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$[Zn_7\{(2\text{-}C_5H_4N)CH(OH)PO_3\}_6(H_2O)_6]SO_4\cdot 4H_2O$: A Zinc Phosphonate Cluster with a Drum-like Cage Structure

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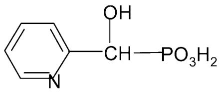
Direct reaction of hydroxy(2-pyridyl)methylphosphonic acid with zinc sulfate under hydrothermal conditions results in the formation of the novel heptanuclear cluster compound $[Zn_7\{(2\text{-}C_5H_4N)CH(OH)PO_3\}_6(H_2O)_6]SO_4\cdot 4H_2O$ (**1**). The inorganic core of the cluster can be described as a cylindrical drum made up of six Zn atoms bridged by six $\{CPO_3\}$ units that is centered by a seventh Zn atom. Crystal data: monoclinic, $C2/c$, $a = 22.690(2)$ Å, $b = 16.675(2)$ Å, $c = 18.151(2)$ Å, $\beta = 93.390(2)°$.

Oligonuclear metal complexes have been studied extensively as catalysts, precursors to metal-oxide-based materials, and models of active sites in metal enzymes. However, cage complexes containing phosphonate ligands are rare, although a number of polymeric metal phosphonate compounds have been prepared because of their potential applications in absorption, ion exchange, and sensors, among others.[1] Several vanadium,[2] aluminum,[3] copper,[4] cobalt,[5] manganese,[5] cadmium,[6] and iron[7] cage complexes have been prepared. To the best of our knowledge, only four zinc phosphonate clusters are known. Compound $[Zn_3Cl_2(3,5\text{-}Me_2PzH)_4(^tBuPO_3)_2]$[8] contains a planar trizinc assembly with two capping $\mu_3\text{-}^tBuPO_3^{2-}$ ligands. In compound $[Zn_6Cl_4(3,5\text{-}Me_2PzH)_8(PhPO_3)_4]$,[8] the six zinc centers are arranged in a chairlike conformation, bridged by tripodal $\mu_3\text{-}PhPO_3^{2-}$ ligands. Compound $[Zn_6\{MeN(CH_2CO_2)(CH_2PO_3)\}_6(Zn)][Zn(H_2O)_6]_2\cdot 22H_2O$[9] contains a heptanuclear zinc phosphonate cluster anion in which the oxo-bridged Zn_6 octahedron is centered by a Zn(II) cation. The dodecanuclear aggregate $[Zn_2(thf)_2(EtZn)_6Zn_4(\mu_4\text{-}O)(^tBuPO_3)_8]$[10] consists of a central $Zn_4(\mu_4\text{-}O)$ core and a zincophosphonate "shell". To produce cluster complexes that contain phosphonate ligands, two approaches are commonly employed. One is to introduce the phosphonate ligand in conjunction with a coligand. The other is to use organometallic precursors to react with the phosphonate ligands. Herein, we report a new heptanuclear cluster complex, $[Zn_7\{(2\text{-}C_5H_4N)CH(OH)PO_3\}_6(H_2O)_6]SO_4\cdot 4H_2O$ (**1**), prepared through direct reaction of the hydroxy(2-pyridyl)methylphosphonic acid (2-hpmpH$_2$, Chart 1) and zinc sulfate.

Chart 1



Compound **1** was prepared through hydrothermal treatment of a mixture of $ZnSO_4\cdot 7H_2O$ (0.292 mmol, 0.0838 g) and 2-hpmpH$_2$ (0.25 mmol, 0.0473 g) in 8 mL of H_2O, adjusted to pH 4.58 with 1 M NaOH, at 140 °C for 24 h. Colorless needlelike crystals were obtained as a monophasic material.[11] Yield: 57%. Single-crystal X-ray diffraction analysis[12] reveals that compound **1** crystallizes in monoclinic space group $C2/c$. There are four crystallographically independent zinc atoms in the structure, each with a distorted octahedral

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(11) Anal. found (calcd) for $C_{36}H_{48}N_6O_{34}P_6SZn_7\cdot 4H_2O$ (%): C, 23.92 (23.27); H, 3.03 (3.02); N, 4.80 (4.53). IR (KBr, cm^{-1}): 3406 (s, br), 1608 (m), 1574 (w), 1482 (m), 1447 (m), 1321 (w), 1131 (s), 1072 (s), 1027 (m), 976 (s), 866 (vw), 813 (w), 764 (w), 746 (vw), 670 (w), 645 (w), 586 (s), 514 (w), 474 (w), 435 (w).

(12) Crystal data: $C_{36}H_{48}N_6O_{34}P_6SZn_7\cdot 2H_2O$, $M_r = 1820.3$, monoclinic, $C2/c$, $a = 22.690(2)$ Å, $b = 16.675(2)$ Å, $c = 18.151(2)$ Å, $\beta = 93.390(2)°$, $V = 6855.1(12)$ Å^3, $Z = 4$, $D_c = 1.764$ g cm^{-3}, μ(Mo Kα) = 26.69 cm^{-1}, $F(000) = 3656$, $\lambda = 0.71073$ Å, graphite monochromator. A crystal of dimensions 0.08 × 0.05 × 0.05 mm was selected for indexing and intensity data collection at 293 K. Unique reflections: 6652 ($R_{int} = 0.0471$). Least-squares refinements were based on F^2 and converged at R1 = 0.0570, wR2 = 0.1159.

