

Electronic Supplementary Information

A Novel Sandwich-Type Tungstoarsenate Containing a Cagelike {Ca₆} Cluster with a Water Molecule Enwrapped †‡

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Discussion on the centre atom of the {Ca₆} cluster

Fig. S1 (a) Cyclic voltammograms of **1** was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO₂: 0, 1.0, 1.5, 2.0, 2.5 and 3.0 mM, respectively (inset, the concentrations of NaNO₂). (b) Cyclic voltammograms of $\{[\text{Ca}(\text{H}_2\text{O})]_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$ was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO₂: 0.5, 1.0, 2.0, 2.5 and 3.5 mM, respectively (inset, the concentrations of NaNO₂). (c) Cyclic voltammograms of $[\text{B}-\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO₂: 0, 0.5, 1.5, 2.5, 3.5 and 4.5 mM, respectively (inset, the concentrations of NaNO₂). (d) Cyclic voltammograms of $[\text{HPW}_7\text{O}_{28}]^{8-}$ was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO₂: 0.5, 1.0, 2.0, 2.5 and 3.0 mM, respectively (inset, the concentrations of NaNO₂). The working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.

Fig. S2 Comparison of the experimental and simulated XRPD patterns of **1**.

Fig. S3 The IR spectrum of **1**.

Fig. S4 Thermogravimetric curve of **1** in the flowing N₂ atmosphere.

Fig. S5 Charge distribution of O atoms in the polyoxotungstate fragment of **1**.

Experimental Details

Discussion on the centre atom of the {Ca₆} cluster:

There should be an atom located in the centre of {Ca₆} cluster based on the results of X-ray diffraction. Considering the starting materials we used, we infer that there are three possibilities which the centre atom should be:

1. When we marked the centre atom to be Cl⁻, there were some mistakes emerged in the check cif report: a. the Ueq value of the Cl⁻ is abnormal higher; b. the average distance between Ca and Cl is 2.6 Å which is obviously shorter than previous reports. If a short Ca-Cl separation of 2.6 Å really exists, it can only be considered Ca-Cl very strong covalent single bond, because it is obviously shorter than the sum of two atomic covalent radii (2.80 Å). However, the current work does not contain such evidence.
2. When we marked the centre atom to be Na⁺, the Ueq value of Na⁺ was normal. However, the average distance between Na⁺ and Ca²⁺ is 2.6 Å, which is unacceptable.
3. Though the Ueq value of the centre atom is a little lower, if we marked it to be O atom. This result is much reasonable than assigning Na⁺ or Cl⁻. Since the O atom has been surrounded by six Ca²⁺, the atomic thermal vibration of O atom is restricted, resulting in the Ueq value of the O atom decreasing in some degree.

In summary, O atom other than Na⁺ or Cl⁻ located in the centre of the cluster is more reasonable in crystallographic discussion. And the elemental analysis result confirmed that no Na⁺ or Cl⁻ atoms were detected.

