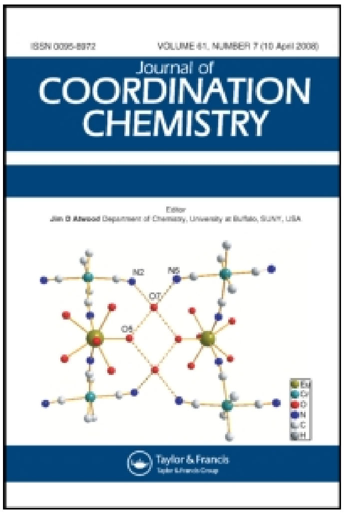

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Two chain-shaped $(H_2O)_4$ clusters: crystallographic, thermal and theoretical studies

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Two chain-shaped $(H_2O)_4$ clusters: crystallographic, thermal and theoretical studies

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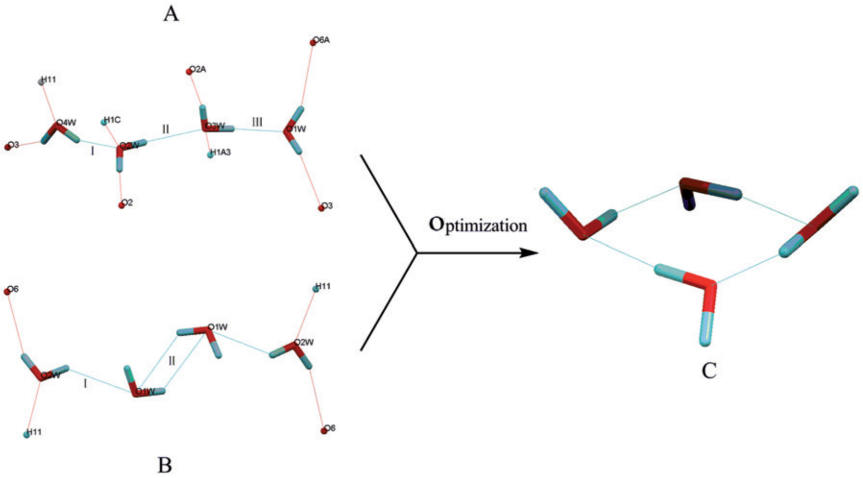
A chain-shaped $(H_2O)_4$ cluster **A** is self-assembled in a metal phosphonate compound, $[Al(phen)(AEDPH_2)(AEDPH_3)] \cdot 4H_2O$ (**1**) ($AEDPH_4 =$ 1-aminoethylidenediphosphonic acid, phen = 1,10-phenanthroline). This water cluster, and another chain-shaped $(H_2O)_4$ cluster **B** which exists in the previously reported compound $[Zn(phen)(AEDPH_2)_2] \cdot 4H_2O$ (**2**), are investigated by X-ray crystallographic, thermal gravimetric analysis (TGA) and theoretical calculations. Both **A** and **B** collapse to ring-shaped $(H_2O)_4$ cluster **C** after geometry optimizations with 6-311+G(d, p) basis set at Hartree-Fock theory as well as density functional theory. Energy calculations reveal the stability is **C** > **B** > **A**, which is consistent with experiment results.



Keywords: Theoretical calculation; Water tetramer; Chain-shaped; Crystallographic; Thermal gravimetric analysis

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1. Introduction

Water clusters, as aggregation of lattice water molecules through hydrogen bonds, can be understood as the simplification of liquid water [1]. Studying water clusters may provide keys to understanding the unusual properties of water [2].

Among various small water clusters, $(H_2O)_4$ and $(H_2O)_6$ are the simplest examples in the two-dimensional (2D) models of liquid water and ice [3]. In $(H_2O)_4$ clusters, there are many reports on ring-shaped water tetramer as the most stable [4] [see figure 3(c)], including some theoretical studies [5]. An unstable isomer of $(H_2O)_4$, a chain-shaped $(H_2O)_4$, only exists in specific hosts restricted by hydrogen bonds and displaying different properties from the ring-shaped one. Such an isomer is rarely reported [6], and theoretical calculations of it are absent.

