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# Polyoxometalates-based chiral frameworks involving helical motifs generated by spontaneous resolution

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ABSTRACT

Two enantiomerically 3D chiral polyoxometalate frameworks L,D-$[K(H_2O)]_6[H_2GeMo_2W_{10}O_{40}]_3 \cdot 40H_2O$ (**1a** and **1b**), were conventionally synthesized and characterized by X-ray single-crystal diffraction, IR spectrum, elemental analysis, powder X-ray diffraction, thermogravimetric analysis, UV–Vis spectroscopy, circular dichroism spectra. Structural analysis indicates that **1a** and **1b** are enantiomers. The terminal O and $\mu_2$-O atoms of Keggin-type polyanion $[GeMo_2W_{10}O_{40}]^{4-}$ and $\{K(H_2O)\}_n$ segments are connected one another to form 1D chiral helical chains, which are further extended by the achiral Keggin-type $[GeMo_2W_{10}O_{40}]^{4-}$ anion to construct 3D 4,8-connected chiral frameworks. The enantiomers were isolated by spontaneous resolution during crystallization without any chiral auxiliary. They represent rare examples of enantiomerically pure chiral polyoxometalate-based inorganic porous frameworks.

## 1. Introduction

Chiral polyoxometalates (POMs) have received much attention, not only owing to their fascinating structures and topologies, but also because of their significant potential applications in nonlinear optics, enantioselective catalysis, chiral separation and molecular recognition [1–3]. Stimulated by these applications, more and more scholars were attracted to design and synthesize chiral POMs-based materials, and many highlighted chiral POMs have been performed [4–6]. To date, two methods have been advanced for the construction of POMs-based chiral compounds. One approach is building chiral POMs backbones by the self-assembly of achiral species including structural distortion, the bond length alteration, the formation of lacunae, or substitution by other metal ions. The second approach is based on the use of chiral sources including chiral POMs, chiral organic connectors or chiral metal–organic complexes. Notably, most of the reported chiral POMs are inclined to generate racemic compounds because of rapid racemization in solution, and spontaneous resolution of chiral POMs were only achieved in a few cases [7]. The first spontaneous resolution of chiral POMs, two enantiomerically pure chiral POMs $[Hf(PW_{11}O_{39})_2]^{10-}$ being separated without any chiral source upon crystallization, was reported by Hill et al., in 2007 [8]. Spontaneous resolution upon crystallization without any chiral auxiliary is very appealing due to its association with homochirality in life and absolute asymmetric synthesis in the solid state. However, only a very limited number (5–10%) of racemates can form a conglomerate (mixture of chiral crystals) through spontaneous resolution [9]. Alternatively, the spontaneous resolution of chiral POMs is still a relatively scarce phenomenon, which confronts more difficulties and challenges, owing to their facile racemization in solution, partial hydrolysis, or fluxional behavior [10].

As is well known, most POM anion clusters possess high symmetry and are very difficult to crystallize in non-centrosymmetric space groups. The symmetry-breaking approach to obtain chiral POMs is possible through assembly of POMs generate POMs-based frameworks. Thus, hunting for a strategy for preparing high-dimensional chiral POMs is extremely challenging but attractive. On the basis of the above points, we synthesized a pair of novel 3D chiral W/Mo mixed POMs-based inorganic framework L,D-$[K(H_2O)]_6[H_2GeMo_2W_{10}O_{40}]_3 \cdot 40H_2O$ (**1a** and **1b**) by self-assembly

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processes under strong acid condition. Structure analysis showed that **1a** and **1b** are enantiomers. They are novel examples of chiral POMs-based 3D chiral inorganic porous framework generated by spontaneous resolution upon crystallization without any chiral influence.

## 2. Experimental section

### 2.1. Materials and measurement

All chemicals were obtained commercially and used without further purification. The $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ precursor was obtained according to the procedure described in the literature and characterized using the IR spectrum [11]. Elemental analyses (K, W, Mo and Ge) were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/MAX-3 instrument with Cu-Ka ($\lambda = 1.5418$ Å) radiation at 293 K. The IR spectrum in KBr pellets was employed in the range of 4000–400 $cm^{-1}$ using an Alpha Centaurt FT-IR spectrophotometer. The UV–visible spectra were recorded utilizing a Hitachi UV-3010 spectrophotometer. Thermogravimetric analyses (TGAs) were operated on a Perkin-Elmer TGA7 instrument, with a heating rate of 10 °C/min under a nitrogen atmosphere. The CD spectra for the enantiomers was conducted by using a Jasco J-810 spectropolarimeter.

### 2.2. Syntheses

#### 2.2.1. *L,D-$[K(H_2O)]_6[H_2GeMo_2W_{10}O_{40}]_3\cdot 40H_2O$ (**1a** and **1b**)*

A mixture of $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ (2.50 g, 0.91 mmol), and $Na_2MoO_4$ (0.4 g, 1.92 mmol) was added to distilled water (40 mL) with stirring and heated to 75 °C, followed by the addition of HCl (6 M, 4.0 mL) to acidize the reaction system to pH 1.5. Subsequently, the mixture was carefully adjusted to pH 3.4 using 1 M $K_2CO_3$ solution and kept at 75 °C for 2 h and then cooled to room temperature and filtered. Slow evaporation of filtrate at room temperature resulted in the yellow rod-like crystals after ten days. Finally, the pair of enantiomers (**1a** and **1b**) were separated manually by using the polarized light microscope and according the differences of morphological characteristic: **1a** are rod-like hexagonal prism and **1b** are dihexagonal prism with vertices (Fig. S1). Yield: 47.32% (based on W). Anal. calcd (%) for 1: K 2.51, Ge 2.32, W 58.75, Mo 6.13. Found (%): K 2.39, Ge 2.36, W 58.62, Mo 6.21.

