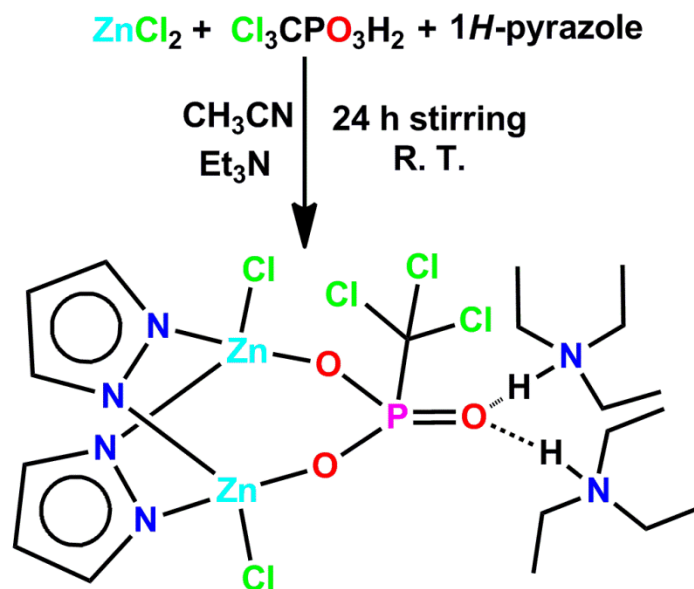
The resulting clear colorless solution was filtered. Removal of the solvent from filtrate *in vacuo* afforded a colorless solid residue which was re-dissolved in toluene and kept for crystallization by vapor diffusion method with *n*-hexane at room temperature. After one week, colorless block-shaped crystals of **4** were obtained. Yield: 0.043 g, 38% (based on zinc) mp: 120 °C (d) Anal. Calcd for C₁₀₂H₁₈₆Cl₆N₄O₂₁P₆Zn₈ (**4**; 2726.20): C, 44.94; H, 6.88; N, 2.06; Found: C, 46.66; H, 7.14; N, 1.96. IR (KBr, ν/cm^{-1}): 3437 (m, br), 2939 (m), 1617 (m), 1473 (s), 1398 (m), 1293 (w), 1081 (s), 989 (s), 864 (w), 778 (m), 731 (m), 643 (w), 575 (m), 501 (m). ESI-MS (*m/z*): Theoretical mass peak: 1147.99, Experimental mass peak: 1148.05, [Zn₄(Cl)₃{2,3,5,6-(Me)₄C₆H-CH₂-PO₃}₃Et₃N + 2H⁺]⁺ (Figure 2). ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.64 (Ar-1H), δ 2.06-2.17 (Ar-CH₃), δ 1.10 [N(CH₂CH₃)₃], δ 2.47 [N(CH₂CH₃)₃], ³¹P NMR (500 MHz, DMSO-*d*₆): δ 21.56 (s) (ESI).



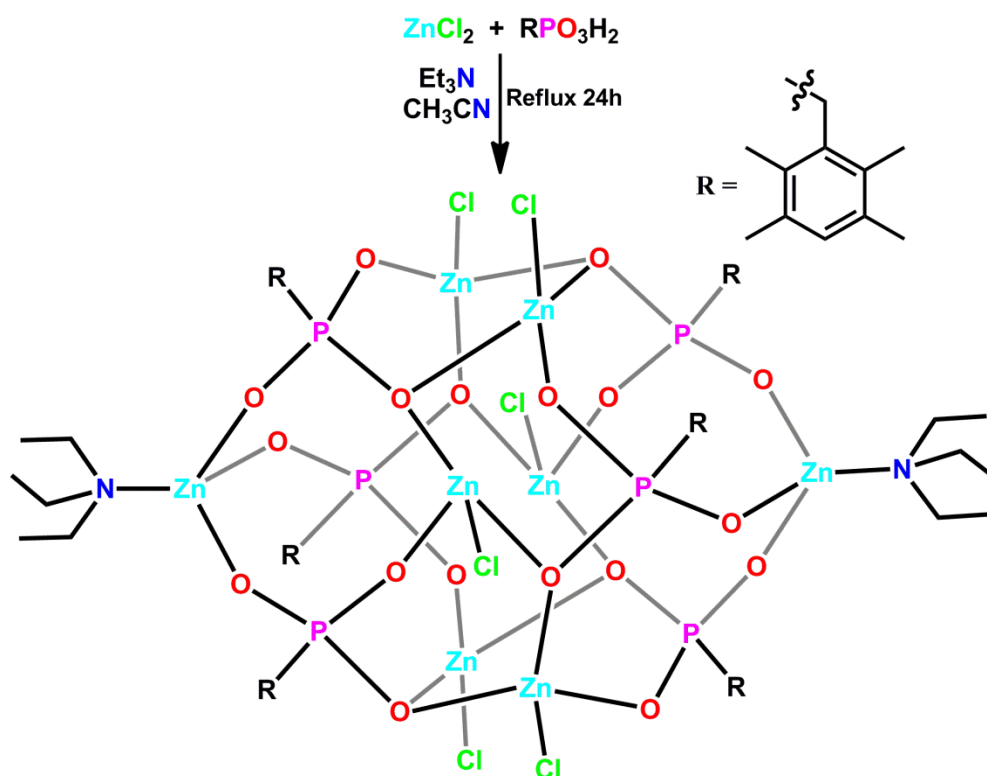
Scheme 1. Synthesis of **1**



Scheme 2. Synthesis of **2**



Scheme 3. Synthesis of 3



Scheme 4. Synthesis of 4

X-ray Crystallography. Data were collected on Bruker APEX II CCD diffractometer (MoK α , λ = 0.71073 Å). Complete hemispheres of data were collected using ω -scans (0.3°, up to 30 s/frame). Integrated intensities were obtained with SAINT+,²² and when they were corrected for absorption SADABS was used.²³ Structure solution and refinement were performed with the SHELXTL-package.²⁴ The structures were solved by direct methods and completed by iterative cycles of difference Fourier syntheses and full-matrix least-squares refinement against F^2 .²⁵ All the other non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms on the carbon frameworks were included in the final stages of the refinement and were refined with a typical riding model. Some solvent molecules could not be modeled satisfactorily as they were located on the symmetry elements of the space group. Therefore the Olex/Mask²⁶ was used to remove such disordered units from the respective overall intensity data. The atoms with large anisotropic displacement parameters were constrained and restrained. These details are found in _refine_special_details of the cif file. The details of the masked electron density are appended to the respective cif files. DIAMOND (version 3.1) has been used for mean-plane analyses as well as molecular drawings. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

Mask Details for **1**.