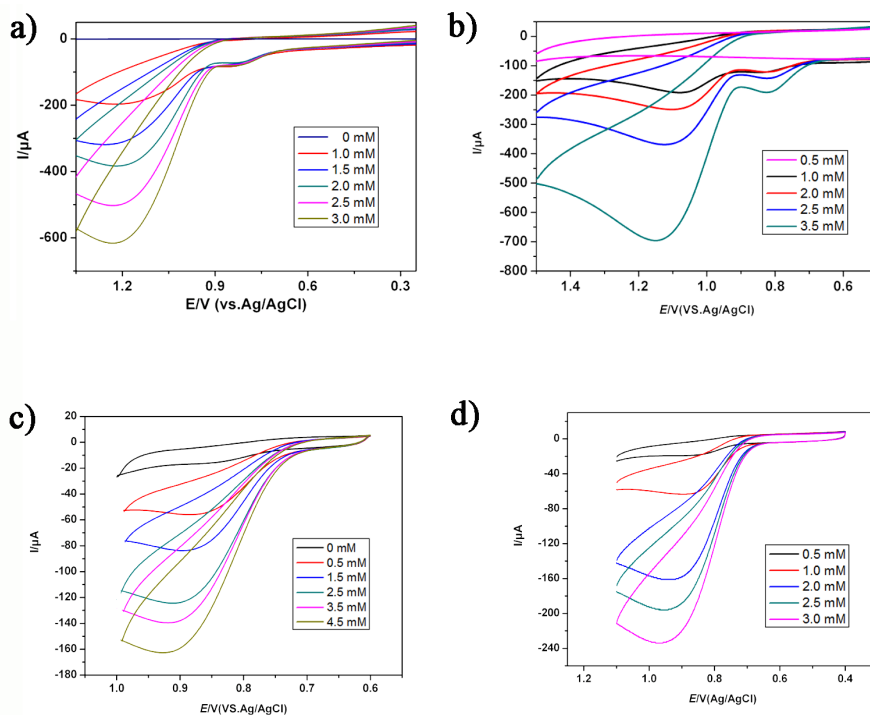


Fig. S1 (a) Cyclic voltammograms of **1** was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO_2 : 0, 1.0, 1.5, 2.0, 2.5 and 3.0mM, respectively (inset, the concentrations of NaNO_2). (b) Cyclic voltammograms of $\{[\text{Ca}(\text{H}_2\text{O})]_6[\text{P}_4\text{W}_6\text{O}_{34}]_2\}^{12-}$ was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO_2 : 0.5, 1.0, 2.0, 2.5 and 3.5 mM, respectively (inset, the concentrations of NaNO_2). (c) Cyclic voltammograms of $[\text{B}-\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO_2 : 0, 0.5, 1.5, 2.5, 3.5 and 4.5 mM, respectively (inset, the concentrations of NaNO_2). (d) Cyclic voltammograms of $[\text{HPW}_7\text{O}_{28}]^{8-}$ was performed in the concentration of 1×10^{-3} at a scan rate of $120 \text{ mV} \cdot \text{s}^{-1}$ with different concentrations of NaNO_2 : 0.5, 1.0, 2.0, 2.5 and 3.0 mM, respectively (inset, the concentrations of NaNO_2). The working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.

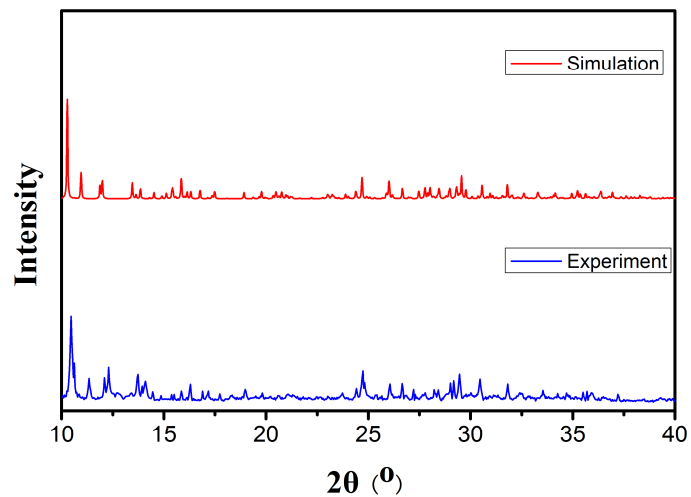


Fig. S2 Comparison of the experimental and simulated XRPD patterns of **1**.

The phase purity of **1** is confirmed by the agreement between the experimental X-ray powder diffraction (XRPD) pattern and the simulated pattern based on single-crystal X-ray diffraction (Fig. S2). The different intensity between them is attributed to the variation in the preferred orientation of the powder sample during collection of the experimental XRPD.

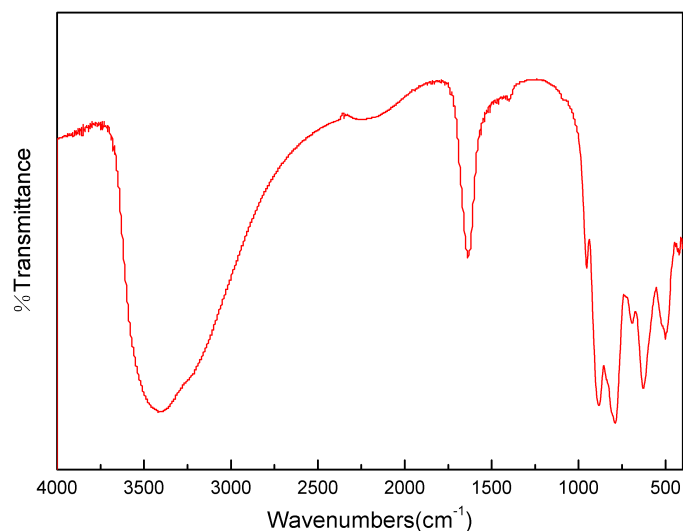


Fig. S3 The IR spectrum of **1**.

The IR spectrum of **1** (Fig. S3) shows the similar characteristic asymmetric vibration mode to other lacunary Keggin-type AT species.¹⁻³ In the IR spectrum of **1**, four characteristic bands assigned to the $\nu(\text{W}-\text{O}_t)$, $\nu(\text{As}-\text{O}_a)$, $\nu(\text{W}-\text{O}_b)$ and $\nu(\text{W}-\text{O}_c)$ vibrations are observed at 951, 885, 792 and 691–625 cm^{-1} , respectively. In comparison with those of $\text{Na}_3[\alpha\text{-AsW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ [987, 872, 781 and 911 cm^{-1} for $\nu(\text{W}-\text{O}_t)$, $\nu(\text{W}-\text{O}_b)$, $\nu(\text{W}-\text{O}_c)$ and $\nu(\text{As}-\text{O}_a)$ asymmetry stretching vibrations]⁴, the obvious Einstein shifts of $\nu(\text{W}-\text{O}_t)$, $\nu(\text{W}-\text{O}_b)$, $\nu(\text{W}-\text{O}_c)$ vibration absorption bands may be attributed to increase of the negative charges in the polyoxoanion.⁵ In addition, the resonance centered at 3416 and 1638 cm^{-1} are ascribed to water molecules.

