A 1-D ladder-like aggregate constructed from Preyssler anion and transition metal linkers

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A 1-D ladder-like aggregate constructed from Preyssler anion and transition metal linkers

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A 1-D ladder-like aggregate, $K_2Na_6[Na(H_2O)Fe_2(H_2O)_8(P_5W_{30}O_{110})] \cdot 23.5H_2O$ (**1**; K_2Na_6[**1a**] $\cdot$ 23.5H_2O) has been obtained by conventional aqueous solution reaction. X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic system, space group $P2_1/m$, $a = 16.938(3)$ Å, $b = 21.396(4)$ Å, $c = 17.520(4)$ Å, $\beta = 98.14(3)°$, $V = 6285(2)$ Å^3, and $Z = 2$. Polyoxoanion **1a** shows a 1-D ladder-like chain, built up of Preyssler anion and Fe^{3+} linkers, which represents the first extended structure based on Preyssler anion and transition metal linkers. The 1-D chains in **1** are further connected into a 3-D open framework by potassium and sodium cations. Compound **1** displays electrocatalytic activity towards the reduction of nitrite.

Keywords: Preyssler anion; Ladder-like; 1-D; Polyoxometalate; Transition metal

1. Introduction

Architecturing of the extended frameworks of interest in materials chemistry stems from potential applications in catalysis, magnetism, and absorption, but also from their versatile architectures and topologies [1]. Polyoxometalates (POMs) are effective building blocks to construct extended frameworks because of their controllable shape and size, their high-negative charges, and their oxo-rich surfaces [2, 3]. POM-based extended frameworks have been reported from 1-D chain to 3-D framework [4]; commonly used POM building blocks focus on small POM clusters such as Keggin-, Anderson-, Silverton-, Lindquist-, and sandwich-type anions [5–7]. In contrast, little attention has been paid to the linkage of large POM clusters [8]. Introduction of large POM clusters into the extended structures could result in POM materials with unprecedented structures and interesting properties, owing to their different structural features and properties, such as more surface oxygens and potential coordinate sites [9]. However, the rational design and synthesis of large POM cluster-based extended structures are a challenge because of the difficulties in choosing appropriate building blocks and linking units, as well as suitable synthetic conditions.

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Preyssler anion, $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$, is a stable, large-sized POM cluster, which may be an excellent building block to construct extended materials [10]. Recently, we introduced the Preyssler anion into extended materials, and several 1-D chain and 2-D layer compounds with Nd^{3+}, Eu^{3+}, and Ce^{3+} linkers were obtained [9], demonstrating that it is possible to design and synthesize compounds with Preyssler anion as building blocks. We are trying to construct extended structures based on Preyssler polyoxoanions and transition metal linkers to introduce centers of magnetism and electrochemistry into the extended structures of functional materials. Here we report the synthesis, characterization, and crystal structure of $K_2Na_6[Na(H_2O)Fe_2(H_2O)_8(P_5W_{30}O_{110})] \cdot 23.5H_2O$, which represent the first extended framework based on Preyssler polyoxoanions and transition metal linkers.

2. Experimental

2.1. *Materials and methods*

All chemicals were purchased and used without purification. $K_{12.5}Na_{1.5}[Na(H_2O)P_5W_{30}O_{110}] \cdot 15H_2O$ was synthesized according to the literature procedure [11] and characterized by IR spectrum. P, W, Fe, K, and Na were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. IR spectrum was recorded from 400 to $4000 \, cm^{-1}$ on an Alpha Centauri FT/IR Spectrophotometer using KBr pellets. Thermal gravimetric (TG) analysis was performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of $10°C \, min^{-1}$. Electrochemical measurements were carried out on a CHI 800A electrochemical workstation at room temperature (25–30°C). A glassy carbon electrode was used as the working electrode, platinum gauze as counter electrode, and Ag/AgCl as reference electrode.