Electron count 129.1 (void of 105 Å³) per unit cell accounts for 1.5 water molecules. [129.1 total no. of calculated e⁻ (Z = 8)]

Mask Details for **4**.

Electron count 440 (void of 1967.7 \AA^3) per unit cell accounts for 4 *n*-hexane and 2 water molecules. [440 total no. of calculated e^- ($Z = 2$)]

RESULTS AND DISCUSSION

Synthesis. Most of the layered transition metal phosphonates reported so far have been synthesized by the hydrothermal synthetic methods.²⁷ But in the present instance the reaction of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cl}_3\text{CPO}_3\text{H}_2$ in the presence of triethylamine (1:1:2) at room temperature under normal solution reaction conditions at ambient temperature afforded a coordination polymer $\{[\text{Zn}_2(\text{Cl}_3\text{CPO}_3)_2(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}\}_n$ (**1**) upon crystallization (Scheme 1).

The importance of the co-ligand in limiting the extended structure is seen in a comparable reaction between $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cl}_3\text{CPO}_3\text{H}_2$ in the presence of 3,5-dimethylpyrazole (as the co-ligand). In this reaction, instead of the coordination polymer **1**, we obtain a tetranuclear derivative, $[\{\text{Zn}_4(\eta^1\text{-DMPzH})_6(\text{Cl}_3\text{C-PO}_3)_2\}(\mu\text{-OH})_2(\text{ClO}_4)_2]$ (**2**) (Scheme 2).

The characterization of **1** and **2**, in solution, was carried out by ESI-MS and ^{31}P NMR. Compound **1** shows a ^{31}P NMR chemical shift of 3.93 ppm in DMSO- d_6 (ESI). ESI-MS of **1** in DMSO reveals that the coordination polymer breaks down to a monomeric unit 596.60 $[\{\text{Zn}_2(\text{Cl}_3\text{CPO}_3)_2(\text{H}_2\text{O})_3\} + \text{H}_2\text{O} - \text{H}^+]^-$ (Figure 1). The ^{31}P NMR chemical shift is presumably due to such a monomeric species. In contrast to the situation found with **1**, the ESI-MS of **2** in DMSO reveals that the tetranuclear ensemble remains intact under these conditions (ESI). The ^{31}P NMR spectrum of **2** reveals the presence of a single chemical shift at 4.30 ppm (ESI) consistent with its molecular structure.

In our previous investigations on molecular metal phosphonates, we have noticed that the nature of the metal salt also has a crucial role in determining the final outcome of the reaction.¹ In most instances when metal chlorides were used as precursors, some of the chloride ligands stayed on in the molecular ensemble either as a terminal or a bridging ligand.^{11a, 15a, 15b, 16} In the current instance the reaction of anhydrous ZnCl_2 with $\text{Cl}_3\text{CPO}_3\text{H}_2$ in the presence of 1*H*-pyrazole afforded a dinuclear derivative $[\{(\text{ZnCl})_2(\eta^2\text{-Pz})_2(\text{Cl}_3\text{CPO}_3)\}(\text{Et}_3\text{NH})_2]$ (**3**) where each Zn(II) retained one chloride ligand. The two Zn(II) ions were bridged by two pyrazolate anions and one phosphonate ligand. ESI-MS of **3** reveals that its molecular integrity is retained in solution (ESI). The ^{31}P NMR of **3** in DMSO-d_6 showed a singlet at 7.56 ppm (ESI).

Previously, we have found that the reaction of CuCl_2 with 2,3,5,6-(Me) $_4\text{C}_6\text{HCH}_2\text{PO}_3\text{H}_2$ afforded a hexaicosametallic derivative, $[\text{Cu}_{26}\{2,3,5,6\text{-(Me)}_4\text{C}_6\text{H-CH}_2\text{-PO}_3\}18(\mu_2\text{-OH})4(\mu_3\text{-OH})_6(\mu_4\text{-Cl})_6(\mu\text{-OH}_2)_2(\text{OH}_2)_2(\text{MeCN})_4]\cdot 6\text{MeCN}\cdot 15\text{H}_2\text{O}$ which is the largest Cu(II) aggregate among phosphonate complexes.¹⁶ In view of this it was of interest to examine if we could isolate a large-nuclearity Zn(II) aggregate utilizing 2,3,5,6-(Me) $_4\text{C}_6\text{HCH}_2\text{PO}_3\text{H}_2$. In accordance with our expectation we were able to isolate an ellipsoidal octanuclear zinc(II) phosphonate $[\{\text{Zn}_8(\text{Cl}_6)\{2,3,5,6\text{-(Me)}_4\text{C}_6\text{HCH}_2\text{PO}_3\}_6(\text{Et}_3\text{N})_2](\text{Et}_3\text{NH})_2\cdot 2\text{ }n\text{-hexane}\cdot 3\text{H}_2\text{O}$ (**4**). To the best of our knowledge **4** has the highest nuclearity among molecular inorganic Zn(II) phosphonates. In this context, it must be mentioned that previously an organometallic dodecanuclear zinc phosphonate, $[\text{Zn}_2(\text{THF})_2(\text{EtZn})_6\text{Zn}_4(\mu_4\text{-O})(t\text{-BuPO}_3)_8]$ was reported by Roesky and co-workers in the reaction between ZnEt_2 and $t\text{-BuPO}_3\text{H}_2$.^{28a} Also two nonanuclear Zn(II) phosphonates, $[\text{Zn}_6\text{L}_6(\text{Zn})\{\text{Zn}(\text{H}_2\text{O})_4\}_2]\cdot 14\text{H}_2\text{O}$ and $[\text{Zn}_7\text{L}_6\{\text{Zn}(2,2'\text{-bipy})(\text{H}_2\text{O})_3\}_2]\cdot 13.5\text{H}_2\text{O}$ [where $\text{L} = \{\text{O}_3\text{PCH}_2\text{NC}_5\text{H}_9\text{COO}\}^{3-}$] were reported by Mao and coworkers but it is to be noted that H_3L used in this case also consists a carboxylate group which provides additional coordination.^{28b} Also,

two heterometallic zinc phosphonates, $[\text{Co}^{\text{II}}(\text{en})_3]_2[\text{Zn}_6\text{P}_8\text{O}_{32}\text{H}_8]$ and $[\text{Co}^{\text{III}}(\text{en})_3][\text{Zn}_8\text{P}_6\text{O}_{24}\text{Cl}]\cdot 2\text{H}_2\text{O}$ were reported by Xu and coworkers.^{28c}

ESI-MS of **4** in DMSO reveals that the ellipsoid aggregate decomposes into two equal halves which could be detected (Figure 2). The ^{31}P NMR of **4** in DMSO- d_6 reveals a singlet resonating at 21.6 ppm consistent with the ESI-MS data (ESI).

