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钌取代的钨锗和钨硼杂多化合物的合成与表征

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本文合成了 Keggin 结构的[GeW11O28(Ru・OH2)]⁵⁻和[BW11O28(Ru・OH2)]⁵⁻杂多阴离子的四 丁基铵盐。通过紫外-可见、红外光谱、核磁共振、顺磁共振和循环伏安法对上述化合物进行了表征。 结果表明 Ru(I)处于一个八面体弱场中、Ru(I)的顺磁性和核四级矩对¹⁴⁸W 的化学位移和强度有 明显的影响,其电化学还原与 W(N → V)相关。Ru(I)填充了缺位杂多阴离子的空位、但仍然保持 Keggin 结构。 关键词: <u>钌</u> 取代型款多钨酸盐 ¹⁸¹W 核磁共振

SYNTHESIS AND CHARACTERIZATION OF THE GERMANIUM AND BORON-CENTERED POLYTUNGSTORUTHENATE

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The syntheses and characterization of organic solvent soluble new tetra- π -butylammonium salts of $[GeW_{11}O_{39}(Ru \cdot OH_2)]^{8-}$ and $[BW_{11}O_{19}(Ru \cdot OH_2)]^{8-}$ are reported. UV-Vis and IR spectra confirm that the ruthenium cation has occupied the lacuna site of the precursor polyoxoanions, and the structure of these substituted derivatives maintains the Keggin type. The sensitive changes in ¹⁸³W NMR, which caused by the paramagnetism and nuclear quadrupolar moment of ruthenium, are discussed in detail. The octahedral weak field coordination of the ruthenium cation, as indicated by EPR, is consistent with the data from UV-vis spectra. The substituted polyanions display two reversible one-electron redox waves in acetonitrile, which are ascribed to the W(N \rightarrow V) process of tungsten-oxo framework.

183W NMR

Keywords: ruthenium substituted heteropolytungstate

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0 Introduction

Heteropoly complexes resemble discrete fragments of metal oxide structures of definite sizes and shapes. They maintain their identities in aqueous and nonaqueous solutions as well as in ionic crytals. Many heteropoly complexes which contain various combinations of d-transition metals at specific sites have been synthesized. In recent years considerable attention has been directed towards the chemistry and potential applications of heteropolyanions, especially with respect to catalysis^[1]. One particular exciting development concerning the use of polyoxoanions of the Keggin type $[XW_{11}O_{39}M \cdot (OH_2)]^{n-1}$ is the "surface" M atom can be dehydrated and become coordinately unsaturated. The resulting anion $[XW_{11}O_{39}M]^{n-1}$ is quite reactive and then considered as an inorganic metalloporphyrin analogue. Neumann and Abu-Gnim have demonstrated hydrocarbon oxidation starting with a polyoxotungstate having the composition of $[SiW_{11}O_{39}Ru \cdot (OH_2)]^{s-}$ and a verity of oxidants^[2]. Rong and Pope have studied the redox properties and atom-transfer reactivity of the $[PW_{11}O_{39}Ru \cdot (OH_2)]^{4-}$ anion^[3]. Polyoxoanions which contain ruthenium element also bring additional interest for two reasons: because of the activation of dioxygen by these metallopotphytin and other complexes and because of the rich and extensive multielectron redox chemistry displayed by ruthenium^[4]. Herein we report the synthesis, $1s_{1}$ lation and characterization of two ruthenium-substituted Keggin type complexes $\alpha = \int XW_{11}O_{39}Ru$ • (OH_2) ^{[a-}, where X = Ge and B. These complexes have been characterized by elemental analysis, IR, UV-vis, CV, EPR and ¹⁸³W NMR. Although these complexes are based on the well-known monosubstituted Keggin anion, we are in the process of exploring some of these species in more detail, with emphasis on those that might be expected to display significant redox and potential catalytic activity.

1 Experiment

1.1 Reagents

The lacunary salts of a-K₃GeW₁₁O₃₉ • 13H₂O and a-K₉BW₁₁O₃₉ • 10H₂O were prepared according to the literature^{15]} and identified by IR spectra. Analytical grade n-Bu₄NBr, n-Bu₄NClO₄, CH₃CN, CD₃CN and RuCl₃ • xH₂O(Ru; 37.0%) from commercial source were used without further purification.

