Inorg. Chem. **2002**, *41*, 1030–1032

Inorganic Chemistry
Communication

New Structural Forms in Molecular Metal Phosphonates: Novel Tri- and Hexanuclear Zinc(II) Cages Containing Phosphonate and Pyrazole Ligands

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Received November 12, 2001

The reaction of $ZnCl_2$ with *tert*-butylphosphonic acid and 3,5-dimethylpyrazole in the presence of triethylamine as a hydrogen chloride scavenger affords a trinuclear molecular zinc phosphonate $[Zn_3Cl_2(3,5\text{-}Me_2Pz)_4(t\text{-}BuPO_3)_2]$. The structure of this compound contains a planar trizinc assembly containing two bicapping μ_3 $[t\text{-}BuPO_3]^{2-}$ ligands and terminal pyrazole and chloride ligands. In contrast an analogous reaction of $ZnCl_2$ with phenylphosphonic acid and 3,5-dimethylpyrazole affords a hexanuclear zinc phosphonate $[Zn_6Cl_4(3,5\text{-}Me_2PzH)_8(PhPO_3)_4]$. The six zinc centers are arranged in a chairlike conformation. The four phosphonates in this complex also act as bridging tripodal μ_3 $[RPO_3]^{2-}$ ligands.

There has been considerable interest in the synthesis and structure of metal phosphates and phosphonates in recent years.[1] Many of these derivatives possess interesting two- and three-dimensional layered structures with well-defined internal voids which allows them to be used in wide-ranging applications such as cation exchangers, a property that could be very useful in the processing of radioactive waste streams,[2] sorption,[3] catalysis,[4] catalyst supports,[4] sensors,[5] and nonlinear optics.[6] Several metal phosphonates containing V,[7] Zr,[8] Al,[9a] Cu,[9b] Ga,[9c] Zn,[9d] Co,[9e] and Cd[9f] are known. An exciting feature of most of these metal phosphonates is the possibility of varying their structures and properties by changing the nature of the alkyl or the aryl group attached to the phosphorus or by the addition of appropriate pillaring agents.[9b]

In contrast to the layered phosphonates, molecular systems of multimetal phosphonates are relatively rare and have been described only recently.[10a−c] Synthesis of multizinc clusters is of considerable contemporary interest.[10d] Thus, trinuclear zinc clusters have attracted attention because such motifs have been implicated in biological systems such as phospholipase C and P1 nuclease.[11] Although Roesky and coworkers have recently described the synthesis of a dodecanuclear zinc phosphonate,[10a] zinc phosphonate clusters

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10.1021/ic011154y CCC: $22.00

containing a smaller number of metal units are extremely rare. In order to achieve the synthesis of such clusters we have decided to utilize an ancillary ligand such as 3,5-dimethylpyrazole in conjunction with phosphonic acids containing substituents with vastly different steric requirements. Herein, we describe the synthesis and structural characterization of two novel zinc(II) phosphonate clusters. The size of the cluster is modulated by the type of phosphonic acid used. Thus use of the bulky *tert*-butylphosphonic acid leads to the formation of a trinuclear cluster while the use of phenylphosphonic acid generates a hexanuclear cluster.

The reaction of $ZnCl_2$ with *tert*-butylphosphonic acid or phenylphosphonic acid in the presence of 3,5-dimethylpyrazole and triethylamine affords the clusters **1** and **2**.

$$3\ ZnCl_2 + 2\ t\text{-BuP(O)(OH)}_2 + 4\ 3{,}5\text{-Me}_2\text{PzH} + 4\ NEt_3 \rightarrow [Zn_3Cl_2(3{,}5\text{-Me}_2\text{PzH})_4(t\text{-BuP(O)}_3)_2]$$

1

$$6\ ZnCl_2 + 4\ PhP(O)(OH)_2 + 8\ 3{,}5\text{-Me}_2\text{PzH} + 8\ NEt_3 \rightarrow [Zn_6Cl_4(3{,}5\text{-Me}_2\text{PzH})_8(PhP(O)_3)_4]$$

2

Clusters **1** and **2** can be isolated in extremely high yields in contrast to the low yield of the previously known molecular zinc cluster.[10a] Remarkably replacing *tert*-butylphosphonic acid with phenylphosphonic acid exactly doubles the aggregation of the zinc. In solution both **1** and **2** show an equivalence of the phosphorus nuclei, which resonate at 39.3 and 16.1 ppm, respectively