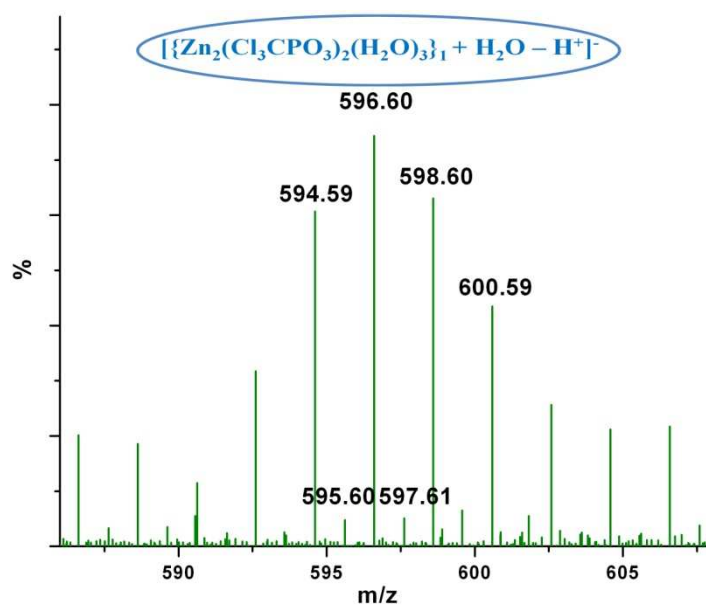


Figure 1. ESI-MS of **1** showing the presence of a dinuclear repeat unit.

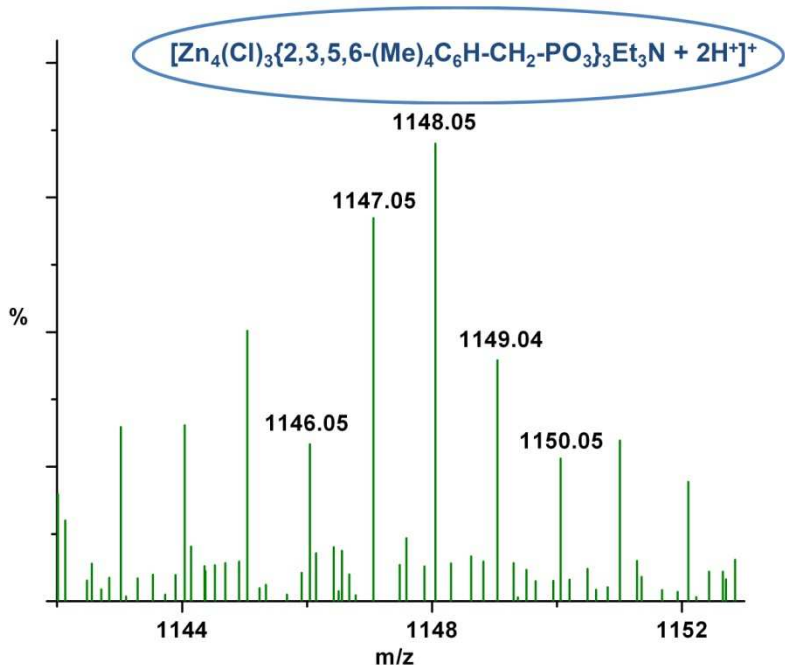


Figure 2. ESI-MS of **4** showing the presence of its half-unit.

Molecular Structures of 1-4. The molecular structures of **1-4** were determined by X-ray crystallography. The crystallographic parameters of these compounds are given in Table 1. CCDC reference numbers for **1-4** are **978373-978376** respectively.

Table 1. Crystal Data and Structure Refinement Parameters of **1-4** (CCDC 978373-978376)

	1	2	3	4
Empirical formula	C ₂ H ₆ Cl ₆ O ₉ P ₂ Zn ₂	C ₃₂ H ₅₀ Cl ₈ N ₁₂ O ₁₆ P ₂ Zn ₄	C ₁₉ H ₃₈ Cl ₅ N ₆ O ₃ PZn ₂	C ₁₈₀ H ₃₀₆ O ₃₈ P ₁₂ Cl ₁₂ Zn ₁₆ N ₈
Formula weight	579.49	1465.94	737.51	5033.27
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	C 2/c	P-1	P2(1)/n	P-1
Unit cell dimensions	$a = 23.691(6)$ $\alpha = 90.00^\circ$	$a = 9.998(5)$ Å $\alpha = 77.438(5)^\circ$	$a = 9.679(5)$ Å $\alpha = 90^\circ$	$a = 14.1126(12)$ Å $\alpha = 93.974(2)^\circ$
	$b = 13.710(4)$ $\beta = 105.048(5)^\circ$	$b = 11.016(5)$ Å $\beta = 72.645(5)^\circ$	$b = 20.502(5)$ Å $\beta = 91.657(5)^\circ$	$b = 26.267(2)$ Å $\beta = 92.518(2)^\circ$
	$c = 10.983(3)$ $\gamma = 90.00^\circ$	$c = 13.645(5)$ Å $\gamma = 77.177(5)^\circ$	$c = 15.715(5)$ Å $\gamma = 90^\circ$	$c = 33.873(3)$ Å $\gamma = 91.439(2)^\circ$