In order to explore the properties of chain-shaped $(H_2O)_4$ clusters, a new phosphonate compound, namely $Al(phen)(AEDPH_2)(AEDPH_3) \cdot 4H_2O$ (**1**) ($AEDPH_4 =$ 1-aminoethylidenediphosphonic acid, phen = 1,10-phenanthroline) and the previously reported $[Zn(phen)(AEDPH_2)_2] \cdot 4H_2O$ (**2**) [7], are hydrothermal synthesized and characterized. They contain different chain-shaped $(H_2O)_4$ clusters. We use both Hartree-Fock theory with 6-311+G(d, p) basis set and density functional theory with the same basis set to investigate the two chain-shaped water tetramers in **1** and **2** and compare them with ring-shaped water tetramer using total energy, binding energies (BEs) and bond lengths.

2. Experimental

2.1. *Materials and measurements*

The 1-aminoethylidenediphosphonic acid ($AEDPH_4$) was prepared according to the US Patent 4239695 [8]. All other starting materials were purchased from commercial sources and used without further purification. Elemental analysis data (C, H, N) were obtained from a Perkin-Elmer 240B elemental analyzer. IR spectra were recorded from KBr pellets from 400–4000 cm^{-1} on a Nicolet 5700 FT-IR spectrometer with a spectral resolution of 4.00 cm^{-1}. TGA studies were carried out on a NETZSCH STA 449C at a heating rate of 20 $K\,min^{-1}$ under air.

2.2. *Synthesis of $Al(phen)(AEDPH_2)(AEDPH_3) \cdot 4H_2O$ (1)*

A mixture of $Al(OH)_3$ (0.0293 g, 0.375 mmol), $AEDPH_4$ (0.1539 g, 0.75 mmol) and phen (0.0894 g, 0.375 mmol) 3.00 mL H_2O was sealed and heated at 80°C. Colorless block crystals were obtained after several days (0.1550 g, Yield: 44.9% based on phen). Anal. found: C, 27.57%; H, 4.71%; N, 7.80%. Calcd for $C_{16}H_{33}N_4O_{16}P_4Al$: C, 27.92%; H, 4.83%; N, 8.14%. IR (KBr pellets, cm^{-1}): 3448s $\{\nu_s(OH)\}$; 1631m $\{\delta(OH)\}$; 1524, 1431, 1383 m {phen skeleton vibration}; 1146, 1107s $\{\nu_{as}(PO_3)\}$; 935 m $\{\nu(POH)\}$.

2.3. *X-ray crystallography*

Single-crystal data were collected on a Bruker SMART CCD area-detector diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

Table 1. Hydrogen bonds for **1** (Å) and (°).

D–H···A	d(D···A)	∠(DHA)	D–H···A	d(D···A)	∠(DHA)
N(1A)–H(1A2)···O(1)	2.922(2)	166.7	O(2W)–H(2W2)···O(3W)#8	2.715(3)	164(3)
N(1)–H(1B)···O(2A)	3.208(2)	127.2	O(2W)–H(1W2)···O(5A)#9	2.986(2)	116(3)
N(1)–H(1B)···O(1A)	3.004(2)	169.9	O(4W)–H(1W4)···O(6)#10	3.079(3)	115(2)
O(1W)–H(2W1)···O(3)	2.761(2)	159(4)	O(4W)–H(1W4)···O(3)#10	2.574(2)	151(3)
N(1A)–H(1A3)···O(3W)#1	2.918(2)	174.2	O(2W)–H(1W2)···O(2)#10	2.765(2)	153(3)
N(1A)–H(1A1)···O(2)#2	2.716(2)	163.4	O(1W)–H(1W1)···O(3A)#10	3.063(2)	116(2)
N(1)–H(1C)···O(2W)#3	2.882(2)	169.5	O(1W)–H(1W1)···O(6A)#10	2.828(2)	157(3)
N(1)–H(1A)···O(2A)#4	2.746(2)	153.3	O(5)–H(13)···O(6A)#11	2.564(2)	168(4)
O(4W)–H(2W4)···O(2W)#5	2.641(3)	151(3)	O(5A)–H(12)···O(6)#12	2.523(2)	173(4)
O(3W)–H(2W3)···O(2A)#6	2.737(2)	154(4)	O(3A)–H(11)···O(4W)#13	2.389(2)	170(4)
O(3W)–H(1W3)···O(1W)#7	2.628(2)	176(3)			

Symmetry transformations used to generate equivalent atoms: #1: $x, y+1, z-1$; #2: $-x+1, -y+2, -z$; #3: $x-1/2, -y+3/2, z-1/2$; #4: $-x, -y+2, -z$; #5: $-x+3/2, y+1/2, -z+3/2$; #6: $x, y-1, z+1$; #7: $-x+1, -y+1, -z+1$; #8: $x+1/2, -y+1/2, z-1/2$; #9: $-x+3/2, y-1/2, -z+1/2$; #10: $x+1/2, -y+3/2, z+1/2$; #11: $x-1/2, -y+3/2, z+1/2$; #12: $x+1/2, -y+3/2, z-1/2$; #13: $x-1, y, z-1$.

