

**Synthesis and Crystal Structure of a Novel 1D Chain-like Organic
Inorganic Hybrid Rare Earth Derivative of Polyoxometalate:
 $H_{0.5}[Sm(H_2O)_6]_{0.25}[Sm(H_2O)_5]_{0.25}\{[Sm(H_2O)_7][Sm(H_2O)_2(DMSO)] [SiW_{11}O_{39}]\} \cdot 4.5H_2O$**

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Abstract: A 1D chain-like organic-inorganic hybrid rare earth derivative of polyoxometalate $H_{0.5}[Sm(H_2O)_6]_{0.25}[Sm(H_2O)_5]_{0.25}\{[Sm(H_2O)_7][Sm(H_2O)_2(DMSO)] [SiW_{11}O_{39}]\} \cdot 4.5H_2O$ has been firstly synthesized by reaction of α - $K_8SiW_{11}O_{39} \cdot 13H_2O$, $HClO_4$, Sm_2O_3 with dimethyl sulfoxide (DMSO) and characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. The neighboring polyanionic units $\{[Sm(H_2O)_7][Sm(H_2O)_2(DMSO)] [SiW_{11}O_{39}]\}^{2-}$ are bridged together to a 1D chain structure by means of $[Sm(H_2O)_2(DMSO)]^{3+}$ ion.

Keywords: Silicotungstic acid, polyoxometalate, mono-vacant Keggin structure, rare earth ions.

Polyoxometalates may be versatile inorganic building blocks for the construction of molecular-based materials. By means of their multiple coordination requirements and oxophilicity, lanthanide cations are suitable to link polyoxometalate building blocks to form new classes of materials with potentially useful magnetic and luminescent properties¹⁻⁴. Peacock and Weakley studied the interactions between the $[\alpha-SiW_{11}O_{39}]^{8-}$ isomer and lanthanide cations⁵, and they reported that the $[\alpha-SiW_{11}O_{39}]^{8-}$ forms both 1:1 and 1:2 compounds with rare earth metals. Recently, Pope *et al.* investigated the structural characterization of the one-dimensional 1:1 $[Ln(\alpha-SiW_{11}O_{39})(H_2O)_3]^{5-}$ ($Ln = La^{III}, Ce^{III}$) compounds, showing that these anions are polymeric in the solid state⁶. Mialane *et al.* also reported the solid-state structures of the $Ln/[\alpha-SiW_{11}O_{39}]^{8-}$ ($Ln = Yb^{III}, Nd^{III}, Eu^{III}, Gd^{III}$)⁷. However, there is not any report about the organic-inorganic hybrid rare earth derivative with mono-vacant $[\alpha-SiW_{11}O_{39}]^{8-}$ building block. Herein, we firstly report the synthesis and crystal structure of an organic-inorganic rare earth derivative $H_{0.5}[Sm(H_2O)_6]_{0.25}[Sm(H_2O)_5]_{0.25}\{[Sm(H_2O)_7][Sm(H_2O)_2(DMSO)] [SiW_{11}O_{39}]\} \cdot 4.5H_2O$ with mono-vacant $[\alpha-SiW_{11}O_{39}]^{8-}$ building block.

Experimental

Preparation of α - $K_8SiW_{11}O_{39} \cdot 13H_2O$: This compound was prepared according to the

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literature⁸ and confirmed by IR spectra.

