

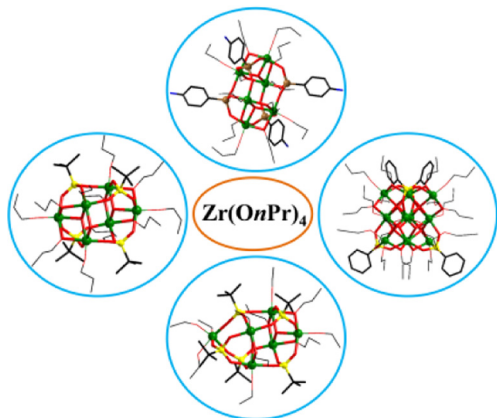
Short communication

A series of zirconium-oxo cluster complexes based on arsenate or phosphonate ligands

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GRAPHICAL ABSTRACT

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ABSTRACT

A series of zirconium-oxo cluster complexes have been prepared by the reaction of $Zr(OnPr)_4$ and arsenate or phosphonate ligands, namely, $Zr_6(\mu_3-O)_2(4-aPhaa)_4(OnPr)_{12}$ (**Zr₆-1**, 4-aPhaa = 4-aminophenylarsonic acid), $Zr_6(\mu_3-O)_2(tbpa)_4(OnPr)_{12}$ (**Zr₆-2**, tbpa = tert-butylphosphonic acid), $H_2[Zr_6(\mu_3-O)(\mu_2-O)(tbpa)_5(OnPr)_{12}]$ (**Zr₆-3**), and $H_4[Zr_{10}(\mu_4-O)_4(\mu_3-O)_4(ppa)_4(OnPr)_{20}]$ (**Zr₁₀**, ppa = phenylphosphonic acid). These complexes have been structurally characterized by the single-crystal X-ray diffraction. Interestingly, the {Zr₁₀} cluster contains a $[Zr_{10}O_4]^{32+}$ supertetrahedron core stabilized by the phosphate groups. In addition, thermal stabilities and phase purities were also investigated in detail.

Polyoxometalates (POMs) have attracted intensive research attention because of their unique structural variety and electronic properties and hence applications in various fields such as catalysis, magnetism, and medicine [1–5]. For the past several decades, most of the research interest in this field has been devoted to d-block elements in high

oxidation states, such as V [6], Nb [7], Mo [8], and W [9], etc. More recently, Zhang and co-workers set a new record for the family of Ti-based clusters and report a {Ti₅₂} cluster [10]. However, the polyoxozirconates (POZs) are less studied [11–14]. In the early time, some low-nuclearity POZs have been reported, such as {Zr₄} [12a], {Zr₆}

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[12b–d], {Zr₇} [12e], {Zr₉} [12f] and {Zr₁₀} [12g]. Meanwhile, some transition metal containing POZs were also prepared and characterized, including {Fe₂Zr₆} [12a], {Pb₄Zr₇} [13b], {Ag₂Zr₈} [13c], {Ti₄Zr₄} [13d], and {Mn₁₀Zr₁₀} [13e], et al. So far, there are only a few reported high-nuclearity POZs, including {Zr₁₂} [14a], {Zr₁₃} [14b], and {Zr₁₈} [14c].

On the other hand, the functionalization of POZs by organic ligands is also of great significance [15]. Apart from the common oxo-alkoxide ligands, other O-donor ligands like carboxylates have been widely employed to construct POZs [12b–g, 13b–d, 14a, c]. However, the arsenate and phosphonate ligands are less applied. Lately, Schubert's group reported a {Zr₆} cluster decorated by phenylphosphonic acid ligand [16].