Volume	3445.1(16)	1380.0(11) Å ³	3117(2) Å ³	12509.3(18)
Z	8	1	4	2
Density (calculated)	2.234 Mg/m ³	1.764 Mg/m ³	1.572 Mg/m ³	1.336 Mg/m ³
Absorption coefficient	3.931 mm ⁻¹	2.235 mm ⁻¹	2.050 mm ⁻¹	1.766 mm ⁻¹
<i>F</i> (000)	2256	740	1512	5220
Crystal size	0.072 × 0.068 × 0.064 mm	0.040 × 0.038 × 0.036 mm	0.084 × 0.082 × 0.078 mm	0.96 × 0.92 × 0.90 mm
Theta range for data collection	2.41 to 25.49 °	1.08 to 28.31°	2.33 to 25.5 °	0.77 to 25.05 °
Index ranges	-27 ≤ <i>h</i> ≤ 31, -18 ≤ <i>k</i> ≤ 18, -14 ≤ <i>l</i> ≤ 10	-13 ≤ <i>h</i> ≤ 12, -9 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 17	11 ≤ <i>h</i> ≤ 7, -24 ≤ <i>k</i> ≤ 24, -19 ≤ <i>l</i> ≤ 19	-17 ≤ <i>h</i> ≤ 17, -28 ≤ <i>k</i> ≤ 33, -43 ≤ <i>l</i> ≤ 32
Reflections collected	14834	8810	20779	74382
Independent reflections	3211 [<i>R</i> (int) = 0.0898]	6138 [<i>R</i> (int) = 0.0424]	5757 [<i>R</i> (int) = 0.0407]	45793 [<i>R</i> (int) = 0.0462]
Completeness to theta	100%	89.3% (28.31°)	99.2%	98.4% (25.5°)
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.745 and 0.550	1 and 0.636984	0.746 and 0.630	1 and 0.087374
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3211/6/193	6138 / 4 / 343	5758/0/337	45793/304/2426
Goodness-of-fit on <i>F</i> ²	1.012	1.088	1.096	0.932
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0390, <i>wR</i> ₂ = 0.0871	<i>R</i> ₁ = 0.0700, <i>wR</i> ₂ = 0.1352	<i>R</i> ₁ = 0.0624, <i>wR</i> ₂ = 0.1666	<i>R</i> ₁ = 0.0878, <i>wR</i> ₂ = 0.2272
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0614, <i>wR</i> ₂ = 0.0930	<i>R</i> ₁ = 0.1274, <i>wR</i> ₂ = 0.2017	<i>R</i> ₁ = 0.0735, <i>wR</i> ₂ = 0.1748	<i>R</i> ₁ = 0.1673, <i>wR</i> ₂ = 0.2738
Largest diff. peak and hole	1.05/-0.70 e.Å ⁻³	1.311 and -1.954 e.Å ⁻³	2.14/-0.68 e.Å ⁻³	1.85 and -0.84 e.Å ⁻³

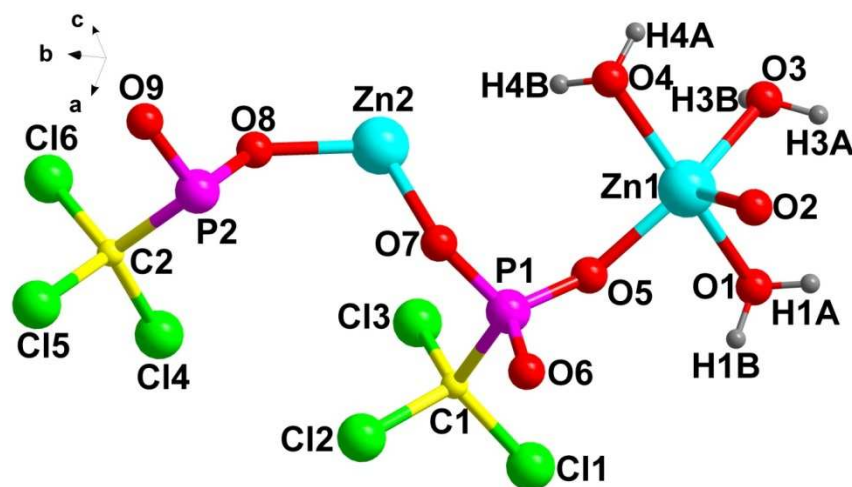


Figure 3. Schematic representation of the asymmetric unit of **1**. Selected bond distances (in Å) and angle (in deg.): Zn1-O2, 1.958(3); Zn1-O5, 1.973(3); Zn1-O3, 2.060(3); Zn1-O4, 2.073(3); Zn1-O1, 2.139(3); Zn2-O8, 1.921(3); Zn2-O7, 1.940(3); Zn2-O6, 1.941(3); Zn2-O9, 1.981(3); P1-O5, 1.503(3); P1-O7, 1.513(3); P1-O6, 1.527(3); P1-C1, 1.854(5); P2-O2, 1.496(3); P2-O9, 1.517(3); P2-O8, 1.526(3); P2-C2, 1.856(5); O2-Zn1-O5, 110.19(13); O2-Zn1-O3, 103.17(13); O2-Zn1-O4, 102.32(16); O5-Zn1-O4, 97.28(14); O3-Zn1-O4, 84.78(14); O2-Zn1-O1, 96.42(14); O5-Zn1-O1, 81.79(13); O3-Zn1-O1, 85.00(14); O4-Zn1-O1, 160.27(17); O8-Zn2-O7, 110.17(13); O5-P1-O7, 115.14(19); O5-P1-O6, 115.14(18); O7-P1-O6, 109.70(17); O9-P2-O8, 111.32(19); O9-P2-C2, 103.2(2); O8-P2-C2, 104.1(2).