2.2. *Gel filtration chromatography*

Gel filtration chromatography was performed by using $0.4 \, M$ $CH_3COONa + CH_3COOH$ (pH = 4) elution buffer for **1** in a $40 \, cm \times 1 \, cm^2$ Sephadex G-50 (fine) column, which allows the separation of species with molecular masses from 500 to $10,000 \, g \, mol^{-1}$ (3 g). The analytical results revealed that **1** was eluted far earlier than $[P_2W_{15}Mo_2VO_{62}]^{8-}$ (ionic mass $= 4055 \, g \, mol^{-1}$) and no other species were detected after $[P_2W_{15}Mo_2VO_{62}]^{8-}$ was eluted. The results suggest that the ionic mass of **1** (ionic masses are about 7639) is much larger than that of $[P_2W_{15}Mo_2VO_{62}]^{8-}$ and even larger than the upper separation limit of Sephadex G-50 ($10,000 \, g \, mol^{-1}$). The result confirms that polyoxoanion **1** keeps its solid structure in aqueous solution.

2.3. *Synthesis*

In a typical synthesis for **1**, $K_{12.5}Na_{1.5}[Na(H_2O)P_5W_{30}O_{110}] \cdot 15H_2O$ (2 g, 0.23 mmol) and $FeCl_3 \cdot 6H_2O$ (2 g, 7.4 mmol) were dissolved in 60 mL of distilled water and 21 mL HAc (glacial acetic acid) was added dropwise with vigorous stirring, and the mixture was boiled for 1 h. On stopping heating, 10 mL of 12 M HCl (0.12 mol) was added to the

solution with stirring and boiled for 12 h. After cooling to room temperature, the solution was filtered and the filtrate was slowly evaporated at room temperature for 6 days, resulting in the yellow blocks (yield 37% based on P). Anal. Calcd for **1** (%): K, 0.93; Na, 1.92; Fe, 1.33; P, 1.85; W, 65.9. Found: K, 0.74; Na, 1.94; Fe, 1.38; P, 1.86; W, 66.2. IR (KBr pellets): 3433(m), 1615(m), 1166(m), 1085(m), 937(s), 756(s), 532(m), 465(m) cm^{-1} (Supplementary material, figure S1).

2.4. *X-ray crystallography*

Single-crystal X-ray data for **1** was collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with a normal focus 18 KW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 KV and 200 mA. Data processing was accomplished with the RAXWISH processing program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL 97 [12]. In the crystal structure, there are a number of short connections between $OW(H_2O) \cdots O(POM)$, indicating extensive H-bonding interactions. All H atoms on solvent water molecules were included directly. The crystal data and structure refinement of **1** are given in table 1.

3. Results and discussion

3.1. *Structure description*

Single-crystal X-ray diffraction reveals that the structure of **1a** is a ladder-like chain $[Na(H_2O)Fe_2(H_2O)_8(P_5W_{30}O_{110})]_n^{8n-}$, constructed from the Preyssler anion $[Na(H_2O)(P_5W_{30}O_{110})]^{14-}$ ($[P_5W_{30}]$) and Fe^{3+} ions (figure 1). $[P_5W_{30}]$ could be regarded as a pentamer composed of five $[PW_6O_{26}]$ subunits, connected by four W–O–W connecting modes resulting in a crown-type structure which possesses a doughnut-shaped cavity with a Na^+ cation residing in it. Studies have shown that the alkali metal ions in the doughnut-shaped cavity can be replaced by other ions with similar size, such as U^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, and Th^{4+}. Therefore, $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$ has been considered as a potentially useful compound in nuclear waste treatment due to its ability to selectively capture lanthanide/actinide cations from neutral aqueous solutions [13]. Alternatively, the 30 W atoms in $[P_5W_{30}]$ could be classified as axial and equatorial tungstens with 10 axial W atoms and 20 equatorial W atoms distributed in four parallel planes, two outer pentatungsten planes, and two inner decatungsten planes (figure 2). In this ladder-like chain, two Fe^{3+} ions coordinate to two neighboring $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$ polyoxoanions through four terminal oxygens from four equivalent tungstens of two inner decatungsten planes to constitute a chain-like structure (as shown in figure 2). The Fe–O bond lengths are 1.99(2) Å and 1.998(18) Å. Residual coordination sites of two six-coordinate irons are filled by water at distances of Fe–Ow, 1.989(19)–2.211(9) Å. The $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$ can be regarded as a tetradentate ligand coordinating to four $Fe(H_2O)_4^{3+}$ groups to constitute a 1-D ladder-like chain along the *c*-axis, representing the first example of an extended framework based on Preyssler anions and transition metal linkers. Polymeric chains of $[Na(H_2O)Fe_2(H_2O)_8(P_5W_{30}O_{110})]_n^{8n-}$ are further connected by potassium and sodium

