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Octanuclear Aluminum(III) and Iron(III) Phosphonate Cages Encapsulating Two Na^I Ions

Zi-Yi Du,[*,†] **Yu-Hui Sun,**[†] **Qing-Yan Liu,**[*,‡] **Yong-Rong Xie,**[†] **and He-Rui Wen**[†]

[†]*College of Chemistry and Life Science, Gannan Normal University, Ganzhou 341000, People's Republic of China, and* [‡]*College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, People's Republic of China*

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Hydrothermal reactions of aluminum(III) nitrate or iron(III) nitrate with *N*,*N*-dimethylaminomethane-1,1-diphosphonic acid (H_4L) and sodium hydroxide lead to two novel isostructural octanuclear metal phosphonate cages encapsulating two Na^I ions, namely, $[Al_8Na_2(HL)_2(H_2L)_{10}(H_2O)_6]\cdot 20H_2O$ (**1**) and $[Fe_8Na_2(HL)_2(H_2L)_{10}(H_2O)_6]\cdot 22H_2O$ (**2**). The molecular structure of **1** can be viewed as a *three-in-one* cluster, in which a central zeolite D6R SBU lookalike aluminophosphonate cage is capped by two symmetry-related aluminophosphonate tetrahedral cages above and below and such a tetrahedral cage, being composed of four zeolite S6R SBU lookalike aluminophosphonate rings, further hexadentately traps one Na^+ ion in its cavity.

Recently, there has been considerable research activity on metal phosphonates with a molecular cluster unit, partly because of their aesthetically appealing structures and partly because of their potential applications in areas such as single-molecule-magnet materials, model compounds for a better understanding of some perplexing chemical mechanisms, and host−guest chemistry, which allows the cages to act as "microreactors" in some cases.[1−8]

One of the principal challenges in this area is to find appropriate synthetic strategies that will allow the formation of metal phosphonate clusters whose nuclearity can be varied. To date, promising approaches toward their syntheses include (i) the use of a sterically hindered phosphonate ligand to stimulate core aggregation,[5] (ii) the use of an ancillary ligand acting as a terminal group to prevent the formation of an extended architecture,[6,7] and (iii) the reaction of a phosphonate ligand with an oligonuclear precursor to generate a high-nuclear cluster compound.[8] By following these strategies, there has been much progress in the preparation of polynuclear metal phosphonate clusters. However, it is worth noting that most of the alkylphosphonate ligands used only possess one phosphonate group, while diphosphonate ligands have rarely been employed in the syntheses of these cluster compounds, with the exception of a few polyoxomolybdenum diphosphonate clusters.[9]

In view of our ongoing research on the design and syntheses of novel molecular polynuclear metal phosphonates,[10] now we are intrigued by the possibility of using diphosphonic acid "$R-CH(PO_3H_2)_2$" as a promising ligand for this purpose. Although it can be viewed as an analogue of

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*To whom correspondence should be addressed. E-mail: ziyidu@gmail.com (Z.-Y.D.), qyliuchemistry@gmail.com (Q.-Y.L.).

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the inorganic pyrophosphate, diphosphonic acid contains a stable, nonhydrolyzable P−C−P bond. Compared with diphosphonic acid "$H_2O_3P-C_nH_{2n}-PO_3H_2$", which is often used for the construction of pillar-layer strucures,[11] "R−CH-$(PO_3H_2)_2$" features a closer linking between the two phosphonate groups, which facilitates their synergic coordination ability of acting as a $[CP_2O_6]$ unit rather than two $[CPO_3]$ units. Additionally, a sterically hindered "R−CH" group between the two phosphonate groups may prevent the formation of an extended architecture.

In order to address the above issue, we initially selected $(CH_3)_2N-CH(PO_3H_2)_2$ (H_4L) as a potential building block. Our such research efforts yielded two novel octanuclear metal phosphonate cages encapsulating two Na^I ions, namely, $[Al_8Na_2(HL)_2(H_2L)_{10}(H_2O)_6]\cdot 20H_2O$ (**1**) and $[Fe_8Na_2(HL)_2(H_2L)_{10}(H_2O)_6]\cdot 22H_2O$ (**2**). As far as we know, they represent the first examples of aluminum(III) or iron(III) phosphonate clusters based on a diphosphonate ligand. Herein, we report their syntheses, crystal structures, and characterizations.