The asymmetric unit of **1** possesses two Zn(II) centers and two fully deprotonated phosphonate ligands (Figure 3). X-ray crystallography reveals that **1** possesses a 2-D layered extended structure (Figure 4a). All the phosphonate ligands bind through the 3.111 coordination mode. There are two types of Zn (II) ions in **1**. Zn1 is five-coordinate [5O, three molecules of water (average Zn-O distance: 2.09 Å) and two phosphonate oxygen atoms (average Zn-O distance: 1.96 Å)] in a square pyramidal geometry. On the other hand Zn2 is tetrahedral (4O, average Zn-O distance: 1.95 Å); the four oxygen atoms are derived from three phosphonate ligands. The coordination polymer of **1** is a network of inter-connected macrocycles. The repeat unit consists of a central 24-membered $\text{Zn}_6\text{P}_6\text{O}_{12}$ macrocycle along with two different 8-membered $\text{Zn}_2\text{P}_2\text{O}_4$ macrocycles (Figure 4b). Interestingly, the 24-membered macrocyclic subunit possesses intricate O-H...O hydrogen bonding interactions (Figure 4c, ESI). The supramolecular packing of the layers, shown in Figure 5 reveals that the inter-layer distance is ~ 3.6 Å while the thickness of each layer is ~ 8.3 Å. Interestingly, Zn(II) phosphonates, known earlier,

$$\text{Zn}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3], \quad \text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl}) \cdot 3\text{H}_2\text{O},$$

$\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$, $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{NH}_2\text{CONH}_2$, $\text{Zn}(\text{O}_3\text{PCH}_2\text{CH}_3)\cdot\text{H}_2\text{O}$,
 $\text{Zn}(\text{O}_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{H})\cdot\text{H}_2\text{O}$, $\text{Zn}(\text{O}_3\text{P}(\text{CH}_2)_2\text{Br})\cdot\text{H}_2\text{O}$ and $\text{Zn}(\text{O}_3\text{P}(\text{CH}_2)_2\text{NH}_3^+\text{NO}_3^-)$ possess structural features that are different from **1**.^{29, 27b}

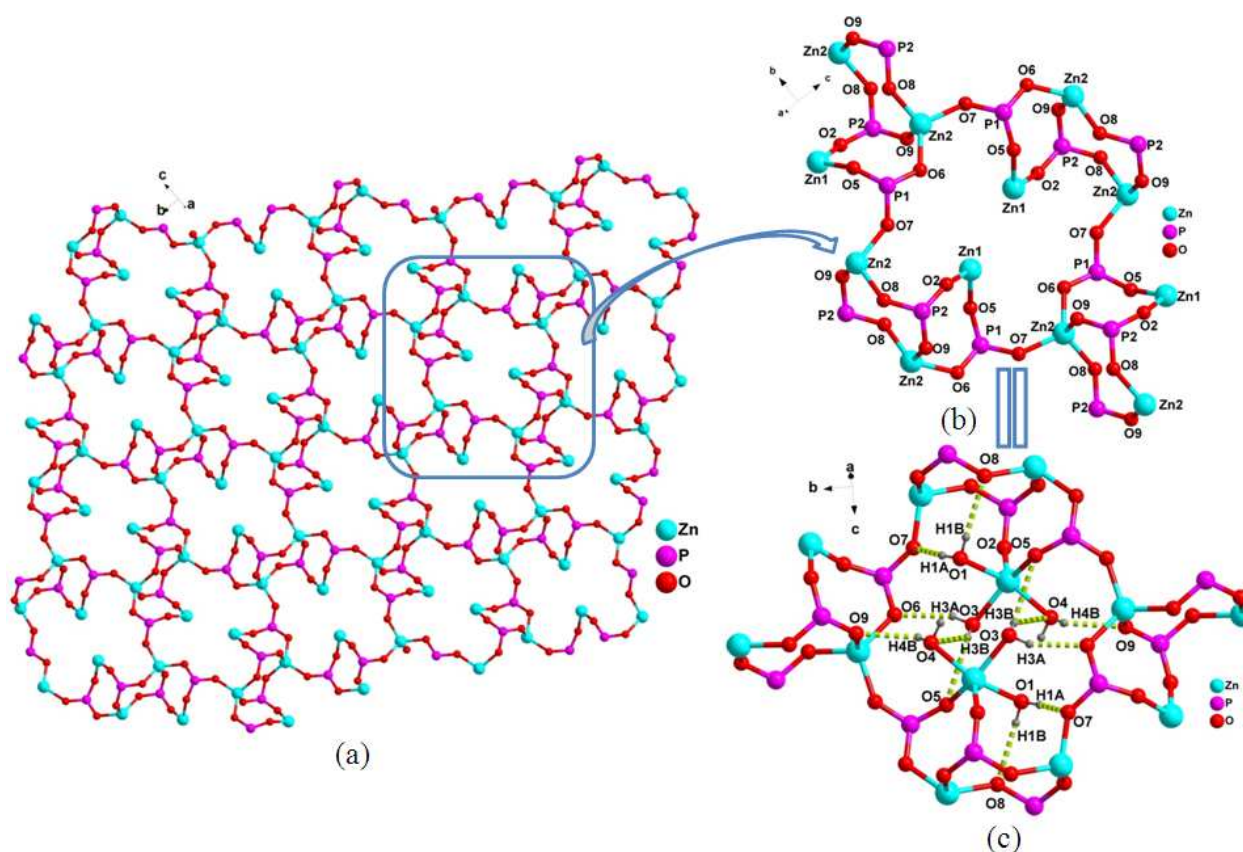


Figure 4. (a) Layered polymeric structure of **1** (CCl_3 group of the phosphonate and some H atoms have been omitted for clarity). (b) Repeat unit of the coordination polymer is shown consisting of a central 24-membered $\text{Zn}_6\text{P}_6\text{O}_{12}$ macrocycle along with two different 8-membered $\text{Zn}_2\text{P}_2\text{O}_4$ macrocycles (c) Some O-H...O hydrogen bonding interactions within the 24-membered macrocycle of **1** (ESI).

