



Two 3D networks based on sandwich-type polyoxometalate units linked by Sr–O clusters: Synthesis, structure, and magnetic property

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ABSTRACT

Two 3D hybrid sandwich-type polyoxometalates, $[\{\text{Sr}(\text{H}_2\text{O})_5\text{Sr}(\text{H}_2\text{O})_6\text{Sr}_{0.5}(\text{H}_2\text{O})_7\}_2\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\{\text{Sr}(\text{H}_2\text{O})_6[\text{Sr}(\text{H}_2\text{O})_8]_2\text{Sr}(\text{H}_2\text{O})_4\}_2\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\beta\beta\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 5\text{H}_2\text{O}$ (**2**), have been obtained by the routine synthetic reactions in aqueous solution and characterized by IR, elemental analysis, thermal analysis, and X-ray single-crystal diffraction. The 3D hybrid framework of **1** and **2** are built by tetra-Mn^{II} substituted sandwich-type polyoxotungstates modified by fourteen Sr(H₂O)_x (x=4–8) units acting as bridges, forming centrosymmetric sandwich structures. The magnetic property of compound **1** has been studied by measuring its magnetic susceptibility in the temperature range of 2–300 K, which indicates predominant ferromagnetic interactions between the Mn^{II}–O–Mn^{II} bridge unit. Additionally, the electrochemical behaviours have been detected on solid bulk modified carbon paste electrodes of compounds (CPEs) and three redox couples are detected.

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1. Introduction

Transition-metal-polyoxometalates (TMSPs) based on lacunary Keggin and Wells–Dawson polyanions precursors exhibit a fascinating variety of structures and properties including catalysis, medicine, and magnetism [1]. The lacunary polyanions, such as monovacant, divacant, trivacant, were important intermediates in POM chemistry and were proved to be metal-accommodated species that can combine with TMs or rare earths including Mn, Cu, Co, Ni, Zn, Zr, Hf, Ce, and so on [2], making the structure stable and polymerization clusters via extremely strong connection. The vacant sites in the surface of POMs can provide more O-donor ligands and more negative charges, which have been proved as the most active sites to react with various metal ions or metal-organic fragments. In the context, trivacant heteropolytungstates, such as $\alpha\text{-PW}_9\text{O}_{34}^{3-}$ or $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$, acting as structural building blocks, are of particular interest because the trivacant species are suitable precursors that can react with d-electron metal ions in their three vacant sites to form dimeric sandwich-type structure [3]. Meanwhile, the structural multiplicities could be adjusted by introducing of diverse bridging units and transition metal ions [4]. The trivacant POMs and the paramagnetic TM aggregations could

combine to novel high-coordinated and high-connected TMSPs. Up to now, numerous sandwich-type POMs have been synthesized, which belong to the well-known Weakley-, Herve-, Krebs- and Knoth-type sandwich structures as the main building blocks with various nuclearities and original topologies. The Yang's and Hill's group have reported plenty of novel sandwich-type structures based on trivacant Keggin (PW₉, SiW₉, and GeW₉) and Wells–Dawson (P₂W₁₅) POMs, respectively [5].

To the best of our knowledge, the multi-dimensional sandwich trivacant heteropolytungstates structures connecting with each other in different ways via some kind of metal–water units (alkaline metal (K, Na), transition metal (Mn, Co), lanthanum (Ce)) have been reported [6], however, the alkaline-earth metal ions act as linkage to form three dimensional structure are never been reported, except that alkaline-earth metal ions (Sr or Ca) fill in vacant position or cavum [7]. Therefore, it is still meaningful and challenging to synthesize new complexes that alkaline-earth metal ions act as linkages. In our work, we try to find the rational reaction condition to obtain stable sandwich-type heteropolytungstates and the alkaline-earth metal Sr^{II} ion. With the aim of extending these new series to other interesting sandwich complexes, we report the synthesis, crystal structures, and magnetic properties of two compounds consisting of $\alpha\text{-PW}_9\text{O}_{34}^{9-}$ or $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$, transition metal, and alkaline-earth metal, $[\{\text{Sr}(\text{H}_2\text{O})_5\text{Sr}(\text{H}_2\text{O})_6\text{Sr}_{0.5}(\text{H}_2\text{O})_7\}_2\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\{\text{Sr}(\text{H}_2\text{O})_6[\text{Sr}(\text{H}_2\text{O})_8]_2\text{Sr}(\text{H}_2\text{O})_4\}_2\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\beta\beta\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 5\text{H}_2\text{O}$ (**2**). The magnetic properties of **1** and the electrochemistry behaviours are studied additionally.