Compound **1** was prepared from a mixture of $Al(NO_3)_3\cdot 9H_2O$, H_4L, and NaOH in an ethanol−water solution, which was sealed in a stainless steel reactor with a 23 mL Teflon liner, heated at 120 °C for 2 days. The final solid product consisted of many colorless octahedron-like crystals of **1** and some indefinite white powder. When $Fe(NO_3)_3\cdot 9H_2O$ was employed instead of $Al(NO_3)_3\cdot 9H_2O$, compound **2** was obtained in a similar procedure.

Compounds **1** and **2** are isostructural; hence, only the structure of **1** will be discussed in detail as a representation. Compound **1** crystallizes in the cubic $Pa\bar{3}$ space group, and it features an isolated octanuclear aluminum(III) phosphonate cage encapsulating two Na^I ions, with a crystallographically imposed -3 symmetry (Figure 1). The cage is rugby-ball-shaped, and the inorganic core is about 12 Å long. Although the cage is large, its architecture can be easily understood by viewing it as a *three-in-one* cluster, in which a central zeolite D6R SBU lookalike aluminophosphonate core is capped by two symmetry-related aluminophosphonate tetrahedral cages above and below. More interestingly, such a tetrahedral cage, being composed of four zeolite S6R SBU lookalike aluminophosphonate rings, further hexadentately traps one Na^+ ion in its cavity.

There are two types of Al^{III} ions in the cluster unit. While the Al1 ion lying on a -3-fold axis is octahedrally coordinated by three pairs of O atoms from three equivalent diphosphonate ligands, the Al2 ion lying on a general position is octahedrally coordinated by five O atoms from four diphosphonate ligands as well as an aqua ligand (Figure 2). The unique Na1 ion in the cluster unit also lies on a -3-fold axis but is six-coordinated by three pairs of O atoms from three pairs of symmetry-related diphosphonate ligands. The Al−O [1.852(7)−1.944(7) Å] and Na−O [2.332(7)−2.395(8) Å] bond distances are comparable to those reported for other aluminum(III) and sodium(I) phosphonates.[12,13] It is observed that the Na−O [2.353(4)−2.415(5) Å] bond distances in compound **2** are slightly longer than those in compound **1**, owing to a slightly larger cavity in compound **2**.

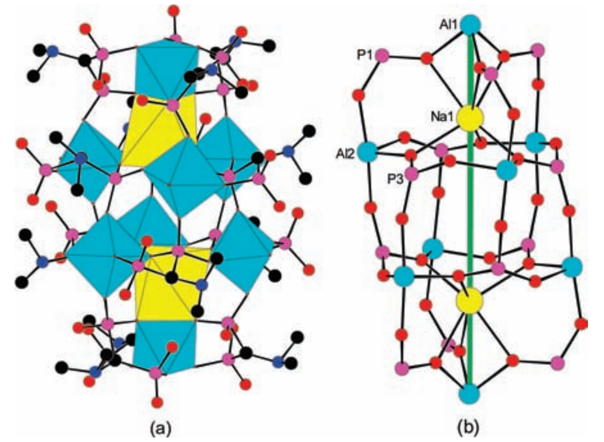

Figure 1. Cluster structure of compound **1** (a) and the inorganic core of the cluster (b). The AlO_6 and NaO_6 octahedra are represented as cyan and yellow, respectively. Al, Na, P, O, N, and C atoms are drawn as cyan, yellow, purple, red, blue, and black circles, respectively. Noncoordinated phosphonate O atoms and monodentate phosphonate groups have been omitted in part b for clarity.

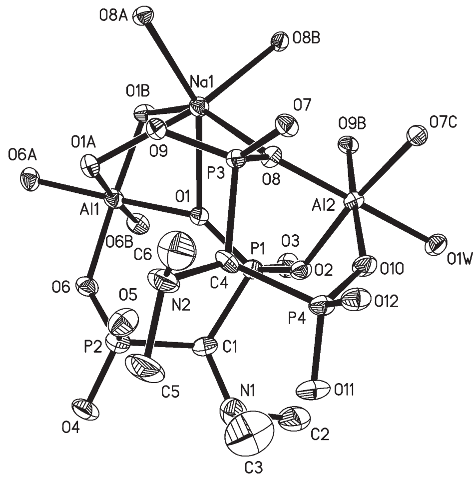

Figure 2. ORTEP representation of the selected unit of **1**. The thermal ellipsoids are drawn at 30% probability. Lattice water molecules have been omitted for clarity. Symmetry codes for the generated atoms: A, *z*, *x*, *y*; B, *y*, *z*, *x*; C, −*z*, −*x*, −*y*.