Crystal data for **1**: $C_{16}H_{33}N_4O_{16}P_4Al$, F.W. = 688.32, monoclinic, $P2(1)/n$, $a = 10.9648(8)$ Å, $b = 14.3280(10)$ Å, $c = 17.4854(12)$ Å, $\beta = 90.4920(10)^\circ$, $V = 2746.9(3)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_{\mathrm{Calcd}} = 1.664\,\mathrm{g\,cm^{-3}}$. A total of 18157 reflections were measured up to $\theta = 28.00^\circ$, of which 6608 [$R_{(\mathrm{int})} = 0.0172$] were unique [$I > 2\sigma(I)$]. All empirical absorption corrections were applied by using the SADABS program [9]. The structure was solved by direct methods using SHELXS-97 [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXL-97. Hydrogen atoms were directly obtained from Difference Fourier Maps and several DFIX commands were applied on hydrogen atoms of water molecules in the compound. Final R indices (all data): $R_1 = 0.0472$, $\omega R_2 = 0.1173$. The ORTEP drawing was produced with PLATON [11]. Water cluster drawings were obtained using Mercury 1.4.2. The details of hydrogen bonds are listed in table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. 650813. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12, Union Road, Cambridge CB21EZ, UK (Fax: (+44) (1223) 336033; Email for inquiry: deposit@ccdc.cam.ac.uk).

2.4. *Theoretical calculations*

Single point energy calculations and geometry optimizations were carried out using Gaussian-03 [12] with Hartree-Fock theory as well as density functional theory with 6-311+G(d, p) basis set.

3. Results and discussion

3.1. *Crystal structures of 1 and $(H_2O)_4$ clusters*

As shown in figure 1(a), in **1**, an $AEDPH_4$ loses one proton and transfers another to the amino-nitrogen atom and serves as $AEDPH_3^-$, while the other one loses two protons to form AEDPH$_2^{2-}$. Each Al^{3+} is six-coordinate with two nitrogens (N1 and N2A) from phen, and four oxygens from an AEDPH$_3^-$ (O1A and O4A) and an AEDPH$_2^{2-}$ (O1 and O4), generating a N$_2$O$_4$ distorted octahedral coordination geometry. The metal-ligand bond distances are in the range 1.843(2)–1.866(2) Å (Al–O) and 2.057(2)–2.062(2) Å (Al–N). The angles of O–Al–O are in the range 90.75(6)–94.22(6)° and that of N–Al–N is 79.18(8)°.

The neighboring Al(phen)(AEDPH$_2$)(AEDPH$_3$) units are self-assembled to form 1D chains by intermolecular P–OH···O–P hydrogen bonds. The P–O H(O5) and H(O5A) form hydrogen bonds of R$_2^2$(8) with neighboring O6A and O6, giving distances of 2.564 and 2.523 Å in the (101) plane. Such hydrogen bond distances are in the range 2.45–2.60 Å for typical P–OH···O–P in the solid state [13]. The 1D chains are further interlinked through π–π interactions of phen (distances between adjacent phen rings are 3.406–3.476 Å) and various strong hydrogen bonds to generate a 3D supramolecule [figure 2(a)].

