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$\{Zn_6[MeN(CH_2CO_2)(CH_2PO_3)]_6(Zn)\}^{4-}$ Anion: The First Example of the Oxo-Bridged Zn_6 Octahedron with a Centered Zn(II) Cation

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Hydrothermal reactions of *N*-(phosphonomethyl)-*N*-methylglycine, $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ (H_3L), with zinc(II) acetate resulted in the formation of a novel zinc carboxylate–phosphonate, $\{Zn_6L_6(Zn)\}\{Zn(H_2O)_6\}_2 \cdot 22H_2O$ (**1**). The structure of **1** contains a heptanuclear zinc phosphonate cluster anion, $\{Zn_6L_6(Zn)\}^{4-}$, in which seven zinc(II) cations form an unusual $Zn_6(Zn)$ centered octahedron with six of its Zn_3 triangle faces each further capped by a phosphonate group. The Zn(II) cations of the Zn_6 octahedron are five-coordinated whereas the centered Zn(II) cation is octahedrally coordinated. Packing of these cluster anions creates micropores occupied by the hydrated zinc(II) cations as well as lattice water molecules. The structural skeleton of **1** is retained after the removal of the lattice water molecules.

The chemistry of metal phosphonates has been a research field of rapid expansion in recent years, mainly due to their potential application in the area of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry.[1] Most of the metal phosphonates have a layered structure in which the metal centers are bridged by the phosphonate group, although a variety of 1D chains and porous 3D networks have also been reported.[1] One main obstacle in metal phosphonate chemistry is that many metal phosphonates normally form poorly crystalline compounds, making their structural studies a rather difficult task. Phosphonic acids with additional functional groups such as aza-crown ethers, amines, and carboxylic groups have been found to be better ligands since they can provide more coordination sites that may not only increase the solubility of the metal phosphonates in water and improve the crystallinity of their metal complexes but also form many new complexes with novel structures.[2−4] Reactions of metal(II) salts with phosphonic acids attached with an aza-crown ether resulted in a number of "macrocyclic leaflets" with a 1D chain structure as well as other structural moieties.[2] Several types of structures have been reported for metal complexes with *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA) under different pH conditions.[4] A number of metal phosphonocarboxylates have been reported; their structures normally feature either a 2D layer or a 3D network with an open framework.[5]

Metal phosphonates with a molecular cluster unit are relatively rare.[6−11] Several cage complexes involving vanadium and aluminum have been reported.[6] The redox-active $\{Mn_4\}$ cages described by the Dismukes group are also very exciting.[7] A novel dodecanuclear copper(II) cage and a few tri- and hexanuclear zinc cages containing phosphonate and pyrazole were reported,[8] and several polymetallic cobalt and

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manganese cages with phosphinate and phosphonate ligands have been isolated by the Winpenny group.[9] Two mixed-valence polyoxomolybdenum diphosphonate anions were reported recently by the Sevov group.[10] A dodecanuclear zincophosphonate aggregate with a $Zn_4(\mu_4\text{-}O)$ core was reported by the Roesky group.[11] Synthesis of multizinc clusters is of considerable contemporary interest, as exemplified by the potential application of the trinuclear clusters in biological systems such as phospholipase C and P1 nuclease.[12] Herein we reported the synthesis and X-ray crystal structure analysis of a novel heptanuclear zinc phosphonate containing an unusual cluster anion, $\{Zn_6[MeN(CH_2CO_2)(CH_2PO_3)]_6(Zn)\}^{4-}$, which features an unusual $Zn_6(Zn)$ centered octahedron.

The phosphonic acid containing an amino−carboxylate moiety, *N*-(phosphonomethyl)-*N*-methylglycine, $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ (H_3L), was prepared by a Mannich type reaction according to the procedures previously described.[3] Its purity was confirmed by elemental analysis and ^1H and ^{31}P NMR measurements.[13] Hydrothermal reactions of the above phosphonic acid with zinc(II) acetate at 170 °C for 5 days resulted in brick-shaped colorless single crystals (62.1% yield) of $\{Zn_6L_6(Zn)\}\{Zn(H_2O)_6\}_2\cdot 22H_2O$ (**1**).[14] One crystal was used for single-crystal structural analysis on a Smart CCD diffractometer at room temperature.[15]