The eight Al^{III} ions and two Na^I ions in the cage are supported by 12 diphosphonate ligands, which adopt two types of coordination modes and can be denoted as $[3.2_{12}1_301_100]$ (Chart 1a) and $[4.2_{12}1_31_41_100]$ (Chart 1b) according to the Harris notation.[14] By using three of its six O atoms, the diphosphonate ligand containing P1 and P2 chelates bidentately with one Al1 ion and bridges with one Al2 ion and one Na1 ion, with group $P1O_3$ being tridentate and group $P2O_3$ being monodentate. In the diphosphonate ligand containing P3 and P4, the monodentate group $P4O_3$ has the same coordination mode as group $P(2)O_3$, whereas the tetradentate group $P3O_3$ is different from group $P1O_3$ in that it further bridges with a Al^{3+} ion through a third phosphonate O atom. Protonation of the

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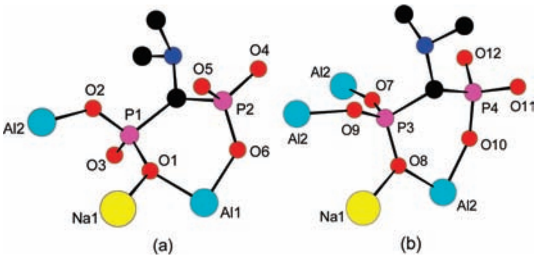
Chart 1. Coordination Modes of the Diphosphonate Ligand in Compounds **1** and **2**



diphosphonate ligand merits special attention. The two isostructural compounds in this report have been formulated based on crystallographic studies and elemental analyses. In the formula of **1**, the removal of 26 protons from 12 neutral H_4L ligands is the only way to balance the overall charge of the molecule because Al^{3+} and Na^+ cations have no other stable oxidation states, and if we assume that H_2L^{2-} and HL^{3-} are the two possible anion forms exiting in the formula, we can easily calculate that the only reasonable numbers of H_2L^{2-} and HL^{3-} anions are 10 and 2, respectively. For each of the HL^{3-} and H_2L^{2-} anions, the N atom is protonated because of the zwitterionic behavior of aminophosphonic acid,[15] and the second proton of the H_2L^{2-} anion is expected to be on the phosphonate O atom with a much longer P−O bond (Table S2 in the Supporting Information). In addition, the 3+ oxidation states of the Fe ions in compound **2** were confirmed by the bond-valence-sum analysis (3.17 for the Fe1 ion and 3.13 for the Fe2 ion).[16]

The discrete clusters in compound **1** are hydrogen-bonded into a 3D supramolecular network via hydrogen bonds among noncoordinated phosphonate O atoms, aqua ligands, and lattice water molecules (Table S2 in the Supporting Information). The O···O contacts range from 2.51(1) to 3.00(2) Å.

The thermal stabilities of **1** and **2** were examined by thermogravimetric analysis (TGA) in a N_2 atmosphere from 30 to 700 °C. Their TGA curves are similar, and both exhibit two main steps of weight loss (Figure S2 in the Supporting Information); hence, only that of **1** is discussed representationally. The first step of weight loss for **1** started at 48 °C and completed at 210 °C, which corresponds to the release of 26 water molecules. The observed weight loss of 15.2% is close to the calculated value (14.1%). The second started at 322 °C and completed at 598 °C, which most likely can be attributed to partial decomposition of the organic component. The total observed weight loss at 700 °C is 30.4%, and the final residuals were not characterized.

In summary, the hydrothermal syntheses, crystal structures, and characterizations of two novel octanuclear metal phosphonate cages encapsulating two Na^I ions, namely, $[Al_8Na_2(HL)_2(H_2L)_{10}(H_2O)_6]\cdot 20H_2O$ (**1**) and $[Fe_8Na_2(HL)_2(H_2L)_{10}(H_2O)_6]\cdot 22H_2O$ (**2**) (where $H_4L = (CH_3)_2N{-}CH(PO_3H_2)_2$), have been reported. The utility of the diphosphonic acid ligand "$(CH_3)_2N{-}CH(PO_3H_2)_2$" provides a new perspective for the isolation of cluster compounds in metal phosphonate chemistry. Further research works will be extended to design other diphosphonic acids "$R{-}CH(PO_3H_2)_2$" by changing the "R−" group and use this type of ligand for the synthesis of more polynuclear metal phosphonates featuring novel structures and properties.

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Supporting Information Available: Experimental details, summary of the crystal data and structural refinements, table of bond lengths, X-ray crystallographic files in CIF format, XRD patterns, and TGA curves for both compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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