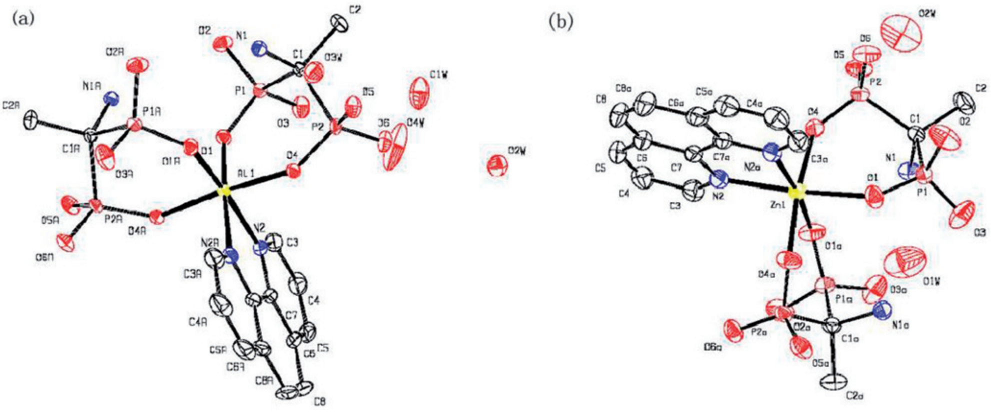

Figure 1. The ORTEP drawing of **1** (a) and **2** (b) with thermal ellipsoids at the 50% probability; all hydrogen atoms are omitted for clarity.

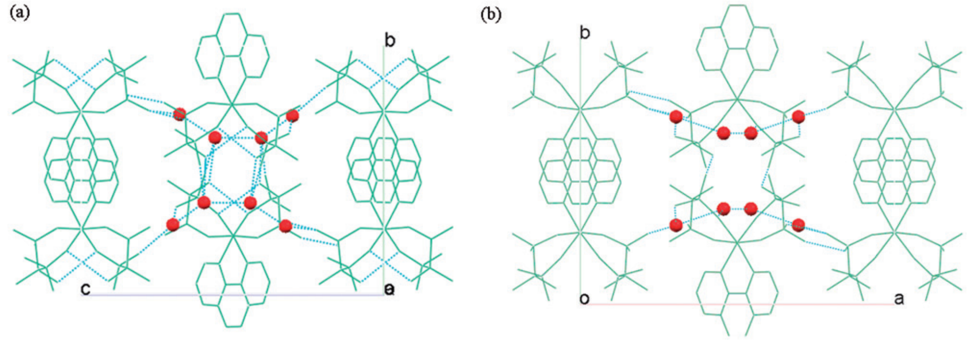

Figure 2. Perspective view of the three-dimensional network of **1** (a) and **2** (b) via hydrogen bonds and π–π interactions. All hydrogen atoms are omitted for clarity.

In **1**, four Al(phen)($AEDPH_2$)($AEDPH_3$) units are connected to form a cavity, in which four lattice waters are assembled to generate a chain-shaped water tetramer **A**, as depicted in figure 3(a). The middle two water oxygens are tetrahedral with two bonds to water molecules and two bonds with two hosts, while the fringe oxygens are three-coordinate. The O–O distances are 2.628 Å–2.715 Å.

However, in **2**, the four water molecules exhibit an unusual Z-shape cluster **B** (figure 3b) with a center of symmetry, in which all water oxygens are three-coordinate. The O–O distances are 2.839 Å–2.859 Å, basically equal to that of liquid water (2.85 Å) [14].

Water cluster **C** is a typical ring-shaped water tetramer (figure 3c). In **C**, all water molecules adopt an alternating pattern. Only the middle two molecules adopt an alternating pattern in **A** and **B**. **C** is expected to be the most stable while **A** is the least stable. The dimer formed by two hydrogen bonds II in **B** contribute to its stability.

3.2. *IR spectra and thermogravimetric (TGA) studies*

Figure S-1 (Supplemental Material) shows the IR spectra of **1** and **2**. The broad-strong peaks centered at 3430–3447 cm^{-1} are from water. The corresponding bending H–O–H (δ_{HOH}) vibrations of the lattice water molecules are at 1630 cm^{-1}. The bands in the region of 1425–1524 cm^{-1} can be attributed to the skeleton vibrations of phen. Sharp bands near 1380 cm^{-1} show the existence of methyl. The P–O stretching vibrations in the region 1146 – 936 cm^{-1} are common.

As shown in figure 4, the TGA curve of **1** shows that the chain-shaped $(H_2O)_4$ cluster is stable to 50°C and then gradually decomposes until 210°C. The weight loss of 10.57% corresponds to loss of all four waters (calculated 10.47%). The dehydrated product, Al(phen)($AEDPH_2$)($AEDPH_3$), is stable to 275°C where it begins to decompose.