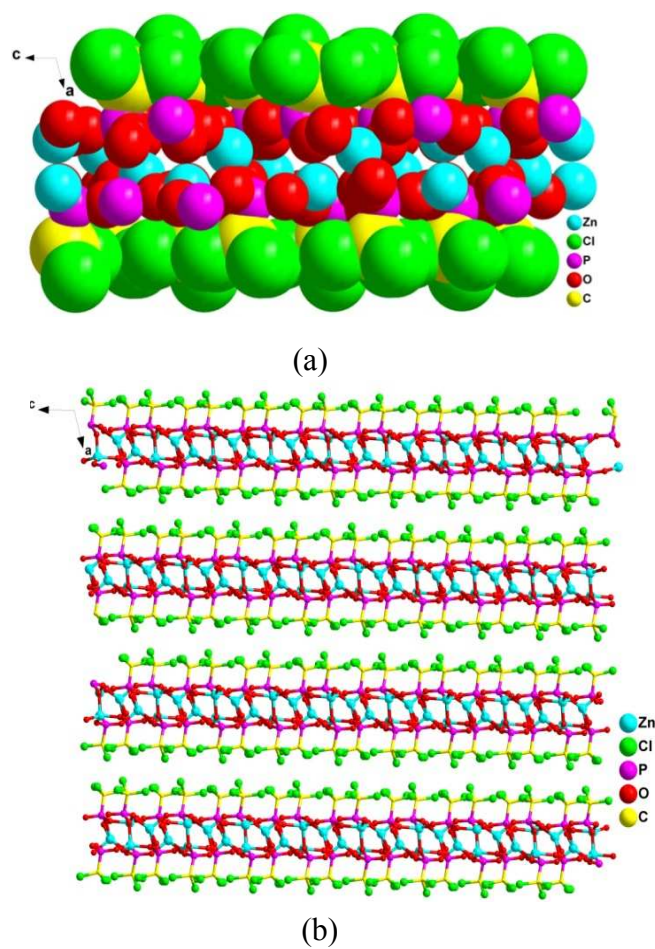


Figure 5. (a) Single layer of the layered structure of **1** along the *b*-axis. (b) Supramolecular packing of layers in **1** along the *b*-axis.

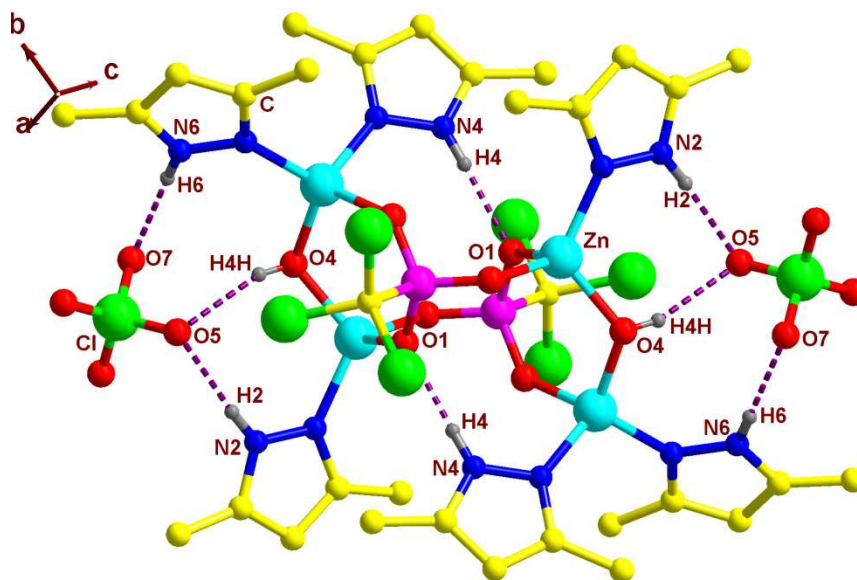


Figure 6. Molecular structure of **2**. Some H atoms have been omitted for clarity. Hydrogen bond parameters for **2**. H4H---O5, 2.298(6) Å; O4-H4H---O5, 161.8°; H2---O5, 2.001(4) Å; N2-H2---O5, 168.6°; H6---O7, 2.068(5) Å; N6-H6---O7, 164.7°; H4---O1, 2.008(3); N4-H4---O1, 171.9°.

The X-ray crystallography of the compound **2** shows that it is a dicationic tetranuclear complex $[\{Zn_4(\eta^1\text{-DMPzH})_6(\text{Cl}_3\text{C-PO}_3)_2\}(\mu\text{-OH})_2(\text{ClO}_4)_2]$ (Figure 6). The metal assembly is enclosed by a lipophilic organic sheath composed of η^1 -3,5-dimethyl-1H-pyrazole ligands. Two types of Zn(II) centers are present; Zn1 possesses a 3O, 1N coordination mode in a tetrahedral geometry (average Zn-O distance: 1.96 Å and Zn-N distance: 1.98 Å) while Zn2 has a 2O, 2N coordination mode also in a tetrahedral geometry (average Zn-O distance: 1.93 Å and average Zn-N distance: 1.99 Å). The structure of **2** contains a $Zn_4P_2O_8$ core which itself consists of a central 8-membered $Zn_2P_2O_4$ ring flanked on either side symmetrically by six-membered Zn_2PO_3 rings; one of the oxygen atoms is derived from a $\mu\text{-OH}$ (Figure 7). The overall $Zn_4P_2O_8$ core has a chair-shaped geometry (Figure 9). Two central phosphonate ligands in a 3.111 coordination

mode hold the tetranuclear ensemble together. The presence of inter- and intramolecular hydrogen bonds in **2** leads to the generation of a 3-D supramolecular assembly (ESI).

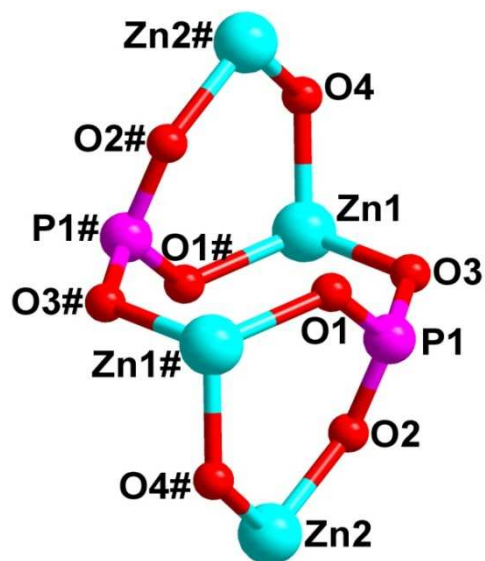


Figure 7. Chair-shaped $\text{Zn}_4\text{P}_2\text{O}_8$ core of **2**. Selected bond lengths (\AA) and bond angles ($^\circ$): Zn1-O4, 1.928(4); Zn1-O3, 1.940(4); Zn1-O1#, 1.999(5); Zn2-O2, 1.938(4); Zn2#-O4, 1.933(4); P1-O3, 1.503(4); P1-O2, 1.513(4); P1-O1, 1.526(4); O4-Zn1-O3, 106.80(17); O4-Zn1-O1#, 109.84(17); O3#-Zn1#-O1, 103.43(16); O4#-Zn2-O2, 104.30(17); O3-P1-O2, 113.1(2); O3-P1-O1, 112.9(2); O2-P1-O1, 114.1(2).

