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

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The ruthenium-substituted polyoxometallic acid \( \text{H}_6[\text{Ru(H}_2\text{O})\text{FeW}_{11}\text{O}_{39}] \cdot 18\text{H}_2\text{O} \) 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

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 \( \text{H}_6\text{Ru(H}_2\text{O})\text{FeW}_{11}\text{O}_{39} \cdot 18\text{H}_2\text{O} \) 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 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 400–4000 cm\(^{-1}\) using KBr pellets. Elemental analyses were carried out using an 8410 inductively coupled plasma (ICP) spectrometer (Australia Labtarm Company). UV spectra were measured on a UV-2550 spectrophotometer (Japan Shimadzu).
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°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.

The obtained oil was dissolved in 80 mL of water and the solution was passed through an Amberlite IR-120 cation-exchange resin was washed several times with deionized water until the pH was less than 1.

The obtained oil was dissolved in 80 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 Fe(NO₃)₃·9H₂O (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 RuCl₃·nH₂O (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 RuCl₃.

Finally, the solid acid was separated by the cooling method.
(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 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

| 2θ (°) | d(nm) | I/I₀ |
|--------|-------|------|
| 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 2 UV spectrum of the complex.

Figure 3 XRD pattern of the complex.

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

Figure 5 Thermogram of the complex.
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 (H₂O₂)₃H₆[Ru(H₂O)FeW₁₁O₃₉] · 16H₂O.

In the DTA curve, the exothermic peak of the product at 422.8°C is clearly smaller than that of H₆[Al(H₂O)FeW₁₁O₃₉] · 4H₂O 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: \( \sigma = \frac{L}{R \times S} \) (L is thickness, S is cross-sectional area) [15].

The calculation shows that at room temperature (22°C), the conductivity of H₆[Ru(H₂O)FeW₁₁O₃₉] · 18H₂O is 4.51 × 10⁻³ S/cm, this shows that the product is a solid high-proton conductor.

3 Conclusion

The ruthenium-substituted polyoxometallic acid H₆[Ru(H₂O)]FeW₁₁O₃₉·18H₂O, a new solid high-proton conductor, was synthesized for the first time and was characterized. We determined the conductivity of H₆[Ru(H₂O)FeW₁₁O₃₉] · 18H₂O by the electrochemical impedance spectroscopy. It is 4.51 × 10⁻³ S/cm at room temperature(22°C).

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