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2. Experimental

2.1. Materials and methods

$K_9[PW_9O_{34}] \cdot nH_2O$ and $K_{12}[P_2W_{15}O_{56}] \cdot nH_2O$ [8] was prepared according to the literature method and confirmed by IR spectroscopy. All of the other chemicals were obtained from commercial sources and used without further purification. P, W, Mn, and Sr were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The IR spectra were obtained on an Alpha Centauri Fourier transform IR (FT-IR) spectrometer with KBr pellets in the 400–4000 cm^{-1} region. The thermo gravimetric analyses (TGA) were carried out in N_2 on a Perkin-Elmer DTA 1700 differential thermal analyzer with a rate of 10 $^{\circ}C/min$. Magnetic susceptibility data were collected over the temperature range of 2–300 K in a magnetic field of 1000 Oe on a Quantum Design MPMS-5 SQUID magnetometer. Electrochemical measurements were performed with a CHI660 electrochemical workstation. A conventional three-electrode system was used. The working electrode was a modified carbon paste electrode (CPE), a platinum wire as the counter electrode and Ag/AgCl (3M KCl) electrode was used as a reference electrode. X-ray powder diffractometry (XRPD) study of **1** was performed with a NETZSCH STA 449C instrument, with a panalytical X-pert pro diffractometer and $CuK\alpha$ radiation.

2.2. Synthesis of **1** and **2**

Compound **1** was synthesized in aqueous condition. $K_9[PW_9O_{34}] \cdot nH_2O$ (0.5 g) was dissolved in 50 mL water, then $MnCl_2 \cdot 2H_2O$ (0.17 g) and $SrCl_2 \cdot 6H_2O$ (0.26 g) were added. The solution was heated to 70 $^{\circ}C$, the pH value was adjusted to 4.6 with 6 M HCl until the precipitation appearing. After 2 h, the solution was cooled to room temperature and 2 days later, the orange block crystals (0.15 g, yield 48%) were obtained based on W. Anal. Calcd. for $H_{68}Mn_4O_{112}P_2Sr_5W_{18}$ (**1**) (Mr=5889.5) (%): W, 56.17; Mn, 3.73; P, 1.05; Sr, 7.44. Found (%): W, 56.16; Mn, 3.78; P, 1.02; Sr, 7.40.

The preparation of **2** was similar to that of **1**, except that $K_{12}[P_2W_{15}O_{56}] \cdot nH_2O$ was instead of $K_9[PW_9O_{34}] \cdot nH_2O$. Anal. Calcd. for $H_{86}Mn_4O_{171}P_4Sr_8W_{30}$ (**2**) (Mr=9382.5) (%): W, 58.77; Mn, 2.34; P, 1.32; Sr, 7.47. Found (%): W, 58.76; Mn, 2.38; P, 1.35; Sr, 7.44.

2.3. X-ray crystallography

The reflection intensities of **1** and **2** were collected on a Bruker SMART CCD diffractometer with $MoK\alpha$ radiation ($\lambda=0.71703 \text{ \AA}$) at 273 K in the range of $2.57^{\circ} < \theta < 28.28^{\circ}$. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares method on F^2 using the SHELXL-97 crystallographic software package [9]. Crystallographic data for the structure of **1** and **2** reported in this paper has been applied CSD numbers 420908 and 421055. Copy of the data can be obtained free of charge from the FIZ Karlsruhe, Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail: crysdata@fiz-karlsruhe.de). The crystallographic data and structure determination parameters for **1** and **2** were summarized in Table 1. Selected bond lengths and bond angles are provided in Tables S1 and S2 in the Supporting Information.

Table 1
Crystal data and structural refinement for compounds **1** and **2**.