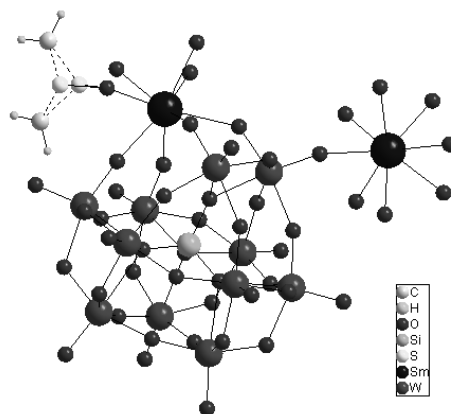
Preparation of $H_{0.5}[Sm(H_2O)_6]_{0.25}[Sm(H_2O)_5]_{0.25}\{[Sm(H_2O)_7][Sm(H_2O)_2(DMSO)][SiW_{11}O_{39}]\} \cdot 4.5H_2O$: The solid oxide Sm_2O_3 (0.52 g, 1.5 mmol) was suspended in distilled water (5 mL), to which a solution of $HClO_4$ (0.80 mL, 12.19 mol/L) was added dropwise under stirring. The mixture was heated at 70 °C under stirring for 1 h, and then the pH value was adjusted to 5.15 by addition of a NaOH solution (0.4 mol/L). Then α - $K_8SiW_{11}O_{39} \cdot 13H_2O$ (1.65 g, 0.5 mmol) and dimethyl sulfoxide (1.5 mL) were added. The mixture was refluxed continuously for 1 h, and then cooled to the ambient temperature. After filtration, water (20 mL) was added to the filtrate, and the obtained solution was left to evaporate slowly at room temperature, polyhedral crystals were obtained after several weeks. Anal. Calcd. for $H_{0.5}[Sm(H_2O)_6]_{0.25}[Sm(H_2O)_5]_{0.25}\{[Sm(H_2O)_7][Sm(H_2O)_2(DMSO)][SiW_{11}O_{39}]\} \cdot 4.5H_2O$: C, 0.70%; H, 1.15%; S, 0.94%; Si, 0.82%; Sm, 10.99%; W, 59.10%; Found: C, 0.77%; H, 1.04%; S, 0.98%; Si, 0.79%; Sm, 11.07%; W, 59.19%.

Structure Determination and Results

Intensity data were collected with a Rigaku RAXIS-IV image plate area detector using graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using SHELXTL-97⁹. Intensity data were corrected for Lorentz and polarization effects as well as for empirical absorption. All of the non-hydrogen atoms were refined anisotropically. This Crystal is monoclinic, space group $P2_1/c$, $a = 23.602(5) \text{ \AA}$, $b = 11.601(2) \text{ \AA}$, $c = 23.545(5) \text{ \AA}$, $\beta = 109.05(3)^\circ$, $Z = 4$, $R_1 = 0.0609$, $wR_2 = 0.1238$.

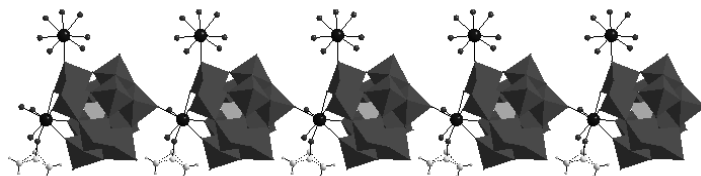
In the IR spectra, the title compound displayed characteristic vibration peaks of the Keggin-type structure, namely, $\nu(W-O_d)$, $\nu(Si-O_a)$, $\nu(W-O_b)$ and $\nu(W-O_c)$, appear at 949; 894; 831 and 703 cm^{-1} , respectively. Compared to IR spectra of α - $K_8SiW_{11}O_{39} \cdot 13H_2O$, the $\nu(W-O_d)$ has a red-shift of 5 cm^{-1} , the major reason for which may be that the charge compensation cations have stronger interaction to the terminal oxygen atoms of the polyoxoanions, impairing the $W-O_d$ bond, reducing the $W-O_d$ bond force constant and leading to decrease the $W-O_d$ vibrational frequency. The $\nu(Si-O_a)$, $\nu(W-O_b-W)$ and $\nu(W-O_c-W)$ have blue-shifts of 7, 31 and 24 cm^{-1} , respectively, the possible reason for which is that the polyoxoanionic symmetry of the title compound increased as compared to that of α - $K_8SiW_{11}O_{39} \cdot 13H_2O$. In addition, the resonance at the 1006 cm^{-1} in the title compound is assigned to $\nu(S=O)$ asymmetric stretching vibration of DMSO molecules. Comparing with that of free DMSO, the $\nu(S=O)$ shift from 1028 to 1006 cm^{-1} . This result confirms that the DMSO ligands are coordinated to the metal ion by means of the oxygen atoms. The UV spectra in aqueous solution for the title compound, α - $K_8SiW_{11}O_{39} \cdot 13H_2O$ and α - $H_4SiW_{12}O_{40} \cdot xH_2O$ revealed an absorption band at 255 nm, which is assigned to the $p\pi - d\pi$ charge transfer transitions of $O_{b(c)} \rightarrow W$ bond¹⁰. The corresponding peak absorption intensity of α - $H_4SiW_{12}O_{40} \cdot xH_2O$ is much stronger than that of the title compound and α - $K_8SiW_{11}O_{39} \cdot 13H_2O$, possibly owing to the lower polyoxoanionic symmetry of the title compound and α - $K_8SiW_{11}O_{39} \cdot 13H_2O$ compared to