1.2 Synthesis

1.2.1 $a_{-}(Bu_{1}N)_{5}GeW_{11}Ru(OH_{2})O_{39}$

To a stirring solution of 3. 2 g(1.0 mmol) of α -K₈GeW₁₁O₃₉ · 13H₂O in 20 mL of hot water was added dropwise a solution of 0. 30 g RuCl₃ · xH₂O (1.1 mmol, 10 mL). The solution was maintained at 90 °C with stirring for about 30 min, then the suspension was cooled to about 50 °C and filtered, leaving a brown product on the filter. Addition a solution of 2.0 g (6.2 mmol) *n*-Bu₄NBt in 10 mL water to the lukewarm filtrate with vigorous stirring provoked the immediate precipitation of a black ruthenium substituted heteropolytungstate salt. The yield was about 70% based on the lacunary polyanion. Elemental analysis calculated (found): C:23.72% (23.59); H: 4.50% (4.33); N;

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1.73%(1.65); Ge: 1.79%(1.83); W: 49.95%(48.97); Ru: 2.50%(2.60); H₂O: 0.44% (0.50). UV-vis(λ_{max} nm, CH₃CN): 263(lge~4); 465(lge~2). ¹⁸³W NMR(δ in ppm, CH₃CN/ CD₃CN): -39.6, -84.7, -89.5, -109.5.

1.2.2 $a_{-}(Bu_4N)_{5}BW_{11}Ru(OH_2)O_{39}$

Since the relative instability of the BW₁₁O⁸₃₀ anion, the order of addition was inversed. To a hot (90 C) solution of 0. 30 g(1.1 mmol) RuCl₃ · xH₂O in 20 mL water was added in one time 3. 2 g (1.0 mmol) of α -K₀BW₁₁O₃₉ · 10H₂O with vigorous stirring. For about 30 min the solution was cooled to ca. 50 C and filtered off the remaining solid (a mixture of paradodecatungstate which was unavoidable impurity contained in the K₉BW₁₁O₃₀ salt, and a brown product). To the lukewarm filtrate was added 2.0 g(6.2 mmol) n-Bu₄NBr in 10 ml water with vigorous stirring, leaded to precipitate a black salt of ruthenium substituted heteropolytungstate. The precipitate was filtered and washed with water, then recrystallized from acetonitrile. The yield was about 60% based on the lacunary polyanion. Elemental analysis calculated (found); C: 27.25% (27.18); H: 5.16% (5.02); N: 1.99% (1.91); B: 0.26% (0.28); W: 47.82% (47.66); Ru: 2.39% (2.45); H₂O; 0.43 (0.50). UV-vis(λ_{max} nm, CH₃CN); 257 (lge~4); 485(lge~2). ¹⁸³W NMR (δ in ppm, CH₃CN/CD₃CN); -52.1, -78.4, -89.2, -112.3.

1.3 Physical Measurements

The elemental analysis was performed on a Perkin-Elmer 240C Analyzer. The number of H_2O was identified by a LCT-2 thermogravimetric analyzer (Beijing Optical Instrument Factory). Atomic absorptions were obtained on a Jarrell-Ash Division Atomscan 2000 ICP Analyzer. UV-visible spectra were measured from 190 nm to 700 nm on a Shimadzu UV-240 spectrophotometer in acetonitrile solution using 1.0 cm quartz cells. IR spectra were recorded on a TJ270-30 IR spectrophotometer using KBr pellets. Cyclic voltammetry were carried out by 0.5 mmol $\cdot 1^{-1}$ of sample in 0.1 mmol $\cdot 1^{-1}$ n-Bu₄NCIO₄ acetonitrile solution from ± 0.5 V to ± 1.5 V at room temperature on MF-1A Potentiostat (Jiangsu Electroanalysis Instrument Factory), the working eletrode was glassy carbon and all potentials were measured relative to a silver chloride-coated silver wire reference electrode, the auxiliary electrode was Pt wire and the scan rate was 50 mV $\cdot s^{-1}$ X-band EPR spectra were registered on a Bruker ER200D-SRC spectrometer at 100K and g-values were determined by calibration to DPPH. ¹⁸³ W NMR spectra were run on a Bruker MSL-300 NMR spectro-meter in CH₃CN/CD₃CN at 20 C, operating at 7.05T (300.13 MHz for proton), resonance frequencies were 12.51 MHz of ¹⁸³W with 10 mm tubes. Chemical shifts were given with respect to saturated Na₂WO₄ in D₂O and the positive chemical shift was referred to downfield.

2 Results and Discussion

For the commercial available "RuCl₃ • xH₂O" is known to be a mixture of Ru^{*} and Ru^{*} complexes^[6], therefore the separation of Ru^{*}-and Ru^{*}-substituted derivative is crucial to synthesis. The Ru^{*} cation is proved to form the oxo-bridge-dimer anion $[O{Ru[*]Cl(\alpha_2-P_2W_{17}O_{61})}_2]^{16-}$ when the commercial "RuCl₃ • xH₂O" solution reacts with analogous lacunary precursor α_2 -P₂W₁₇O₆₁ in the similar con-