In this work, a series of zirconium-oxo cluster complexes have been prepared by the reaction of Zr(OnPr)₄ and arsenate or phosphonate ligands, namely, Zr₆(μ₃-O)₂(4-aPhaa)₄(OnPr)₁₂ (**Zr₆-1**, 4-aPhaa = 4-aminophenylarsonic acid), Zr₆(μ₃-O)₂(tbpa)₄(OnPr)₁₂ (**Zr₆-2**, tbpa = tert-butylphosphonic acid), H₂[Zr₆(μ₃-O)(μ₂-O)(tbpa)₅(OnPr)₁₂] (**Zr₆-3**), H₄[Zr₁₀(μ₄-O)₄(μ₃-O)₄(ppa)₄(OnPr)₂₀] (**Zr₁₀**, ppa = phenylphosphonic acid). These complexes have been structurally characterized by the single-crystal X-ray diffraction. In addition, thermal stabilities and phase purities were also investigated in detail.

The solvothermal reaction between Zr(OnPr)₄ and 4-aminophenylarsonic acid (4-aPhaa) in *n*-propanol produces colorless crystals of Zr₆(μ₃-O)₂(4-aPhaa)₄(OnPr)₁₂ (**Zr₆-1**) in good yields. Single-crystal X-ray analysis reveals that the geometry of the inorganic core of **Zr₆-1** is similar to that of those {Zr₆} clusters reported by Schubert [12b–d], except that arsenate ligand is firstly applied to stabilize this {Zr₆} complex. The {Zr₆} core consists of two triangular {Zr₃(μ₃-O)} subunits which are held together by four bridging 4-aPhaa ligands (Fig. 1a). It is worth noting that Zr1, Zr2, Zr3 atoms bridged by *n*-propanol are six-coordinated, and all of them capture one terminal *n*-propanol to fulfil octahedral coordination environments. In **Zr₆-1**, arsenate groups show a tri-monodentate coordination mode. Moreover, the Zr–O bond lengths are in the range from 1.951 Å to 2.194 Å, comparable to these values reported in POZs [12g, 14a]. Interestingly, there are medium strength N–H...O (2.99 Å) and weak C–H...O hydrogen bonds (3.27 Å) as well as π–π interactions (3.95 Å) between adjacent clusters (Fig. 1b and S1). The three-dimensional (3D) packing superstructure of these clusters is shown in Fig. S2, see supporting information.

Interestingly, by substituting 4-aminophenylarsonic acid with tert-butylphosphonic acid (tbpa) in the above synthetic procedure for **Zr₆-1**, colorless block crystals of Zr₆(μ₃-O)₂(tbpa)₄(OnPr)₁₂ (**Zr₆-2**) can be readily obtained. The structural analysis of **Zr₆-2** shows that it has similar structure as **Zr₆-1**, only the tbpa ligand replaces 4-aPhaa (Fig. 2a). The Zr–O bond distances vary from 1.928 Å to 2.179 Å. However, on the basis of the same reaction starting materials as **Zr₆-2**, low yield crystals of H₂[Zr₆(μ₃-O)(μ₂-O)(tbpa)₅(OnPr)₁₂] (**Zr₆-3**) were obtained by adopting a mixed solvothermal method (*n*-propanol/DMF). **Zr₆-3** is non-centrosymmetric and crystallizes in the monoclinic space group,

Cc. Its structure consists of six zirconium atoms, two hydroxo groups, five terminal tbpa ligands, twelve coordinated propanol molecules (Fig. 2b). There has one similar triangular {Zr₃(μ₃-O)} subunit in **Zr₆-3** (Fig. 2c and d). However, compared to **Zr₆-2**, the leftmost Zr6 atom of **Zr₆-3** moves outward, and the P–O–Zr angles increase as well as the original μ₃-O becomes μ₂-O, which endows the space that can introduce the fifth tbpa ligand. In **Zr₆-3**, all the Zr atoms are six-coordinated and all the tbpa ligands adopt the tri-monodentate coordination mode. The Zr–O bond lengths range from 1.920 Å to 2.270 Å. There is no typical hydrogen bond and the binding interaction may be due to weak van der Waals force between two adjacent clusters in **Zr₆-2** and **Zr₆-3**, and their 3D packing superstructures are shown in Fig. S3 and S4. From above results, it can be seen that the solvent system plays a very important role in constructing different POZs.