Figure 1 The polyanionic unit of the title compound



the $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion.

To the best of our knowledge, the crystal structure of the 1D chain-like organic-inorganic rare earth derivative with mono-vacant $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ building block is not reported up to now. The X-ray single-crystal structure of $\text{H}_{0.5}[\text{Sm}(\text{H}_2\text{O})_6]_{0.25}[\text{Sm}(\text{H}_2\text{O})_5]_{0.25}\{[\text{Sm}(\text{H}_2\text{O})_7][\text{Sm}(\text{H}_2\text{O})_2(\text{DMSO})][\text{SiW}_{11}\text{O}_{39}]\} \cdot 4.5\text{H}_2\text{O}$ was investigated. The structural unit of the title compound consists of 0.5 H^+ , 0.25 discrete $[\text{Sm}(3)(\text{H}_2\text{O})_6]^{3+}$, 0.25 discrete $[\text{Sm}(4)(\text{H}_2\text{O})_5]^{3+}$, one $\{[\text{Sm}(2)(\text{H}_2\text{O})_7][\text{Sm}(1)(\text{H}_2\text{O})_2(\text{DMSO})][\text{SiW}_{11}\text{O}_{39}]\}^{2-}$ polyoxoanionic unit and 4.5 crystal water molecules (**Figure 1**). The neighboring polyoxoanionic units $\{[\text{Sm}(2)(\text{H}_2\text{O})_7][\text{Sm}(1)(\text{H}_2\text{O})_2(\text{DMSO})][\text{SiW}_{11}\text{O}_{39}]\}^{2-}$ are bridged together to a novel 1D chain structure by means of $[\text{Sm}(1)(\text{H}_2\text{O})_2(\text{DMSO})]^{3+}$ (**Figure 2**). $\text{Sm}^{3+}(1)$ coordination cation, which is incorporated into the defect site of the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ fragment, is eight-coordinate, adopting a distorted square antiprismatic geometry, in which two coordination oxygen atoms come from water molecules, one from the DMSO and five from the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ fragment. $\text{Sm}^{3+}(2)$ coordination cation is also eight-coordinate with a distorted square antiprismatic environment, defined by eight coordination oxygen atoms, seven from water molecules and one from the $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ framework. The isolated $\text{Sm}^{3+}(3)$ and $\text{Sm}^{3+}(4)$ coordination cations are six-coordinate and five-coordinate, respectively. The occupancy of $[\text{Sm}(3)(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Sm}(4)(\text{H}_2\text{O})_5]^{3+}$ is 0.25 in the crystal lattice. In addition, DMSO in the $[\text{Sm}(1)(\text{H}_2\text{O})_2(\text{DMSO})]^{3+}$ is crystallographically disordered and occupied two positions. In the polyanionic unit, the Si atom resided in the SiO_4 tetrahedron, which has been somewhat deformed resulting from the removal of one $[\text{W}=\text{O}_d]^{4+}$ group and the complete incorporation of a Sm^{III} atom into the monovacant polyoxometalate framework as compared to saturated Keggin structure. The Si-O bond distances in the SiO_4 polyhedra vary between $1.606(12)$ and $1.642(13)$ Å and the O-Si-O bond angles are in the range of $101.7(6) - 112.6(6)^\circ$. Similarly, all the WO_6 octahedra are distorted to some extent. In summary, the successful synthesis and construction of the title compound provide a rational strategy for the novel 1D chain-like organic-inorganic hybrid rare earth derivatives with mono-vacant Keggin-type structural building block.

Figure 2 The 1D chain motif of the polyanionic unit

Acknowledgments

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