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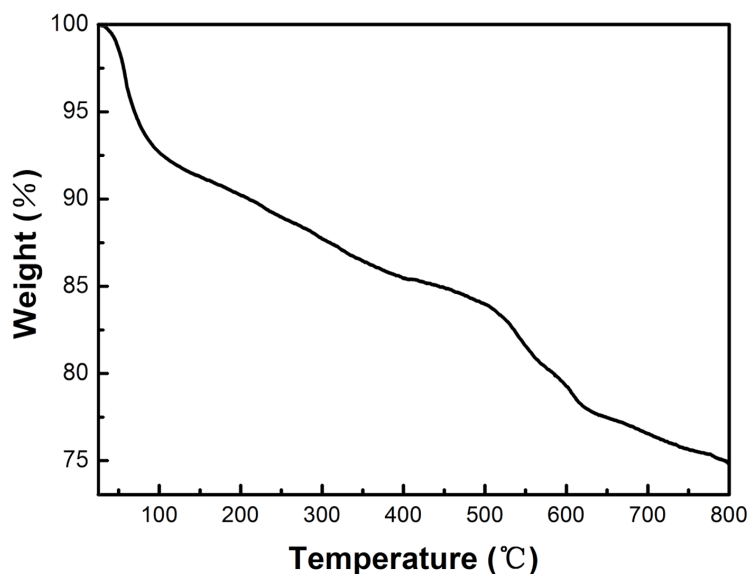
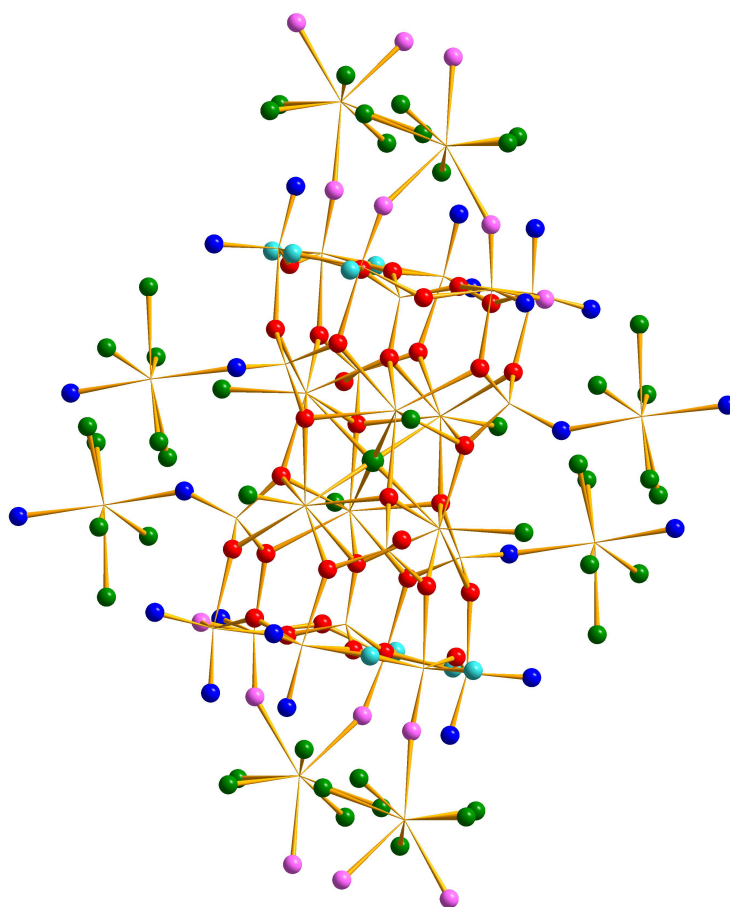


Fig. S4 Thermogravimetric curve of **1** in the flowing N₂ atmosphere.