When tert-butylphosphonic acid is replaced by Phenylphosphonic acid (ppa) in the above synthetic procedure for **Zr₆-3**, colorless needle crystals of H₄[Zr₁₀(μ₄-O)₄(μ₃-O)₄(ppa)₄(OnPr)₂₀] (**Zr₁₀**) was produced. Structural analysis revealed that **Zr₁₀** crystallizes in the tetragonal crystal system with space group *P4₂/n*. The molecular structure of **Zr₁₀** comprises a supertetrahedral [Zr₁₀O₄]³²⁺ core stabilized by four phosphate groups coordinated to Zr atoms in μ₃-bridging modes, forming a cluster of the S4 point group symmetry (Fig. 3). As clearly presented in Fig. 3a, among ten Zr atoms, four adopt six-coordination mode (blue) and four are coordinated with seven oxygen atoms as marked with green; the other two Zr atoms adopt eight-coordination mode (purple). In each tetrahedron of the [Zr₁₀O₄]³²⁺ core, there is one longer Zr–O length of 2.460 Å, and the other three Zr–O distances are within the range of 2.106 Å–2.181 Å, which is common. While Zr–O–Zr angles exhibit significant distortions from the ideal tetrahedral angle, which may be due to the strain induced by the bridging ppa ligands. Indeed, the analysis of the crystal structure of **Zr₁₀** reveals that the {Zr₁₀} clusters further pack into a 3D superstructure (Fig. 3c) by very weak C31–H31B...O6 (3.53 Å) hydrogen bonding interaction between adjacent clusters (Fig. S5).

To investigate the thermal stability and phase purity of these compounds, thermogravimetric analyses (TGA) and X-ray powder diffraction (PXRD) patterns were measured. TGA curve of **Zr₆-1** shows a weight loss of ~12% before 100 °C (Fig. S6), which is related to the removal of guest molecules, followed by the structure decomposes. For **Zr₆-2**, there is a weight loss of ~5% before 350 °C (Fig. S8), corresponding to the release of guest molecules. Compound **Zr₆-2** is thermally stable only up to 380 °C before their structures collapse. However, the TGA curve of **Zr₁₀** exhibits continuous weightlessness as the temperature rises (Fig. S10), which show poor thermal stability. The residues of these compounds after decomposition may be ZrO₂. The PXRD patterns of them confirmed the phase purity of the samples (Fig. S7, S9 and S11), because their patterns are quite similar to the one simulated from their single-crystal data. It's worth pointing out that **Zr₆-2** is stable in water, which can also be demonstrated by the PXRD pattern. We didn't do any characterization test for compound **Zr₆-3** because of lower yield.

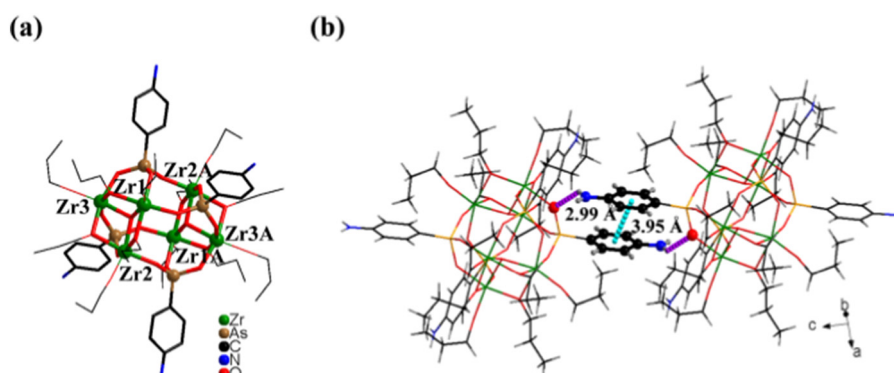


Fig. 1. (a) The molecule structure of **Zr₆-1** and the hydrogen bonding and π–π stacking interaction between adjacent clusters (b).

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