Compound	1	2
Empirical formula	$H_{68}Mn_4O_{112}P_2Sr_5W_{18}$	$H_{86}Mn_4O_{171}P_4Sr_8W_{30}$
Formula weight	5889.5	9382.5
Crystal system	Triclinic	Triclinic
space group	$P-1$	$P-1$
Unit-cell dimensions	$a=12.1382(4),$ $b=12.7200(5),$ $c=18.2212(9),$ $\alpha=104.0780(10),$ $\beta=97.9210(10),$ $\gamma=114.7620(10)$	$a=14.624(3),$ $b=16.590(3),$ $c=16.628(3),$ $\alpha=89.16(3),$ $\beta=88.52(3),$ $\gamma=78.37(3)$
Volume	$2384.40(17)(\text{\AA}^3)$	$3949.8(14)$
Z	1	1
ρ_{calc} (g/cm^3)	4.102	3.944
μ (mm^{-1})	25.054	24.886
$F(000)$	2616.0	4138.0
Crystal size (mm)	$0.38 \times 0.36 \times 0.14$	$0.18 \times 0.15 \times 0.12$
Goodness-of-fit on F^2	1.042	1.035
Final R indices	$R_1=0.0473,$ $wR_2=0.1407$	$R_1=0.0591,$ $wR_2=0.1413$
($I > 2\sigma(I)$)	$R_1=0.0511,$ $wR_2=0.1442$	$R_1=0.0805,$ $wR_2=0.1620$

3. Results and discussions

3.1. Synthesis

Compounds **1** and **2** were synthesized by treating precursors of $K_9[PW_9O_{34}] \cdot nH_2O$ (for **1**) and $K_{12}[P_2W_{15}O_{56}] \cdot nH_2O$ (for **2**), $MnCl_2 \cdot 2H_2O$, and $SrCl_2 \cdot 2H_2O$ at 70 $^{\circ}C$. The successful syntheses indicate that the $Sr(H_2O)_x$ unit is an effective linker in these reaction system because Sr^{II} ions have multi-coordinated environments. We have studied diverse different reaction environment: (1) change the reaction system into H_3PO_4 , Na_2WO_4 , $MnCl_2 \cdot 2H_2O$, and $SrCl_2 \cdot 2H_2O$ according to the P-W ratio of POMs; (2) change the same group $MgCl_2$, $CaCl_2$, $BaCl_2$ instead of $SrCl_2$; (3) adjust the pH value to the lower or the higher level; and (4) utilize the hydrothermal synthesis method maintaining the same reactants. The results are we fail to obtain **1** and **2**. Through the exploring experiments, we can conclude that both type of precursors (POMs and salt), the pH value, synthesis methods are key factors for synthesizing these two complexes.

3.2. Structure descriptions

Single-crystal X-ray diffraction analysis reveals that **1** exhibits a sandwich-type structure constructed from two α - $PW_9O_{34}^{9-}$ units, four Mn^{2+} ions, five $Sr(H_2O)_x$ ($x=5, 6, 7$) units, and six lattice waters, resulting in a rarely 14-supported structure (Fig. 1a). In the cluster, α - $PW_9O_{34}^{9-}$ units possess the well-known trivacant Keggin structural A- α -type, resulting from the removal of three edge-sharing {WO6} octahedral in the α -Keggin-type structure. All W centers display the octahedral coordination geometry. The W–O bond lengths vary from 1.710(11) to 2.443(11) \AA and the O–W–O angles in the range of 72.8(4)–170.0(5) $^{\circ}$. The central belt of **1** is composed of a rhombic Mn_4O_{16} group, in which four coplanar MnO_6 octahedra connected with each other in an edge-sharing mode. The bond lengths of Mn–O are in the range of 2.066(10)–2.311(10) \AA (Fig. 1b). The distances of Mn···Mn along the sides of the rhombus are 3.37 \AA while along the diagonal of the rhombus are 3.35 and 5.80 \AA . The crystallographically independent Sr–O clusters have different coordination environments. Sr1 center is coordinated with a terminal oxygen atom derived from $\{PW_9O_{34}\}$ units, two μ -O bridge (O55) from adjacent Sr1 center and six

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