### 2.3. X-ray crystallography study

The crystallographic data of **1** was recorded on a Bruker Smart Apex CCD diffractometer with Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods using SHELXS-97 crystallographic software package [12]. In the process of refinement, all non-H-atoms were refined with anisotropic displacement parameters. The H-atoms of the water molecules were not located and just put into the final molecular formula. The numbers of crystallization water molecules in the compounds were verified by thermogravimetry, and only partial O atoms of water molecules were achieved with the X-ray structure analysis. The crystal data and structure-refinement results of compounds **1a** and **1b** are summarized in Table 1. CCDC 1543845 (**1a**) and CCDC 1543844 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Table 1**
Crystal data and structural refinement for compound **1a** and **1b**.

| Compound | 1a | 1b |
|---|---|---|
| Formula | $H_{98}K_6Ge_3Mo_6W_{30}O_{166}$ | $H_{98}K_6Ge_3Mo_6W_{30}O_{166}$ |
| M (g $mol^{-1}$) | 9298.19 | 9298.19 |
| T (K) | 293 (2) | 293 (2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Cryst. syst. | Hexagonal | Hexagonal |
| Space group | $P6_222$ | $P6_222$ |
| a (Å) | 19.081(4) | 19.106(3) |
| b (Å) | 19.081(4) | 19.106(3) |
| c (Å) | 12.637(4) | 12.622(5) |
| α (°) | 90 | 90 |
| β (°) | 90 | 90 |
| γ (°) | 120 | 120 |
| V($Å^3$) | 3984(3) | 3990(3) |
| Z | 1 | 1 |
| $D_{calc}$ (mg $m^{-3}$) | 3.657 | 3.652 |
| μ($mm^{-1}$) | 22.812 | 22.779 |
| F(000) | 3810.0 | 3810.0 |
| R(int) | 0.1222 | 0.0743 |
| GOF on $F^2$ | 1.074 | 1.040 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0364 | 0.0328 |
| $wR_2$ (all data)[b] | 0.0916 | 0.0819 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

## 3. Results and discussion

### 3.1. Synthesis and structure description of compound 1

Compounds **1a** and **1b** were obtained by the reaction of $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$, $Na_2MoO_4$ and $K_2CO_3$ in solution at 75 °C for 2 h. In the reaction system, we added 6 M HCl to acidize the reaction system and then chose $K_2CO_3$ to adjust pH value to 3.4 to isolate enantiomers **1a** and **1b**. Notably, we explored using other alkali metal to replace $K^+$ under the same conditions, but, unfortunately, no analogous products were harvest. Single-crystal X-ray structure analyses show that they were crystallize in hexagonal space group $P6_222$. The Keggin polyanion $[GeMo_2W_{10}O_{40}]^{4-}$ in **1** is a dimolybdenum-substituted Keggin-type germanotungstate, obtained by reassembly of the vacant anions $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ and $Na_2MoO_4$ in acid medium. Structurally, each W sites are found to be disordered on the surface of POMs cluster, with the occupancy 83.33% W, 16.67% Mo (W/Mo = 5:1). So, a total of two Mo atoms are given per cluster. And a $GeO_4$ tetrahedron resides in central position of the cluster (Fig. 1a). Bond-valence sum (BVS) [13] calculations show that the oxidation states of all the W, Mo Ge and O atoms are +6, +6, +4 and −2, respectively. In the Keggin cluster, there are three types of O atoms: central O atoms ($O_c$), terminal O atoms ($O_t$) and bridging atoms($O_b$). The bond lengths of W–$O_c$, W–$O_t$ and W–$O_b$ are in the range of 2.276(9)-2.306(9) Å, 1.680(10)-1.691(10) Å, and 1.896(11)-1.955(10), respectively. The $K^+$ ion is octa-coordinated by two $\mu_2$-O atoms from two $[GeMo_2W_{10}O_{40}]^{4-}$ polyoxoanions and four $O_t$ atoms from four $[GeMo_2W_{10}O_{40}]^{4-}$ polyoxoanions and two $H_2O$ molecules (Fig. S2). The bond lengths of K–O are in the range of 2.762(10)–3.168(10) Å. The structures of **1a** and **1b** display analogical chiral inorganic porous framework assembled from $[GeMo_2W_{10}O_{40}]^{4-}$ clusters and $\{K(H_2O)\}_n$ linkers. The $K^+$ ions connect pairs of terminal O and $\mu_2$-O atoms of $[GeMo_2W_{10}O_{40}]^{4-}$ to constructe 1D chiral helixes (Fig. 1b). The helixes with the composition $\{K(H_2O)\}_n$ are built by the bridging octa-coordinated $K^+$ ions. The chains of edge-shared $KO_8$ polyhedra are arranged along the c axis. The similar connection modes have been observed in the other literature [14].

Notably, the helixes in **1a** and **1b** are further extended by $[GeMo_2W_{10}O_{40}]^{4-}$ cluster to build an intriguing 3D POMs-based