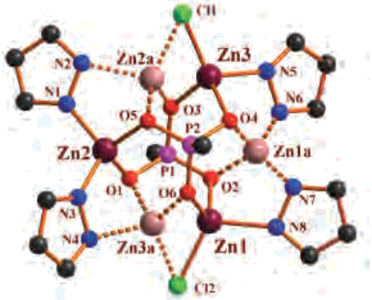

Figure 1. DIAMOND view of the trinuclear cluster **1** also showing the positionally disordered zinc atoms. Important bond lengths (Å) and bond angles (deg): Zn1−O2, 1.985(3); Zn1−O6, 1.930(3); Zn1−N8, 2.078(5); Zn1−Cl2, 2.2144(14); Zn2−O1, 1.996(3); Zn2−O5, 1.964(3); Zn2−N1, 1.942(6); Zn2−N3, 1.934(5); Zn3−O3, 1.937(3); Zn3−O4, 2.018(3); Zn3−N5, 2.062(5); Zn3−Cl1, 2.1976(15); P1−O1, 1.540(3); P1−O2, 1.537(3); P1−O3, 1.517(3); P2−O4, 1.552(3); P2−O5, 1.533(4); P2−O6, 1.522(3); O6−Zn1−O2, 109.51(14); O6−Zn1−Cl2, 113.66(11); N1−Zn2−N3, 117.3(2); O1−Zn2−O5, 116.06(14).

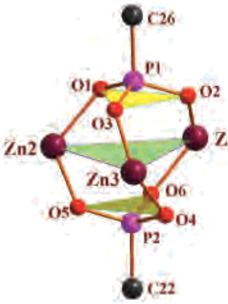

Figure 2. DIAMOND view of **1** showing the planar triangular Zn_3 array bicapped by the $[t\text{-BuPO}_3]^{2-}$ moiety. The internuclear distances (Å) are Zn1−Zn3, 4.408; Zn1−Zn2, 3.855; Zn2−Zn3, 3.935; P1−P2, 3.855. (The pyrazole and chloride ligands on the zinc atoms and the methyl substituents of the *tert*-butyl groups on phosphorus have been removed for clarity.)

The X-ray crystal structure[12a] of **1** is shown in Figure 1. The three zinc centers are held in place by two bicapping tridentate $[t\text{-BuPO}_3]^{2-}$ ligands, Figure 2. Each zinc is tetracoordinate and tetrahedral and is linked with two oxygen atoms derived from two different phosphonate units. Among the two Zn−O bonds one is slightly shorter than the other. While Zn1 and Zn3 have terminal chloride and pyrazole as ligands, Zn2 has two pyrazoles to complete the coordination sphere. The P−O distances although slightly different from each other have an average value of 1.534 Å, which is longer than the P═O bond but shorter than a normal P−O single bond.[13] The three atoms are in the same plane; however, the zinc centers are not equidistant from each other. Two of these are close to each other. Thus, the distances (Å) involved are Zn1−Zn2, 3.892; Zn2−Zn3, 3.935; and Zn1−Zn3, 4.408. It may be noted that in a different trinuclear zinc derivative $Zn_3(tib)_2(OAc)_6$ (tib = 1,3,5-tris(imidazol-1-ylmethyl)benzene) the interzinc distances are extremely long (9.10 Å).[14] Variation of interzinc distances such as found for **1** but with an even larger magnitude has been estimated for the trinuclear zinc active site reported previously for phospholipase C and P1 nuclease.[11a]

An interesting feature of the X-ray structure of **1** is the disorder in the position of the three zinc centers. Thus the occupancy of Zn1a, Zn2a, and Zn3a is 40%. The positions of these are so precisely placed that they are in perfect coordination ambit of pyrazole, chloride, and phosphonate oxygens; thus for example the position of Zn2a is within the bonding distance of Cl1, O3, O5, and N2. The overall effect of this is to generate the appearance of a star-shaped hexanuclear cluster (Figure 1).

The X-ray crystal structure of **2**[12b] is shown in Figure 3. This represents a rare example of a hexazinc phosphonate. The structure consists of two trinuclear arrays related to each other by means of a center of symmetry. The six zinc atoms