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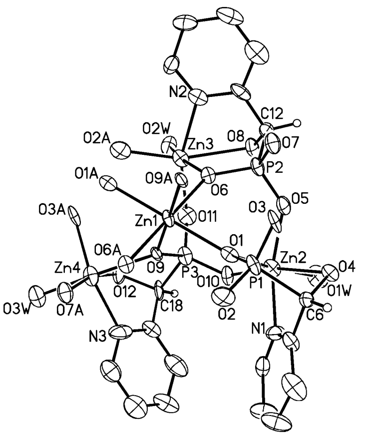

Figure 1. Coordination geometries of zinc in compound **1** with the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level. All H atoms are omitted for clarity.

geometry (Figure 1). The Zn1 atom locates at a special position (0.25, 0.25, 0), while the other three are in general positions. Each Zn1 atom is surrounded by three pairs of phosphonate oxygen atoms (O1, O1A; O6, O6A; and O9, O9A) from three pairs of 2-hpmp^{2-} ligands. The coordination environments around the Zn2, Zn3, and Zn4 atoms are similar. Three of the six binding sites are filled with a phosphonate oxygen, a pyridyl nitrogen, and a hydroxyl oxygen atom from the same 2-hpmp^{2-} ligand. The remaining positions are occupied by two phosphonate oxygens from two different 2-hpmp^{2-} ligands and a water molecule. The Zn−O and Zn−N bond lengths are normal, although the Zn−O (hydroxy) distances (Zn2−O4, Zn3−O8, Zn4−O12) are obviously longer [2.375(3)−2.391(4) Å].

Three crystallographically distinct 2-hpmp^{2-} ligands are found in the molecule. Each acts as a pentadentate ligand. Three donors, i.e., one pyridyl nitrogen, one hydroxyl oxygen, and one phosphonate oxygen, are coordinated to the same Zn2 (or Zn3 or Zn4) atom. The remaining two phosphonate oxygen atoms are linked to the neighboring Zn atoms, leading to a cationic cluster compound. As a consequence, each {CPO_3} tetrahedron is corner-shared with four zinc octahedra. The resulting inorganic core of $Zn_7O_{24}P_6$ can be described as a centered cylindrical drum (Figure 2). The top and bottom faces of the "drum" each contain three Zn atoms, and in each face, neighboring Zn atoms are linked through the "(μ_2-O)−P−(μ_3-O)" bridge, forming a 12-membered ring of $Zn_3O_6P_3$. The zinc atoms within each face are almost equidistant from each other, with interzinc distances of Zn2···Zn3A = 5.668 Å, Zn2···Zn4 = 5.677 Å, and Zn3A···Zn4 = 5.616 Å (symmetry code: A, $0.5 - x$, $0.5 - y$, $-z$). Six side faces of the cylinder are made up of eight-membered rings of {Zn−O−P−O−Zn−O−P−O}. The Zn1 atom lies in the center of the cylinder, coordinated by six μ_3-O of six {CPO_3} from the top and bottom face of the drum. The Zn1···Zn distances are 3.743 Å for Zn1···Zn2, 3.701 Å for Zn1···Zn3, and 3.685 Å for Zn1···Zn4. The pyridyl rings reside on the top and bottom of the drum, leading to a hydrophobic area in the molecule. The SO_4^{2-} anions and the unbonded water molecules occupy the intermolecular space in the lattice. Extensive hydrogen-bonding interactions are observed among the water molecules, the SO_4^{2-} oxygens, and the hydroxy groups of the phosphonate ligands.

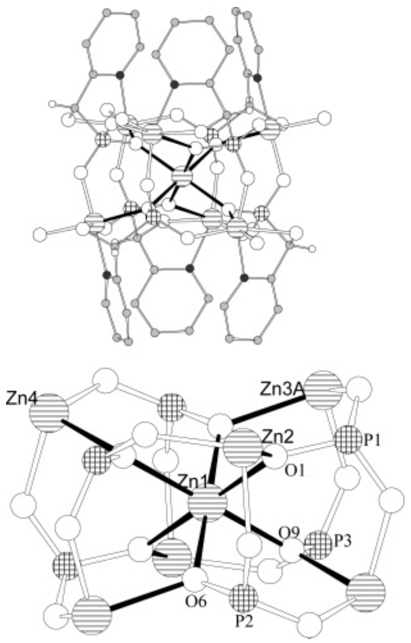

Figure 2. Heptanuclear cluster of compound **1** (top) and inorganic core of the cluster (bottom).

The heptanuclear core of structure **1** is unique compared to another heptanuclear cluster, i.e., $\{Zn_6[MeN(CH_2CO_2)(CH_2PO_3)]_6(Zn)\}^{4-}$.[9] In the latter case, six equivalent Zn atoms are each five-coordinated with distorted trigonal-bipyramidal geometry and are linked into an oxo-bridged Zn_6 octahedron. In **1**, three pairs of Zn atoms are all six-coordinated and are connected purely through the O−P−O bridges forming a cylindrical drum.

TG analysis shows that compound **1** experiences a two-step weight loss in the temperature range 50−800 °C. The weight loss between 50 and 210 °C is 10%, corresponding to the removal of four lattice and six coordinated water molecules (calcd 9.7%). The weight loss above 250 °C is due to the decomposition of the organophosphonate ligand and the collapse of the structure.

In summary, we report the synthesis and structure of compound $[Zn_7\{(2\text{-}C_5H_4N)CH(OH)PO_3\}_6(H_2O)_6]SO_4{\cdot}4H_2O$ (**1**), which exhibits a novel drum-like heptanuclear structure. The results demonstrate that metal phosphonate clusters can be achieved by direct reactions between metal salts and a suitable phosphonate ligand. Further work is in progress to design and synthesize particular phosphonate ligands to produce novel cluster compounds.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org

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