The thermogravimetric (TG) curve of **1** displays three stages of weight loss (Fig. S4) in the temperature range of 25 - 800 °C. The first stage from 25 °C to about 100 °C is attributed to the loss of 19 lattice water molecules, and the observed weight loss 7.01 % is consistent with the calculated value 6.67 %. The second stage with the weight loss of 9.29 % occurs between about 100 °C to 500 °C, which may be assigned to the removal of 27 coordinated water molecules (calcd. 9.48 %). The weight loss of the third stage from 500 °C to 800 °C is 9.07 %, corresponding to the release of two structural water from the dehydration of 4 protons and two As₂O₅, which decomposed to As₂O₅ and O₂ molecules (calcd. 9.04 %).¹

¹ C.-Y. Sun, Y.-G. Li, E.-B. Wang, D.-R. Xiao, H.-Y. An and L. Xu, *Inorg. Chem.*, 2007, **46**, 1563.








Oxygen atom	Bond valence sum range	number	Oxygen atom	Bond valence sum range	number
	-2.2 – -2.0	32		-2.0 – -1.9	8
	-1.9 – -1.7	8		-1.7 – -1.5	18
	-0.35 – 0.0	28			

Fig. S5 Charge distribution of O atoms in the polyoxotungstate fragment of **1**. Oxygen atoms with different bond valence sums are represented by different colours.

The multiply protonated polyoxotungstate fragment in **1** are reasonable. The reasons are as follows:

- (1) The polyoxotungstate fragment in **1** has high negative charges and rich basic surface oxygen atoms, which can easily be protonated.
- (2) On the basis of valence sum (Σ_s) calculation,¹ the oxidation states of 94 O atoms in **1** can be divided into five groups according to their bond valence sums (Fig. S7). Excepting 28 waters ($\Sigma_s = -0.35 - 0.0$) group, there are eight atoms with their Σ_s in the range of $-1.9 - -1.7$ and eighteen O atoms with their Σ_s in the range of $-1.7 - -1.5$. So the six protons are likely to be delocalized on these O atoms.
- (3) About the synthetic condition, the pH values before the reactions are 5.50, and the pH after the reactions are 5.20, which exhibit acidity. According to the above comments, the multiple protonations of the polyoxoanion in **1** with high negative charges are likely under weak acidic conditions for the requirement of the charge balance.
- (4) In generally, the multiply protons can not be located in polyoxometalate fragments by X-ray diffraction. They are usually assigned to be delocalized on the whole polyoxoanion only for the charge balance of the polyoxoanion. The phenomenon is common in POM chemistry and has been reported in many literatures. For example, $[(H_3O)_9\{(PY_2W_{10}O_{38})_4(W_3O_{14})\}]^{21-}$,² $[(H_3O)_{13.5}\{(PEu_2W_{10}O_{38})_4(W_3O_{14})\}]^{16.5-}$,² $[H_3W_{12}O_{40}]^{5-}$,³ $[H_{12}V_{13}O_{40}]^{3-}$,⁴ $[HW_9O_{33}Ru^{II}_2(dmsO)_6]^{7-}$,⁵ $[Ni(enMe)_2]_3 [H_6Ni_{20}P_4W_{34}(OH)_4O_{136}(enMe)_8(H_2O)_6] \cdot 12H_2O$ ⁶ and $[Ni(en)_2(H_2O)]_2 [H_8Ni_{20}P_4W_{34}(OH)_4O_{136}(en)_9(H_2O)_4] \cdot 16H_2O$.⁶

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Experimental Details:

Syntheses of 1: Na₂WO₄·2H₂O (1.0 g, 3.03 mmol), Na₃AsO₄·12H₂O (0.63 g, 1.49 mmol) and CaCl₂ (0.17 g, 1.53 mmol) were dissolved in water (10 mL) under stirring. After dissolution, the pH value was adjusted to 5.50 by adding 0.1 M HCl dropwise. The solution was kept at 80–90 °C for 0.5 h, then filtered and evaporated slowly at ambient temperature. After three weeks, colorless crystals of **1** suitable for X-ray crystallography were obtained (Yield: ca 26% based on Na₂WO₄·2H₂O).

X-ray Crystallography: Crystal data for **1**, H₉₄As₈Ca₁₀O₁₁₄W₁₂, Mr = 5125.11, triclinic, space group *P*-1, *a* = 13.157(3), *b* = 13.260(3), *c* = 18.015(4) Å, α = 74.436(4)°, β = 89.226(3)°, γ = 61.881(3)°, *V* = 2646.5(9) Å³, *Z* = 1, μ = 16.108 mm⁻¹, *F*(000) = 2358, *GOF* = 1.008. Of 12769 total reflections collected, 9107 were unique (*R*_{int} = 0.0443). *R*₁(*wR*₂) = 0.1031 for 683 parameters and 6182 reflections [*I* > 2σ(*I*)]. Intensity data were collected at 296(2) K on a Bruker Smart APEXII CCD diffractometer for **1** using graphite-monochromated *Mo Kα* radiation (λ = 0.71073 Å), respectively. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structure and refined by full-matrix least-squares on *F*² using the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically. CCDC 858792 contain the supplementary crystallographic data for this paper for **1**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.