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describe here^[4]; however, Ru the cation forms monomer anion dition as we $[P_2W_{(i}O_{bi}Ru^{1}(OH_{i})]^{i-}$ only^{(3]}. The similarities of the lacunary precursor $[P_2W_{(i}O_{bi}] + 10 - and$ $[GeW, O_{35}]^{\epsilon_1}$ as well as $[BW_{\epsilon\epsilon}O_{35}]^{s_1}$, lead us to presume that the analogous oxo-bridge-dimer of Ru^k-substituted derivatives also may exist in our synthesis process (the brown product on the filter, see Experiment Section), and the ion-charge of dimer polyanion is much higher than that of the relative monomer. Therefore, the temperature dependence of solubility curve of the mono-or dimer species may be used to separate the Ru^{μ} -and Ru^{μ} -substituted derivatives. The ultimate goal of these syntheses and characterization studies is to prepare pure $XW_{t1}O_{15}(Ru^1 \cdot OH_2)^{n-1}$ as their organic solvent soluble $n-Bu_4N^+$ salts, because most catalysis reactions are carried out in the organic phase.

The UV-vis spectra of both ruthenium-substituted compounds are characterized by a strong absorption band at about 260 nm and a weak shoulder band at about 460~490 nm, respectively. (see Experiment Section) The maximum at about 260 nm is attributed to the O→W charge-transfer band, almost identical with that of the parental lacunary compounds, which infers the expected Keggin structure of the substituted derivatives. The lower energy band at about 460~490 nm probably corresponds to a ${}^{t}T_{26} \rightarrow {}^{1}A_{8}$ transition of Ru³⁺ and indicates an approximate octahedral weak field coordination of the ruthenium cation in the pseudo-porphyrin environment^[7].

The infrared spectra of ruthenium-substituted derivatives are similar to those of the first row transition-metal-substituted homologues. Their spectra data in the X-O and W-O stretching region are summarized in Table 1, along with those of α -[BW₁₂O₄₀]⁶⁻, α -[GeW₁₂O₁₀]⁴⁻ and α -[GeW₁₁O₃₆]⁶⁻ anions as their Bu₄N⁺ salts. The similarity of the spectra of all 12-nucleate anions strongly indicates that they have the same structure as α -[GeW₁₂O₄₀]⁴⁻ (Figure 1). The lacunary anions such as [GeW₁₁O₃₉]⁶⁻ are known to have the same structure minus a WO⁴⁺ group from one of the four W₃O₁₃ units. Compare with the lacunary precursor, the whole structure becomes integral again after the vacancy is inserted by a transition metal cation, which caused the disappearance of v(W-O₆-O) splittung.

compound	$v(X - O_{i})$	$v(W - O_d)$	$v(W - O_b - W)$	v(W-O_e0)
a-GeW ₁₂ O ₃₀ [1]	830(vs)	965(s)	895(vs)	780(vs)
ά- Ge₩ λ[O ₃₉	848(vs)	958(s)	884(vs)	796(s), 716(s)
a-GeW(IO₃9Ru	832(vs)	964(s)	886(vs)	786(vs)
a-BW10010[1]	900(s)	950(s)		B17(vs)
a-BW _{ℓ1} O ₃₉ Ru	900(s)	948(s)		826(vs)

Table 1 Infrared Data for Ge-and B-centered Heteropolyanions (cm^{-1})

The 185 W NMR results also confirm the incorporation of the ruthenium atom in the polyoxoanions by refilling the lacuna. (Figure 2) Since the *mono*-substituted α -Keggin derivative displays the anticipated C_s structure, therefore six possible resonances would be expected in the 183 W NMR spectrum. We note that only four of the six possible lines appear in the 183 W NMR spectra of these ruthenium-substituted derivatives, and the relative intensity of the lines for tungsten nuclei does not coincide with the number of the tungsten atoms. The substitution of ruthenium atom is responsible for the changes of 183 W NMR spectra. The signals from the four tungsten nuclei in sites adjacent to the ruthenium atom are not 第3期

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observed. presumably owing to their signals having been broadened into nonobservation. Both the paramagnetic Ru³⁺ cation and the nuclear quadrupolar moment of ³⁹Ru, ¹⁰¹Ru can provide a strong mechanism for the rapid telaxation of the ¹⁸³W nuclei closest to the substituted Ru atom^[3,9]. As a result of short relaxation time, the lines for those W's should became broad and eventually could not be observed; furthermore, they should be highly deshielded, since the *d*-electrons of $\mathbb{R}u^{3+}$ delocalize partially into vacant d-orbitals of the adacent tungsten atoms^[4], which cause an increase in electronic anisotropy of W's near the substituted site and produce a counterbalancing downfield Fig. 1 shift for the resonances of those tungstens^[9]. On the other hand, relaxation time of the other tungsten nuclei which are not directly adjacent to the ruthenium atom in polyanion also would be shortened to some extent consequently, based on the distance between these tungsten nuclei and substituted ruthenium atom. The resonance signals are therefore also partial broadened while the relative intensities of lines should decrease as a result of shortened relaxation time. Unfortunately, our hope to solve the number of tungsten nuclei just by studying the relative intensities of lines in ¹⁸³ W NMR