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$H_{65}Fe_2K_2Na_7O_{142.5}P_5W_{30}$
Formula weight	8366.70
Wavelength (Å)	0.71073
Temperature (K)	150(2)
Crystal size (mm^3)	$0.31 \times 0.14 \times 0.13$
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions (Å, °)	
a	16.938(3)
b	21.396(4)
c	17.520(4)
β	98.14(3)
Volume ($Å^3$), Z	6285(2), 2
Calculated density ($mg\,m^{-3}$)	4.421
Absorption coefficient (mm^{-1})	27.831
$F(000)$	7334
θ range for data collection (°)	3.00–25.00
Measured reflections	45,165
Independent reflections	10,939
Data/restraints/parameters	10,939/320/833
R_{int}	0.0959
$R_1(I > 2\sigma(I))^a$	0.0812
wR_2 (all data)^a	0.2453
Goodness-of-fit on F^2	1.161

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.
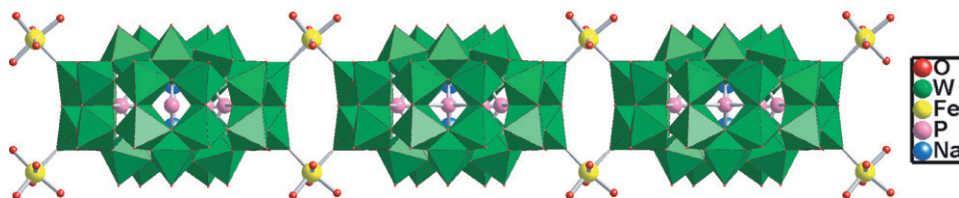
Figure 1. Chain structure of polyoxoanion **1a**.

cations into a 3-D framework (figure 3). The oxidation states of Fe and W sites were determined based on the bond lengths and angles and the bond valence sum (BVS) calculations (The valence sum calculations are performed on a program of bond valence calculator, version 2.00 on February 1993, written by C. Hormillosa with assistance from S. Healy distributed by I.D. Brown). Results indicate that all Fe and W sites are +3 and +6, respectively (table S1).