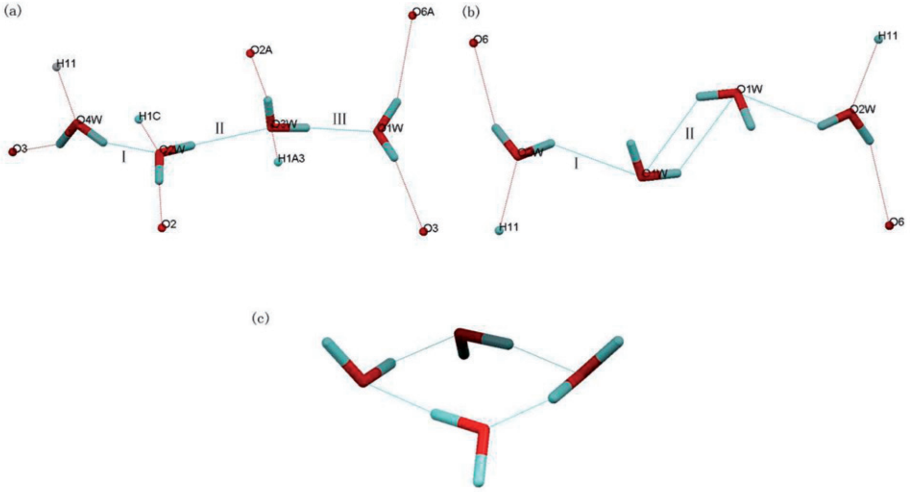

Figure 3. (a) Lattice $(H_2O)_4$ cluster **A** including hydrogen-bonds with the phosphonate oxygens and hydrogens in **1** and definition of hydrogen bonds I, II and III. (b) Lattice $(H_2O)_4$ cluster **B** including hydrogen-bond contacts with the phosphonate oxygen atoms and hydrogen atoms in **2** and definition of I and II. (c) Ring-shaped $(H_2O)_4$ cluster **C**.

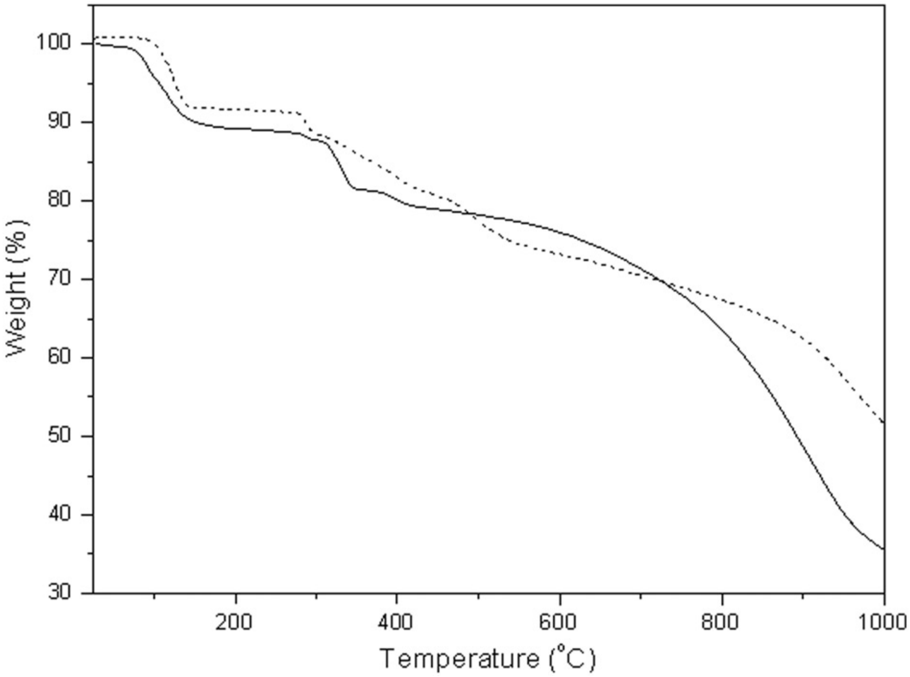

Figure 4. TG of **1** (solid line) and **2** (dashed line).