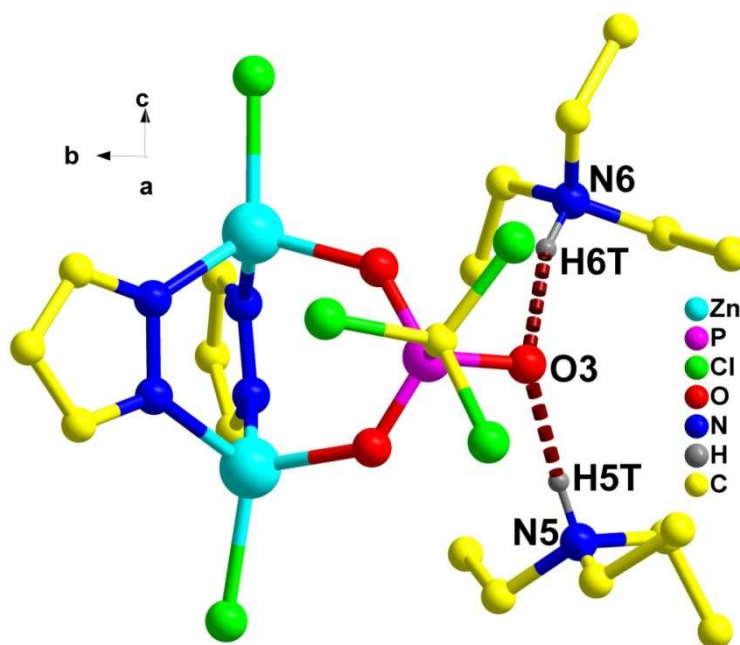


Figure 8. Molecular structure of **3** (some H atoms have been omitted for clarity). Hydrogen bond parameters for **3**: H5T---O3, 1.829(8) Å; N5-H5T---O3 166.3°; H6T---O3, 1.829(8) Å; N5-H6T---O3, 164.6°.

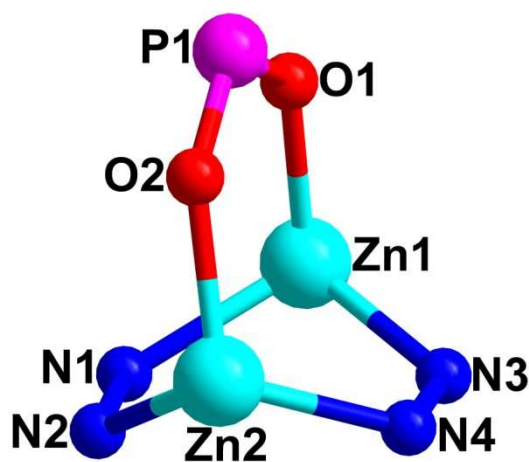


Figure 9. Bicyclic 7-membered $\text{Zn}_2\text{N}_4\text{O}_2\text{P}$ ring of **3**. Selected bond lengths (Å) and angles (°): Zn1-N3, 1.995(5); Zn1-N1, 2.043(5); Zn1-O1, 1.963(4); Zn2-O2, 1.955(4); Zn2-N4, 1.996(5); Zn2-N2, 2.004(6); P1-O1, 1.513(4); P1-O2, 1.508(4); O1-Zn1-N3, 106.2(2); O1-Zn1-N1,

108.9(2); N3-Zn1-N1, 101.9(2); O2-Zn2-N4, 110.6(2); O2-Zn2-N2, 103.0(2); N4-Zn2-N2, 100.4(2); O1-P1-O2, 116.0(2).

The molecular structure of **3** reveals that it is a dianionic complex possessing two triethylammonium cations, $\{(ZnCl)_2(\eta^2-Pz)_2(Cl_3CPO_3)\}(Et_3NH)_2$ (Figure 8). In general, dinuclear metal phosphonates contain two symmetric phosphonate ligands that bridge the metal centers.^{1f, 13a, 15a} In **3**, however, this is different. The two tetrahedral zinc(II) centers are bridged to each other by one $\eta^2-[Cl_3CPO_3]^{2-}$ and two η^2 -[pyazolate]⁻ ligands. The core structure of **3** possesses a bicyclic ring including a rare 7-membered $Zn_2N_2O_2P$ ring; the two Zn(II) ions are further bridged by a η^2 -[pyazolate]⁻ ligand (Figure 9). The phosphoryl oxygen atom is involved in a bifurcated hydrogen bonding with the triethylammonium cation (Figure 8). Hydrogen bonding interactions in **3** allow it to form a 3D-supramolecular assembly in the solid-state (ESI).

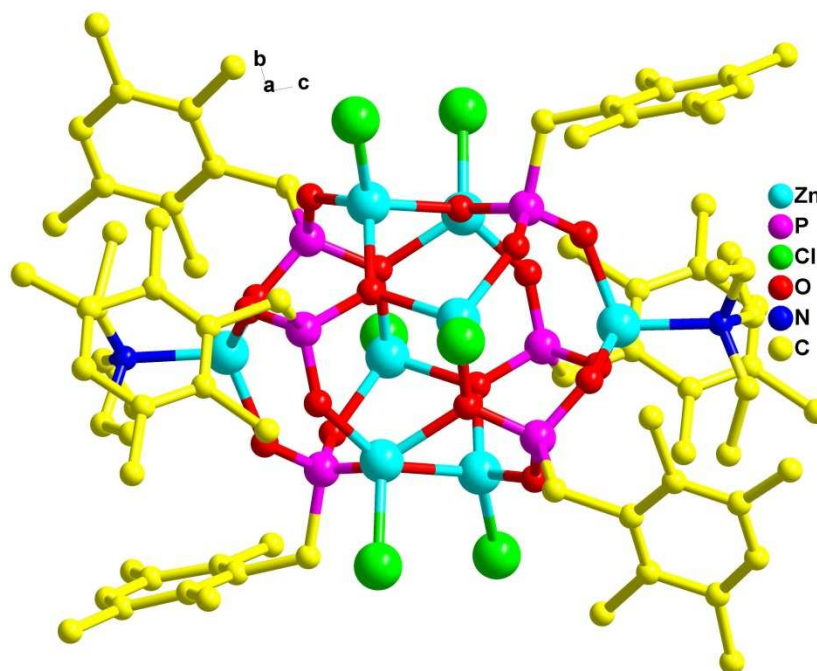


Figure 10. Molecular structure of **4** (the triethylammonium cations and some other H atoms have been omitted for clarity).

