Synthesis, characterization and properties of ruthenium-substituted polyoxometallic acid $\text{H}_6\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39} \cdot 18\text{H}_2\text{O}$ with Keggin structure

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Received October 28, 2010; accepted January 7, 2011

The ruthenium-substituted polyoxometallic acid $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$ was synthesized by stepwise acidification and stepwise addition of solutions of the component elements, and an ion-exchange-cooling method. The product was characterized using inductively coupled plasma spectrometry (ICP), Infrared Spectroscopy (IR), Ultraviolet Spectroscopy (UV), and X-ray diffraction (XRD). The results show that this complex has the Keggin structure. The determination of the thermal stability and proton conductivity of this polyoxometallic acid was carried out by a thermogravimetric-differential thermal analysis (TG-DTA) and electrochemical impedance spectroscopy (EIS).

ruthenium, polyoxometallic acid, Keggin structure, synthesis, characterization

Citation: Xu S X, Wu X F, Wu Q Y, et al. Synthesis, characterization and properties of ruthenium-substituted polyoxometallic acid $\text{H}_6\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39} \cdot 18\text{H}_2\text{O}$ with Keggin structure. Chinese Sci Bull, 2011, 56: 2679–2682, doi: 10.1007/s11434-011-4490-3

In recent years, polyoxometallic acids and their salts, which have a unique molecular structure and are easy to design and assemble, have been widely used as new and efficient catalysts, supramolecular materials, magnetic materials, photochromic materials, electrochromic materials, high-quality sub-conductors, selective electrodes, recording materials, and in gas equipment, drugs, and fuel cells [1–9]. Complexes containing the precious metal ruthenium have excellent reactivity and selectivity in many catalytic oxidations of organic compounds. Ruthenium complexes with anti-tumor activity have low toxicity. Few studies have investigated polyoxometallic acids and their salts containing ruthenium and have only recently attracted much interest [10]. Therefore, research on the synthesis, characterization, properties, and applications of new polyoxometallic acids and their salts containing ruthenium is a major challenge. We report the synthesis, characterization, and properties of the new

ruthenium-substituted polyoxometallic acid $\text{H}_6\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39} \cdot 18\text{H}_2\text{O}$ in this paper.

1 Experimental

1.1 Instruments and reagents

The purity of the copper powder was 200 meshes. $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with $\text{Ru} \geq 37\%$ was used, purchased from Xi'an catalyst chemical Co., Ltd. All other reagents were of reagent grade, purchased from China medicine (Group) Shanghai chemical reagent company.

IR spectra were recorded on a Nicolet Nexus 470 spectrometer (America Thermo Nicolet Company) in the range $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets. Elemental analyses were carried out using an 8410 inductively coupled plasma (ICP) spectrometer (Australia Labtam Company). UV spectra were measured on a UV-2550 spectrophotometer (Japan Shimadzu

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Company) in the range 190–400 nm. TG-DTA was carried out on a STA-409 thermal analyzer (Germany NETZSCH Instruments Manufacturing Co., Ltd) in a dynamic nitrogen atmosphere with a temperature increase rate of $10^{\circ}\text{C min}^{-1}$. Impedance measurements were performed on a VMP2 electrochemical impedance analyzer (America Princeton Applied Research Company) with copper electrodes over the frequency 0.01 Hz to 99.9 kHz. $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$ was pressed into tablets 10 mm in diameter and 3.74 mm in thickness under a pressure of 15 MPa at room temperature (22°C) and a relative humidity of 75%. A copper sheet was attached to each side of the tablet. The proton conductivity was measured using a copper | sample | copper cell.

1.2 Preparation and processing of raw materials

(1) Preparation of RuCl_3 solution. $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (5.46 g) was dissolved in water in a 100 mL flask and diluted to the scale to give a 0.02 mol L^{-1} aqueous solution of RuCl_3 .

(2) Treatment of cation-exchange resin. The cation-exchange resin was washed several times with deionized water until the pH value was the same as that of the deionized water, and then bottled.