For **2**, dehydration begins at 90°C with weight loss of 9.02%, which is slightly lower than the theoretical value (10.02%) corresponding to loss of four waters. Comparing **1** with **2**, the dehydration temperature of **2** is higher, which shows that the water tetramer is more tightly fixed in **2** than in **1**.

3.3. *Theoretical calculations*

In order to contrast the stability of the water tetramers and verify the experiment results, we performed single point energy calculations on **A** and **B** and geometry optimization on ring-shaped tetramer **C**, all with 6-311+G(d, p) basis set at Hartree-Fock theory, as well as density functional theory. The tetramers **A** and **B** are not stable state at these theory levels, collapsing to **C** after geometry optimizations, confirming that **C** is the most stable water tetramer [5]. Comparing the structure parameters of **A**, **B** and **C** (table 2), we find the shortest R(O–O) and R(O $\cdots$ H) occur in **A** and **C** optimized with DFT theory. From comparison of bond lengths, **B** is less stable than **A**. However, the BEs (table 3) of **A** are less positive than **B**, which is due to more hydrogen bonds and the existence of double hydrogen bonds II between the middle two water molecules in **B**. Although the R(O–O) and R(O $\cdots$ H) of these are almost the longest, single point energy calculations indicate the BE of this dimer is 60.85 kcal mol^{-1}, smaller than in **A** (I: 115.52, II: 146.91, III: 80.73 kcal mol^{-1}) and **B** (I: 63.39 kcal mol^{-1}), using B3LYP/6-311+G(d, p) basis set, which is due to the particular molecular arrangement.

Table 2. Geometric parameters for $(H_2O)_4$ clusters **A**, **B** and **C**. The definition of hydrogen bonds I, II or III for **A** and **B** are given in figure 3.

Clusters	HB	R(O–O)/Å	R(O···H)/Å	α (°)[a]	β (°)[a]
A	I	2.6281	1.8848	151.0	108.3
	II	2.7150	1.9799	164.1	103.1
	III	2.6408	1.7747	176.9	106.5
B	I	2.8594	2.1893	138.1	110.1
	II	2.8385	2.2293	131.0	106.9
C(I)		2.8666	1.9378	164.7	106.9
C(II)		2.7393	1.7759	165.8	106.5

C(I) and **C**(II) are the geometry optimization results at HF/6-311+G(d, p) level and B3LYP/6-311+G(d, p) level, respectively.
[a] Angles α and β correspond, respectively, to the angle between the acceptor OH group and the axis of the hydrogen bond and to the HOH angle of the acceptor molecule.

Table 3. HF and DFT results for $(H_2O)_4$ clusters **A**, **B** and **C**.

Species	Basis (I)	Basis (II)	BE (I)	BE (II)
H_2O	−76.05331	−76.45846		
A	−303.94772	−305.53038	166.61	190.43
B	−304.03386	−305.62061	112.55	133.81
C	−304.25161	−305.88287	−24.09	−30.76

Single point energy calculation for **A** and **B** and geometry optimization for **C**. Energies in Hartrees using HF/6-311+G(d, p) basis set (basis I) and DFT-B3LYP/6-311+G(d, p) basis set (basis II); BE (I) and (II): binding energy in kcal mol^{-1}.

The above results demonstrate tetramers **A** and **B** are very unstable in **1** and **2**, existing in small cavities formed by four metal phosphonate units. Energy comparison of **A** and **B** proves **B** is more stable, consistent with the TGA where **A** starts to decompose at 50°C while **B** is stable to 90°C.

4. Conclusion

In order to investigate chain-shaped $(H_2O)_4$ clusters, two metal phosphonate compounds with 1-aminoethylidenediphosphonic acid have been synthesized, characterized and theoretically studied, $Al(phen)(AEDPH_2)(AEDPH_3) \cdot 4H_2O$ (**1**) and $Zn(phen)(AEDPH_3)_2 \cdot 4H_2O$ (**2**). Compound **2** was reported recently. In **1** and **2**, the $(H_2O)_4$ clusters are at higher energy than the ring-shaped tetramer, occurring due to hydrogen bonds and the space restriction effect. Geometry optimizations of **A** and **B** both lead to **C** at two theory levels, revealing chain-shaped water clusters are unstable state in comparison to ring-shaped water clusters. Current work is underway to further investigate the formation rules and mechanism of such $(H_2O)_4$ clusters, and to explore transformations between different $(H_2O)_4$ clusters.

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