3.2. *Thermal analyses*

To examine the thermal stability of **1**, TG analyses were carried out. Compound **1** shows two continuous weight loss steps from 40 to 430°C, attributed to the loss of all lattice and coordinated water (figure S2). The total weight loss is 8.2%, a little higher than the calculated value of 7.21%. Fourier maps showed 25.5 lattice water molecules during refinement; however, there are still large accessible voids in the crystal structure,
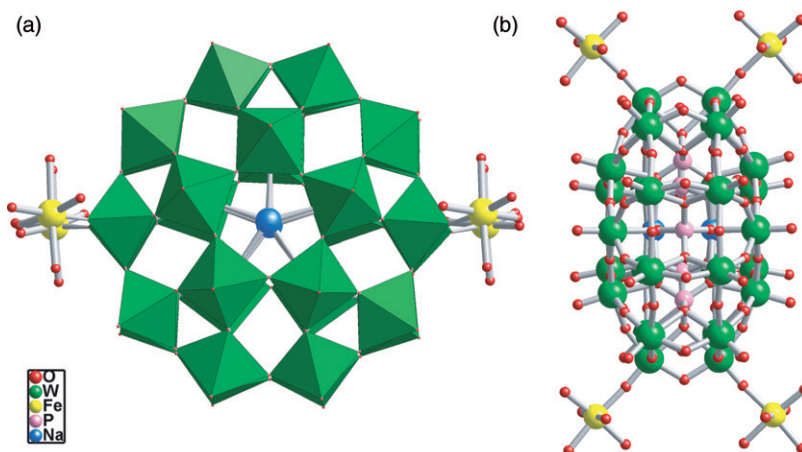
Figure 2.   (a) Polyhedral representation of $[Na(H_2O)(P_5W_{30}O_{110})]^{14-}$ subunit and Fe^{3+} linkers. (b) Ball-and-stick representation of $[Na(H_2O)(P_5W_{30}O_{110})]^{14-}$ subunit and Fe^{3+} linkers.
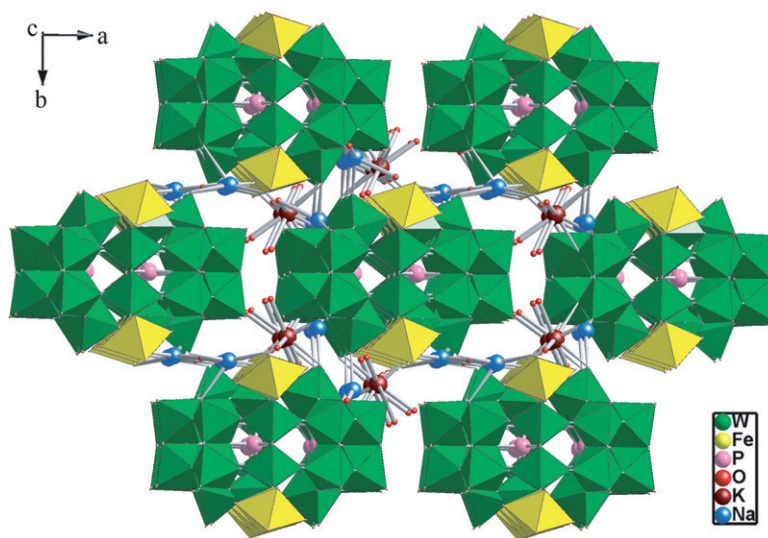
Figure 3.   View of the 3-D framework along the *c* axis.

indicating that more water could exist in the structure, but cannot be found from the weak residual electron peaks.

3.3. *Aqueous solution stability and electrochemistry*

The aqueous solution stability of **1** has been investigated. Polyoxoanion **1** was dissolved in a pH = 4 (0.4 M $CH_3COONa + CH_3COOH$) buffer solution and kept at room temperature. The cyclic voltammetric behavior of the solution was detected every 6 h for six times. The solution showed no voltammetric change (figure S3). Further, the

Figure 4. Cyclic voltammograms of **1** in a pH = 4 (0.4 M CH$_3$COONa + CH$_3$COOH) buffer solution at different scan rates (from inner to outer: 20, 50, 100, 120, 150, 200, 250, and 300 mV s^{-1}).

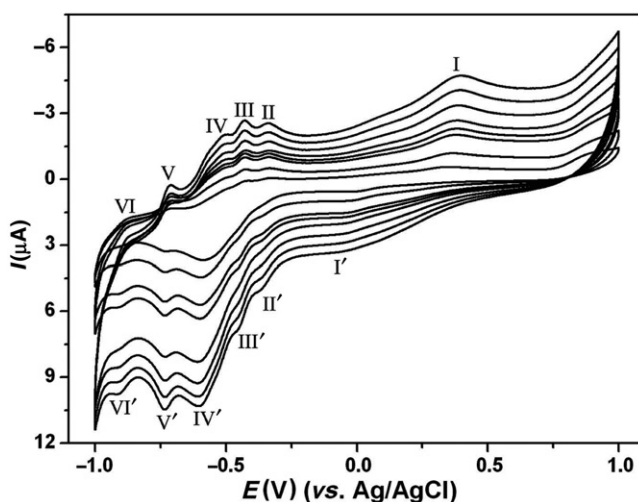UV-Vis spectrum of the above solution was checked simultaneously and no changes were observed (figure S4). These characterizations indicate that **1** is structurally stable in the pH = 4 (0.4 M CH$_3$COONa + CH$_3$COOH) buffer solution. Gel filtration chromatography experiments confirm that **1** is stable in buffer solution.