(3) Synthesis of $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (18.1 g; 0.055 mol) was dissolved in 100 mL of water and the pH of the solution was adjusted to 6.3 with acetic acid. The solution was then heated to boiling and a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.02 g; 0.005 mol) in 30 mL of hot water was added dropwise with stirring. After 30 min, 50 mL of a solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (1.37 g; 0.005 mol) was added dropwise. The pH was readjusted to 5.0 and stirring was continued for 1.5 h. After cooling, grayish brown oil was obtained by adding absolute ethanol. The oily product was extracted three times by the dissolving-cooling method. The obtained oil was dissolved in 80 mL of water and the solution was passed through an Amberlite IR-120 cation-exchange column in H^+ form until the pH was less than 1. Finally, the solid acid was separated by the cooling method. The final yield was about 60.9%, based on W.

2 Results and discussion

2.1 Elemental analysis

Ruthenium, iron, and tungsten were analyzed using ICP spectrometry. The water content was determined by thermogravimetry. Found: Ru, 3.18%; Fe, 1.73%; W, 64.36%; H_2O , 10.69%. Calculated for $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$: Ru, 3.21%; Fe, 1.77%; W, 64.18%; H_2O , 10.85%.

2.2 IR spectra

The infrared spectra and crystal structures of the 1:11 series of polyoxometallic acids $\text{H}_n\text{M}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$ and the 1:12

series of Keggin polyoxometallic acids are similar.

The $[\text{M}(\text{H}_2\text{O})\text{XW}_{11}\text{O}_{39}]^{n-}$ anion (Keggin structure) consists of one XO_4 tetrahedron surrounded by 4 W_3O_{13} sets formed by 3 edge-sharing octahedra. The W_3O_{13} sets are linked by oxygen atoms. Thus, there are 4 kinds of oxygen atoms in $[\text{M}(\text{H}_2\text{O})\text{XW}_{11}\text{O}_{39}]^{n-}$: 4 $\text{X}-\text{O}_a$ groups, in which the oxygen atoms are connected to a heteroatom (X), 12 $\text{W}-\text{O}_b-\text{W}$ oxygen bridges (corner-sharing oxygen bridges between different W_3O_{13} sets), 12 $\text{W}-\text{O}_c-\text{W}$ oxygen bridges (edge-sharing oxygen bridges within W_3O_{13} sets) and 11 $\text{W}-\text{O}_d$ terminal oxygen atoms [11].

In the IR spectrum of $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$ (Figure 1), there are 4 characteristic bands: 957.53 cm^{-1} , $\nu_{\text{as}}(\text{W}-\text{O}_d)$; 879.40 cm^{-1} , $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$; 769.47 cm^{-1} , $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$; 503.34 cm^{-1} , 441.63 cm^{-1} , $\nu_{\text{as}}(\text{Fe}-\text{O}_a)$ or $\delta(\text{O}-\text{Fe}-\text{O})$ [12].

Comparing the 4 characteristic bands of the IR spectra of $\text{H}_6[\text{Al}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 14\text{H}_2\text{O}$ and $\text{H}_6[\text{In}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 10\text{H}_2\text{O}$ (Table 1) shows that the $\nu_{\text{as}}(\text{W}-\text{O}_d)$ bands of the 3 acids shift to a lower wavenumber and the $\nu_{\text{as}}(\text{W}-\text{O}_a)$ bands shift to a higher wavenumber as the ionic radius increases from Al^{III} (0.05 nm) to Ru^{III} (0.077 nm) to In^{III} (0.081 nm).

In the high wavenumber region, there are two absorption peaks at 3448.16 cm^{-1} (ν_{OH} modes) and 1624.80 cm^{-1} (δ_{OH} modes) associated with the OH modes (the stretching vibration ν and bending vibration δ) of the acidic hydroxyls and water molecules; the latter absorption peak indicates the presence of H_3O^+ (Brønsted acid).

2.3 UV spectrum

Crystals of the 1:11 series of polyoxometallic acids $\text{H}_n\text{Ru}-$

Figure 1 IR spectrum of the complex.

Table 1 IR spectral data for polyoxometallic acids (cm^{-1})

	ν_{as} ($\text{W}-\text{O}_d$)	ν_{as} ($\text{W}-\text{O}_b-\text{W}$)	ν_{as} ($\text{W}-\text{O}_c-\text{W}$)	ν_{as} ($\text{Fe}-\text{O}_a$)
$\text{Al}(\text{H}_2\text{O})\text{FeW}_{11}$	962	893	784	474
$\text{In}(\text{H}_2\text{O})\text{FeW}_{11}$	956.54	883.25	777.18	565.10
$\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}$	957.53	879.40	769.47	503.34

(H₂O)XW₁₁O₃₉ have two characteristic strong absorption bands in the UV region. The higher energy peak and the lower energy peak were generated by charge-transfer transitions of the side oxygen atoms, O_d→W, and charge-transfer transitions of the bridging oxygen, O_b/O_c→W, respectively [13].