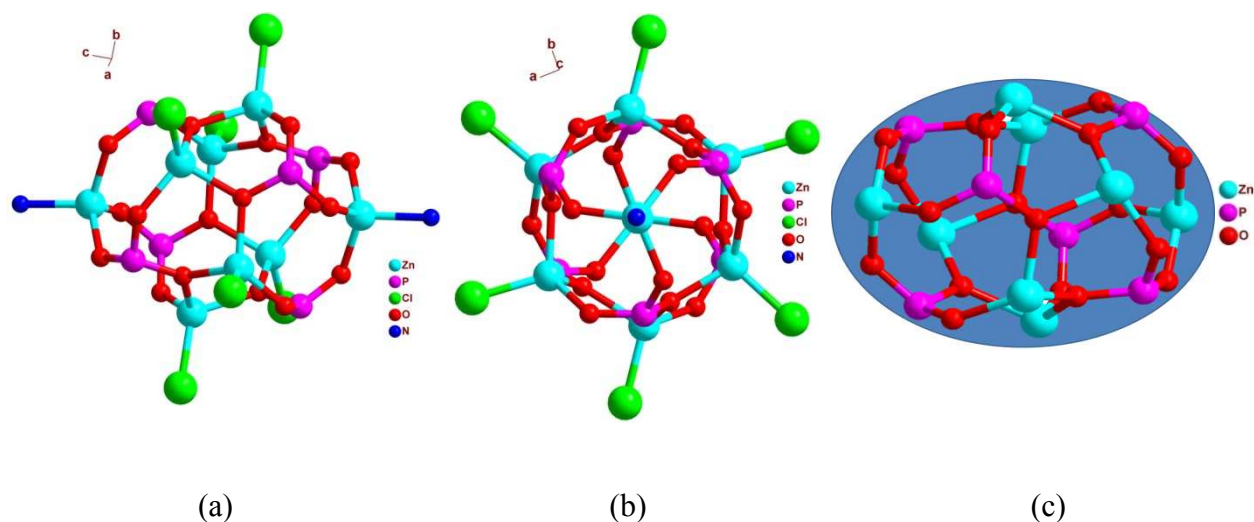


Figure 11. Core structure of **4** (a) as viewed from the side (b) as viewed from the polar end. Notice the symmetric arrangement of the Zn-Cl bonds about this axis. (c) Ellipsoid core of **4** (all the C and H atoms have been omitted for clarity).

The X-ray crystal structure analysis of **4** reveals that it is a dianionic octanuclear complex $[\{Zn_8(Cl)_6\{2,3,5,6-(Me)_4C_6H-CH_2-PO_3\}_6(Et_3N)_2\}(Et_3NH)_2 \cdot 2 \text{ n-hexane} \cdot 3H_2O]$ (Figure 10). This is a new structural type among molecular Zn(II) phosphonates. **4** is a cage where 8 metal ions are held together by six 2,3,5,6-(Me)₄C₆HCH₂PO₃ ligands. The presence of the organic substituents in the periphery of the cage allows this compound to be soluble in a number of organic solvents. All the six phosphonate $[2,3,5,6-(Me)_4C_6HCH_2PO_3]^{2-}$ ligands bind in a 3.111 mode and are present in a similar chemical environment. The Zn₈P₆O₁₈ cage of **4** is shaped like an ellipsoid (Figure 11c) containing six symmetry-related 8-membered Zn₂P₂O₄ rings and six 6-membered Zn₂O₃P (ESI). Six of the Zn(II) ions have a terminal chloride ligand which project out of the cage (Figure 11). The ellipsoid contains two polar Zn(II) ions which are bound to neutral triethylamine ligands (Figure 11). The six Zn(II) ions in **4** possess a 3O, 1Cl coordination environment in a tetrahedral geometry while the other two Zn(II) ions are in a 3O, 1N

coordination environment, also in a tetrahedral geometry. Interestingly, the size of the octa Zn(II) molecular aggregate, **4**, is larger than any of the carbon-based fullerenes. Thus, the end-end distances in **4** range from 7.79 Å (end to end Zn1-Zn8 distance) to 6.96 Å (end to end P3-P4 distance) [if we consider the full molecular aggregate including the hydrogen atoms, the end-end distances range from 18.46 Å (end to end C64-C10 distance) to 20.15 Å (end to end H10B-H64A distance)]. In contrast to these metric parameters found in **4**, the diameter of fullerene C₆₀ is 7.0 Å while diameters of higher fullerenes (i.e., C_n with $n > 60$) are in the range of 8-11 Å.³⁰

Summary

Subtle variation of reaction conditions is a powerful means of modulating the nuclearity as well as other structural features of molecular phosphonates. Admittedly, at the present moment, predicting the precise outcome of the reaction in these multi-component syntheses is difficult. Be that as may, this methodology, seems to be the only powerful synthetic protocol for achieving the assembly of polynuclear aggregates possessing interesting structural features. This synthetic paradigm has been used effectively, as shown above, for tuning the Zn(II) phosphonate ensembles from extended to molecular structures. In the process, we have also been able to isolate and structurally characterize an octanuclear zinc(II) phosphonate, possessing an ellipsoidal core. The latter happens to be the largest-sized molecular inorganic zinc(II) phosphonate.

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ASSOCIATED CONTENT

Electronic Supplementary Information (ESI). Crystallographic information files (CIF), CCDC 978373-978376 for **1-4**. Coordination environments of the metal centers, Tables of bond distance (Å) and bond angle (°), TGA plots, Figure S1-S17, Chart S1, and Table S1-S7.

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Graphical Abstract

**Molecular and Polymeric Zinc(II) Phosphonates:
Isolation of an Octanuclear Ellipsoidal Ensemble**

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