The structure of $\{Zn_6L_6(Zn)\}\{Zn(H_2O)_6\}_2\cdot 22H_2O$ (**1**) contains a novel polynuclear zinc(II) phosphonate anion, two hexahydrated zinc(II) cations, and 22 lattice water molecules. As shown in Figure 1a, there are two independent zinc cations in the polynuclear zinc(II) phosphonate anion; Zn1 is 5-coordinated by a chelate ligand (N1, O2, O5) and two phosphonate oxygen atoms (O3a, O4a) from two neighboring Zn(1)(L) units in a distorted trigonal bipyramidal geometry. The Zn−N and Zn−O(carboxylate) distances are 2.118(4) and 2.119(3) Å, respectively. The Zn−O(phosphonate) distances are in the range 1.957(3)−2.182(3) Å. These distances are comparable to those in other zinc phosphonates.[3,4,8]

The Zn2 atom lies on a position of −3 symmetry, and it is octahedrally coordinated by 6-phosphonate oxygen atoms from six neighboring Zn(1)(L) units. The Zn−O distance of 2.115(3) Å is close to those for Zn1. The *N*-(phosphonomethyl)-*N*-methylglycine ligand acts as a hexadentate ligand. It chelates with a Zn1 atom tridentately and also bridges with three other Zn(II) cations (Zn2, Zn1a, Zn1b). Chelating and bridging coordination mode has also been adopted in Co(II), Zn(II) complexes with *N*-(phosphonomethyl)iminodiacetic acid.[4c] O(5) of the phosphonate group bridges with one Zn1 atom and one Zn2 atom. The other carboxylate oxygen atom (O1) remains noncoordinated. Since all C−O and P−O bonds have very close distances, we would expect that both phosphonate and carboxylate groups of the ligand have been completely deprotonated. Therefore, each ligand carries three negative charges, thus the cluster anion is 4−.

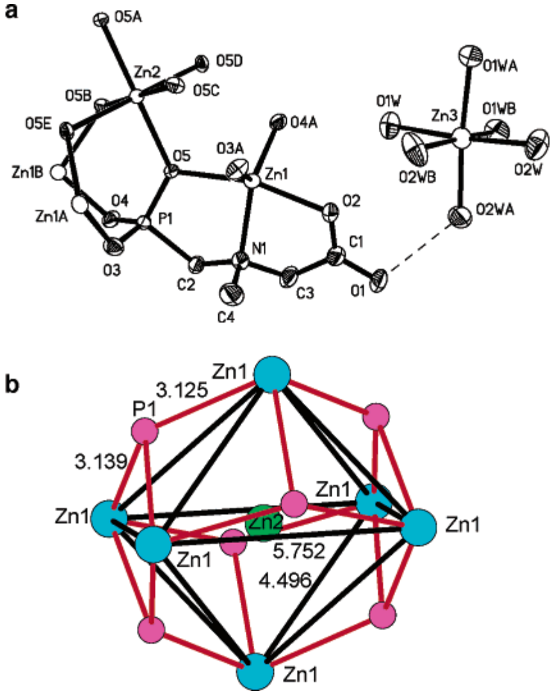

Figure 1. (a) ORTEP representations of **1**. The thermal ellipsoids are drawn at 50% probability. The lattice water molecules have been omitted for clarity. The hydrogen bond is shown as a dotted line. (b) View of the Zn centered Zn_6 octahedron with six capping phosphonate groups. The octahedral Zn, centered Zn, and phosphonate group are drawn as cyan, green, and purple circles.

The seven Zn(II) cations in an anion form an unusual centered octahedron (Figure 1b). The octahedron is created by six 5-coordinated zinc(II) cations (Zn1) with the 6-coordinated Zn2 atom as the centered atom. The edges of the octahedron have Zn···Zn distances of 4.496(1) and 5.752(1) Å, respectively. The distance from the centered Zn(II) to the apex of the octahedron is 3.650(1) Å. Six Zn_3 faces of the octahedron are further capped, each by a phosphonate group. A pair of trans triangle faces remain uncapped. These six P atoms of the phosphonate groups also form an octahedron centered also by the Zn2 atom. It is interesting to compare the heptanuclear zinc(II) phosphonate anion with $[Mo_7O_{16}(O_3PCH_2PO_3)_3]^{8-}$ reported previously, in which three pairs of edge-sharing $Mo^{V}O_6$ octahedra form a ring through corner-sharing; the ring is further “capped” by a $Mo^{VI}O_4$ tetrahedron. In the hexanuclear zinc cages containing phosphonate and pyrazole, the six zinc atoms are arranged in a chairlike conformation.[8a]

The four negative charges of the cluster are balanced by two hexahydrated zinc(II) cations. These zinc atoms (Zn3) are located at positions with 3-fold symmetry (Figure 1a). The Zn−O distances are 2.099(4) and 2.107(3) Å, respectively. Its coordination geometry is a slightly distorted octahedron. The aqua ligand (O(2wa), symmetry operator: *y*, *z*,

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(13) Elemental analysis for $C_4H_{10}NO_5P$: C, 26.05%; H, 5.14%; N, 7.44%. Calcd: C, 26.24%; H, 5.50%; N, 7.65%. ^{31}P NMR shows only one single peak at 7.542 ppm. ^1H NMR: 3.115 ppm ($-CH_3$, s, 3H), 3.448 ppm ($-CH_2-PO_3$, d, 2H, $J_{H-P} = 11.0$ Hz), 4.177 ppm ($-CH_2-COO$, s, 2H).