The electrochemical behavior of **1** and its electrocatalytic reduction of nitrite were investigated by cyclic voltammetry (CV). Figure 4 shows typical cyclic voltammetric behaviors of **1** in a pH = 4 (0.4 M CH$_3$COONa + CH$_3$COOH) buffer solution. In the potential range of +1.0 to −1.0 V, six reduction peaks were observed with the mean peak potentials at −0.064 V, −0.357 V, −0.445 V, −0.601 V, −0.733 V, and −0.903 V (*vs.* the Ag/AgCl reference electrode). The reduction peak located at −0.064 V and its oxidation counterpart at +0.400 are attributed to redox of Fe^{3+} [14]. The five redox peaks in the negative domain and the mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are −0.344 V (II–II′), −0.435 V (III–III′), −0.552 V (IV–IV′), −0.720 V (V–V′), and −0.890 V (VI–VI′) (*vs.* Ag/AgCl) corresponding to redox of the W^{VI} in the polyoxoanion framework, as observed in other polytungstates [14, 15]. The effect of scan rates (*v*) on the peak currents (i_{pa} and i_{pc}) has been investigated from 20 to 300 mV s^{-1}. Taking redox peak (I) as representative, the relationship between the anodic and cathodic peak currents and the scan rates are linear at scan rates lower than 120 mV s^{-1}, indicating that the electrode process is surface-controlled at lower scan rates [16]. However, at higher scan rates (150, 200, 250, and 300 mV s^{-1}) the i_{pa} and i_{pc} values are linearly dependent on the square root of the scan rate ($v^{1/2}$), indicating that the electrode process is diffusion controlled.

Polyoxoanion **1a** displays electrocatalytic activity toward reduction of nitrite. Upon the addition of modest amounts of nitrite, the reduction peak currents at the potential domain of tungsten increase dramatically (figure 5). In the explored potential domain, no reduction of nitrite could be obtained in the absence of POM, indicating that the reduced species of **1** have electrocatalytic activity for nitrite reduction.
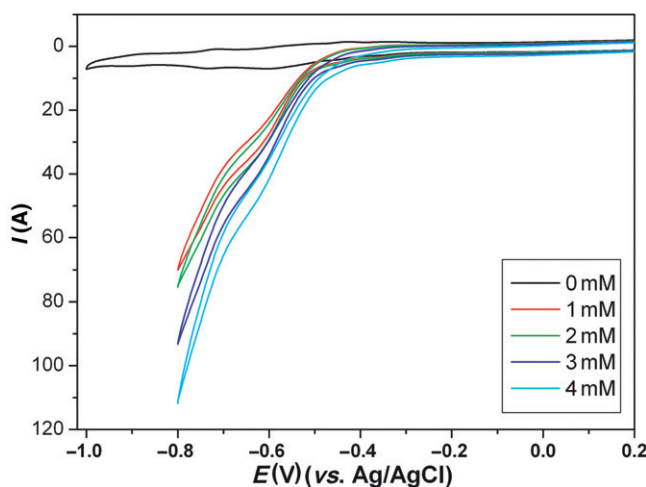
Figure 5. Electrocatalysis of the reduction of NO^{2-} in a pH $= 4$ (0.4 M $CH_3COONa + CH_3COOH$) buffer solution at a scan rate of $150\,mV\,s^{-1}$. The legends correspond to NO_2^- concentrations with unit mmol.

4. Conclusion

The reaction of $K_{12.5}Na_{1.5}[Na(H_2O)P_5W_{30}O_{110}] \cdot 15H_2O$ and $FeCl_3 \cdot 6H_2O$ under routine synthetic conditions in aqueous solution afforded a new polyoxotungstate. The synthesis of **1** offers the first extended framework constructed from Preyssler anion and transition metal linkers and confirms that large POM clusters can be building blocks. The electrochemical properties of **1** reveal that **1a** is stable at pH $= 4$ (0.4 M $CH_3COONa + CH_3COOH$ buffer solution) and the reduced species of **1** has electrocatalytic activity for nitrite reduction.

Supplementary material

TG curves, IR spectra, additional figures, and X-ray crystallographic information file (CIF) are available for **1**. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; Email: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-419860.

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