In the UV spectrum of the target complex (Figure 2), there are two characteristic bands: 200.00 nm, O_d→W, and 262.00 nm, O_b/O_c→W.

2.4 X-ray powder diffraction

The X-ray powder diffraction pattern of H₆[Ru(H₂O)-FeW₁₁O₃₉]·18H₂O is shown in Figure 3, and X-ray powder diffraction data are listed in Table 2.

In each of the four 2θ ranges, i.e., 7°–10°, 16°–22°, 25°–30°, and 33°–38°, the patterns were similar to those of complexes with the Keggin structure [1]. The X-ray diffraction data, combined with IR and UV spectra, confirm that H₆[Ru(H₂O)FeW₁₁O₃₉]·18H₂O has the Keggin structure (Figure 4).

2.5 Thermal analysis

Figure 5 shows the thermogram of H₆[Ru(H₂O)FeW₁₁O₃₉]·18H₂O in a nitrogen atmosphere. The TG curve shows that

Figure 2 UV spectrum of the complex.

Figure 3 XRD pattern of the complex.

Table 2 X-ray powder diffraction data for the complex

2θ (°)	d(nm)	I/I ₀
8.42	1.050	100
9.22	0.959	71.47
10.60	0.835	44.71
17.36	0.511	33.81
18.80	0.472	32.69
23.24	0.383	36.36
25.26	0.352	36.88
26.86	0.332	50.35
27.94	0.319	46.30
29.12	0.307	39.44
31.08	0.288	41.95
33.26	0.269	47.71
34.36	0.261	37.62
36.24	0.248	32.48
38.18	0.236	33.04

Figure 4 Schematic diagram of the tripolyoxometallic acid structure. The Ru^{III} ion, which is in the upper left-hand corner, is depicted as a darker sphere with a terminally coordinated H₂O molecule. The Fe^{III} heteroatom resides in a central pseudo-tetrahedral hole in the structure and is the dark central atom.

Figure 5 Thermogram of the complex.

the total percentage weight loss was 10.47%, which indicates that each product molecule has 19 molecules of water, and that there are three weight-loss steps. The first step is the loss of 16 molecules of hydration water, the second step

is the loss of two molecules of protonated water, and the third step is the loss of one molecule of structural water. Thus, the precise molecular formula of the product is $(\text{H}_5\text{O}_2^+)\text{H}_5[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 16\text{H}_2\text{O}$.

In the DTA curve, the exothermic peak of the product at 422.8°C is clearly smaller than that of $\text{H}_6[\text{Al}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ at 470°C , this is related to the respective ionic radii of Ru and Al [14].

2.6 Conductivity

Electrochemical impedance spectroscopy is a frequency domain measurement method which measures the impedance over a very wide frequency range to study electrode systems. This is a better method than other conventional electrochemical methods because more information can be obtained. We recorded the results of complex impedance measurements for the polyoxometallic acid (the frequency range was 0.01 Hz to 99.9 kHz) at room temperature (Figure 6). The resistance of the product can be obtained by electrochemical impedance spectroscopy analysis of an equivalent circuit, and then converting to the corresponding conductivity: $\sigma = L/(R \times S)$ (L is thickness, S is cross-sectional area) [15].

The calculation shows that at room temperature (22°C), the conductivity of $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$ is $4.51 \times 10^{-3} \text{ S/cm}$, this shows that the product is a solid high-proton conductor.

3 Conclusion

The ruthenium-substituted polyoxometallic acid $\text{H}_6[\text{Ru}(\text{H}_2\text{O})-$

Figure 6 EIS of the complex at 22°C .

$\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$, a new solid high-proton conductor, was synthesized for the first time and was characterized. We determined the conductivity of $\text{H}_6[\text{Ru}(\text{H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O}$ by the electrochemical impedance spectroscopy. It is $4.51 \times 10^{-3} \text{ S/cm}$ at room temperature (22°C).

This work was supported by the National Natural Science Foundation of China (21071124), the Foundation of Jiangxi Educational Committee (GJJ09310), and the Foundation of the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University (2010-16).

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