(14) Anal. Found for $C_{24}H_{110}N_6O_{64}P_6Zn_9$: C, 12.76; H, 4.74; N, 3.50; P, 8.08. Calcd: C, 12.63; H, 4.86; N, 3.68; P, 8.14.

(15) Crystal data for $\{Zn_6L_6(Zn)\}\{Zn(H_2O)_6\}_2\cdot 22H_2O$ **(1)**: space group $Pa\bar{3}$ (No. 205), $Z = 4$, Mo Kα radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 50.02°$, $a = 20.1198(4)$ Å, $V = 8144.6(3)$ Å^3, 0.40 × 0.36 × 0.32 mm, refinement on F^2, R1 = 3.62%, wR2 = 8.14%, GOF = 1.153 for 166 parameters and 1929 reflections with $I > 2.0\sigma(I)$.

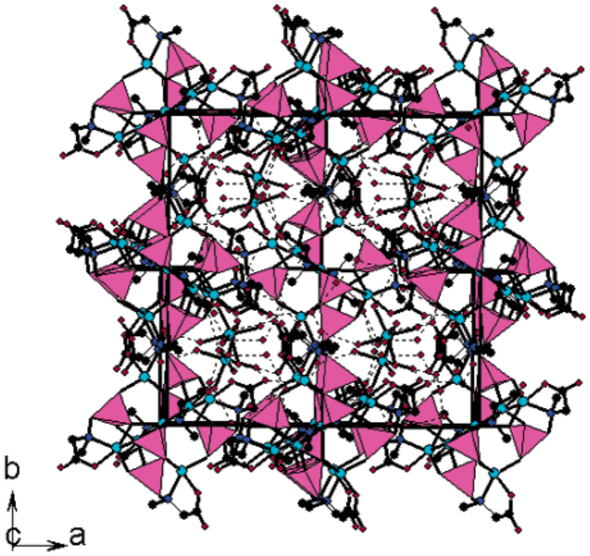

Figure 2. View of the structure of **1** down the *c*-axis. The C−PO_3 groups are drawn as purple tetrahedra, and Zn, N, C and O atoms are represented by cyan, blue, black, and red circles, respectively. Hydrogen bonds are shown as dotted lines.

x) forms a hydrogen bond with the noncoordinated carboxylate oxygen atom (O1); the O···O separation is 2.740 Å.

The packing of the cluster anions creates micropores occupied by the hexahydrated zinc(II) cations as well as lattice water molecules (Figure 2). The polynuclear cluster anions are located at the centers of the cell edges as well as the cell body center. A number of hydrogen bonds are formed among the noncoordinated carboxylate oxygen atoms, aqua ligands, and lattice water molecules; the O···O contacts range from 2.738 to 2.796 Å.

TGA analysis of complex **1** shows three major steps of weight loss: first, the loss of 22 lattice water molecules starting from 65 °C (the weight loss of 17.6% matches with the theoretical one (17.3%)); second, the loss of the 12 coordination water molecules completed at 235 °C (the observed weight loss of 8.9% is in good agreement with the calculated value (9.5%)); and third, the burning of the organic groups starting from 428 °C and completed at 960 °C. It is noticed that the structural skeleton of **1** is retained after the loss of the lattice water molecules, as supported by the results of the X-ray powder diffraction analysis. Such a skeleton can be maintained due to the hydrogen bonding between the noncoordinated carboxylate oxygen atoms of the cluster anions and the aqua ligands of the hydrated zinc(II) cations, as discussed previously. The final products are ZnO and $Zn_2P_2O_7$ in a 1:1 molar ratio based on its XRD powder pattern. The total weight loss of 48.7% is very close to the calculated value (49.2%).

In conclusion, we present here the first example of the oxo-bridged Zn_6 octahedron further centered by a Zn(II) cation. Future efforts will be focused on the syntheses and magnetic properties of analogue cluster units containing magnetic centers such as Mn(II), Co(II), Cu(II), and Fe(II) ions, and the ion-exchange behavior of the hexahydrated zinc(II) cations. By affixing different functional groups on the phosphonic acids, we believe more unusual metal clusters as well as new inorganic−organic hybrid layered and porous materials will be developed.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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