Structure of α -XW₁₃O₄₀^{r=} (Keggin structure). Each vertex of a polyhedron locates the center of a close-packed O atom. The X atom is located at the interior (hatched) tetrahedra. Every octahedron contains a W atom. There are four kinds of oxygen atom in this structure, which are labeled with O_a , O_b , O_c , O_d respectively. The a-XW₁₁ O_{39}^{n-} has a structure identical with that illustrated except that one W atom (labeled "v" in the figure) and its unshared O atom have been removed from the threefold W_3O_{13} cap on the top of the complex. The structurally unique W in 11tungsto derivatives is labeled "u" in the figure. Each member of a pair of structurally equivalent W's in the 11-tungsto derivatives is designated by a given letter, identical for those two W's.

pattern is vanished, since it is difficult to obtain the accurate relaxation time for each kind of tungsten nuclei in polyanion. Further discussion of the ¹⁸³ W NMR line broadening and chemical shifts, although tempting, is not warranted because the assignments of tungsten signals in the paramagnetic species would have to be very speculative^[10]. Finally, our observation is consistent with Rong and Pope's phenomenon in ¹⁸³W NMR of $[PW_{11}O_{30}(Ru \cdot OH_2)]^{4-}$.

The EPR spectra of both ruthenium-substituted derivatives in acetonitrile solution show a peak at $g_{\perp} = 2.04$ and a minum at $g_{\cdot} = 1.83$, which is typical of a ruthenium (I) octahedral metal center coordinated by oxo or aqua ligand with a low-spin d^{s} electronic configuration, and this observation is similar to the value reported for $[SiW_{11}O_{39}Ru(OH_2)]$ in dichloromethane solution^[2].



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Fig. 2 ¹¹³W NMR spectra of ruthenium-substituted derivatives (a) α -GeW₁₁O₃₃Ru(OH₂) (b) α -BW₁₁O₃₃Ru(OH₂)

compound	$E_{ m pa}$ ($ abla$)	$E_{\rm pc}(V)$	dE(mV)	$E_{1/2}(\mathbf{V})$	Ipc/Ipa
[BW ₁₂ O ₁₃] ⁵⁻	-0.97	-1.05	80±2	-1.01	
	-1.46	-1.58	120 ± 2	-1.52	_
[BW ₁₁ O ₃₉ Ru] ⁹⁻	-1.13	-1.25	120 ± 2	-1.19	1,04±0.04
	-1.60	-1.69	90±2	-1.65	0.98±0.04
[GeW ₁₂ O ₄₀]4-	-0.48	-0.64	160 ± 2	-0.56	
	<u> </u>	-1.15	160 ± 2	1.07	
[GeW ₁₁ O ₃₉ Ru] ⁵ −	-0.66	- 0.74	80±2	-0.70	1.02±0.04
	- 1. 10	<u> </u>	80±2	-1.14	0.98±0.04

Table 2	Cyclic	Voltammogram	Data of	Ruthenium-substituted	Derivatives
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Cyclic voltammogram data of ruthenium-substituted derivatives are summerized in Table 2. The $[\text{GeW}_{11}\text{O}_{39}(\text{Ru} \cdot \text{OH}_2)]^{6-}$ anion shows two well-defined one-electron reversible waves with mid-point potentials $(E_{1/2})$ equal to -0.70V and -1.14V respectively; where $E_{1/2} = (E_{pe} + E_{pi})/2$, while E_{pe} and E_{pi} are the cathodic and anodic peak potentials. These waves correspond to the reduction and reoxi-

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dation of the tungsten-oxo cage, which parallel the W($V \rightarrow V$) processes in $[XW_{12}O_{40}]^{n-1}$ anions. Each peak current depends on the square root of the scan rate ($20 \sim 100 \text{ mV/s}$), indicating that the electrode process is diffusion-limiting. Coulometric studies show that each reduction wave corresponds to an one-electron transfer. The E_{ps} and E_{ps} values are independent of the scan rate, and the separation of the peak potential for each redox couple remains constant throughout at $80\pm2 \text{ mV}$, indicating the reversible nature of each wave. In a similar manner, $[BW_{11}O_{39}(Ru \cdot OH_2)]^{3-}$ also exhibits two reversible one-electron redox waves. We note that the reduction of Ru(II) in the substituted polyanions is not observed in the cyclic voltammogram, presumably owning to the absence of proton in acetonitrile solution since the $Ru^{1/n}$ redox potential is pH dependent in aqueous solution^[3].

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