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(12) (a) Crystallographic data for **1**: size = 0.60 × 0.45 × 0.40 mm^3, formula $C_{28}H_{46}Cl_2N_8O_6P_2Zn_3$, MW = 919.73, triclinic, space group $P\bar{1}$, $a = 11.4031(20)$ Å, $b = 12.0802(20)$ Å, $c = 16.9566(20)$ Å, $\alpha = 89.9634(60)°$, $\beta = 71.9449(50)°$, $\gamma = 67.4876(70)°$, $V = 2032.94(3)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\rho_{calcd} = 1.503$ Mg/m^3, total of 17800 reflections were collected, 8260 independent reflections ($R_{int} = 0.0289$), for observed data R1 = 0.0749, wR2 = 0.2788, for all data R1 = 0.0857, wR2 = 0.2943, GOF = 2.372, maximum and minimum residual electron density are 1.148 and −0.991 e Å^{-3}. (b) Crystallograhic data for **2**: size = 0.30 × 0.20 × 0.10 mm^3, formula $C_{88}H_{108}Cl_4N_{16}O_{12}P_4Zn_6$, MW = 2239.90, triclinic, space group $P\bar{1}$, $a = 12.7594(20)$ Å, $b = 14.5816(20)$ Å, $c = 15.1866(20)$ Å, $\alpha = 97.4881(50)°$, $\beta = 94.3542(70)°$, $\gamma = 112.0637(60)°$, $V = 2572.17(2)$Å^3, Z = 1, $T = 203(2)$ K, $\rho_{calcd} = 1.446$ Mg/m^3, total of 13321 reflections were collected, 7392 independent reflections ($R_{int} = 0.0601$), for observed data R1 = 0.0912, wR2 = 0.339, for all data R1 = 0.113, wR2 = 0.3484, maximum and minimum residual electron density are 0.647 and −0.710 e Å^{-3}.

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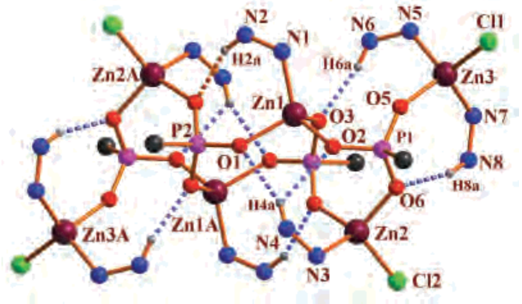

Figure 3. Diagram of **2** also showing the intramolecular N−H···O hydrogen bonding. Important bond lengths (Å) and bond angles (deg): Zn3−Cl1, 2.217(3); Zn3−N7, 2.005(10); Zn3−O5, 1.929(8); Zn3−N5, 2.026(10); Zn2−O6, 1.956(7); Zn2−N3, 2.041(11); Zn2−Cl2, 2.234(3); Zn1−O1, 1.961(8); Zn1−O2, 1.913(7); Zn1−O3, 1.976(7); Zn1−N1, 2.020(9); Cl1−Zn3−N7, 116.4(3); Cl1−Zn3−O5, 111.8(3); N5−Zn3−N7, 108.3(5); O5−Zn3−N7, 105.4(4); O7−Zn2−O6, 109.1(3); N3−Zn2−Cl2, 114.6(3); O1−Zn1−O2, 101.1(3); O1−Zn1−O3, 113.7(3); O2−Zn1−N1, 121.0(4).

are arranged in a chairlike conformation with the central zinc atoms Zn1, Zn2, Zn1A, and Zn2A being in the same plane while Zn3 and Zn3A are present above and below the plane, respectively. As in the case of **1** the four phosphonate units in **2** also act as tripodal $[RPO_3]^{2-}$ ligands; each phosphonate is involved in joining three adjacent zinc centers. Thus the phosphonate ligand both in **1** and in **2** behaves as a *bridging* and *not* a chelating ligand.

Also, in both **1** and **2** the chloride and pyrazole ligands do not function as bridging ligands but are present as terminal ligands. The various metric parameters found for **2** are comparable to that observed in **1** (Figure 3). Three different types of zinc centers are present with varying coordination environment; thus Zn1 and Zn1A have NO_3, Zn2 and Zn2A have $NClO_2$, and Zn3 and Zn3A have N_2ClO coordination environments. Interestingly the N−H's of the pyrazole ligands are involved in intramolecular hydrogen bonding with adjacent oxygen atoms.

In conclusion we have been able to design a rational and quantitative synthesis of tri- and hexanuclear zinc clusters which are new structural forms among molecular transition metal phosphonates. We anticipate that the synthetic strategy described in this work will be extremely useful in cluster assembly reactions involving other kinds of transition metal ions.

Acknowledgment. This work was supported by a grant from Department of Science and Technology (DST), New Delhi, India. S.K is thankful to the Council of Scientific and Industrial Research (India) for a senior research fellowship.

Supporting Information Available: Experimental details describing the synthesis and characterization data for **1** and **2** as well as crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC011154Y