Inorganica Chimica Acta, *183* (1991) 157–160

Preparation and characterization of α- and β-trichromicononatungstosilicate isomers

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(Received May 7, 1990; revised October 26, 1990)

Abstract

Eight new compounds of α- and β-$M_aH_bSiW_9Cr_3(OH_2)_3O_{37}\cdot xH_2O$ types ($M = K^+$, Me_4N^+, Et_4N^+ or n-Bu_4N^+; $a + b = 7$) were synthesized from trivacant heteropoly tungstate α- and β-$[SiW_9O_{34}]^{10-}$ precursors and products were characterized by IR, UV, X-ray photoelectron spectroscopy, polarography, cyclic voltammetry and their magnetic moments. The two kinds of isomers were identified by cyclic voltammetry. The α isomer has two reversible bielectron waves, the β isomer has two irreversible waves.

Introduction

Since the 1970s, there have been many studies on the syntheses of heteropoly anions with Keggin structure from SiW_9 [1]. The Keggin-type heteropolyanions substituted by transition metal ions have more negative charges on the surface than normal Keggin-type polyanions, and enhanced basicity. The high catalytic activity and selectivity of the heteropolyanions in some organic syntheses have been demonstrated in our laboratory. 1:9 Heteropolyanions can be obtained by removing three WO_6 octahedra from α and β isomers of 1:12 (Keggin) heteropolyanions, e.g. $[SiW_{12}O_{40}]^{4-}$. The differences in the sites of the three tungsten atoms removed lead to the isomeric $SiW_9O_{34}{}^{10-}$ polyanion. The removal of three WO_6 octahedra from different W_3O_{13} groups produces an A-type isomer, but the removal of three WO_6 octahedra from the same W_3O_{13} group will generate a B-type isomer (shown in Fig. 1). This paper describes the synthesis and characterization of trisubstituted Keggin structure isomeric heteropolyanions formed by introducing three Cr^{3+} ions into the α- or β-$[SiW_9O_{34}]^{10-}$ (A-type) anions with K^+ or R_4N^+ countercations (R = Me, Et or Bu).

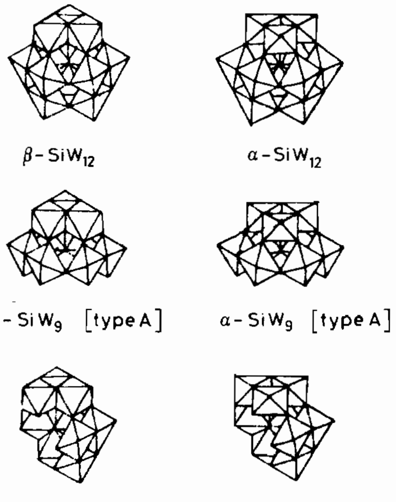

Fig. 1. Structures of α and β isomers of dodecatungstosilicates (Keggin), and type A or B ennea heteropolyanions. The central tetrahedron has been omitted for clarity.

Experimental

Reagents and apparatus

All reagents were of analytical or guaranteed quality. The preparations of α- and β-$Na_9HSiW_9O_{34}\cdot xH_2O$ (noted α-SiW_9 and β-SiW_9) have been described in the literature [2].

IR spectra were obtained on a Nicolet 5DX FT infrared spectrometer with KBr pellets. UV and visible absorption spectra were measured on a DU-8B UV spectrophotometer (Beckman). ESCA data were obtained on a ESCA-650B spectrometer and were calibrated by carbon. Polarograms and cyclic voltammograms were obtained using a 384B polarographic analyser with 303A type electrodes. Magnetic susceptibility measurement was

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0020-1693/91/$3.50

carried out by the Faraday method with an MB-2 magnetic balance at room temperature. Thermogravimetric experiments were conducted on a Q-Derivatograph between room temperature and 800 °C. A P-E 3030 atomic absorption spectrometer, a pH S-2 acidimeter and a DDS-11A conductometer were also used.

The elements were determined by the following methods: tungsten was determined by 8-hydroxyquinoline–tannin acid–methylviolet gravimetry [3]; chromium by ammonium ferrous sulfate volammetry; potassium and silicon by atomic absorption spectrophotometry; water and tetraalkylammonium by thermogravimetric analysis; proton by conductometric titration with MeONa as a titrant, in a solution of ethylene glycol under the protection of nitrogen. The anion charges were confirmed by conductometric titration with $AgNO_3$ solution (0.1 mol l^{-1}) as precipitant.

Synthesis of α-trichromicononatungstosilicates

α-SiW_9 (10 g) was dissolved in H_2O (90 ml, 10 °C). An aqueous solution of $Cr(NO_3)_3 \cdot 9H_2O$ was added stoichiometrically to the above suspension. After adjusting the pH with NaOH (pH is about 4), the solution was heated for 30 min on a water bath. KCl (12.5 g) was then added to the solution. The green crystals were isolated and recrystallized in water. The potassium salt was filtered and washed with a dilute solution of KCl, then EtOH and Et_2O-dried, respectively. *Anal.* Calc. for α-$K_{4.5}H_{2.5}[SiW_9Cr_3(OH_2)_3O_{37}] \cdot 10H_2O$ (noted α-K-SiW_9Cr_3): W, 58.2: Cr, 5.5; Si, 1.0; K, 6.2; H_2O, 9.0. Found: W, 57.7; Cr, 5.4; Si, 0.8; K, 6.0; H_2O, 9.0%. IR: 958, 914, 785 cm^{-1}.

Tetraalkylammonium salts were obtained by adding Me_4NCl, Et_4NCl or n-Bu_4NCl in solution (pH 2), respectively to the solution of α-K-SiW_9Cr_3. *Anal.* Calc. for α-$(Me_4N)_3H_4[SiW_9Cr_3(OH_2)_3O_{37}) \cdot 7H_2O$: W, 58,4; Cr, 5.5; H_2O, 7.6; $(Me_4N)_2O$, 8.7. Found: W, 58.1; Cr, 5.5; H_2O, 7.9; $(Me_4N)_2O$, 9.3%. IR: 960, 914, 794 cm^{-1}. Calc. for α-$(Et_4N)_2H_5[SiW_9Cr_3(OH_2)_3O_{37}] \cdot 6H_2O$: W, 57.9; Cr, 5.5; H_2O, 7.2; $(Et_4N)_2O$, 9.7. Found: W, 57.1; Cr, 5.5; H_2O, 7.4; $(Et_4N)_2O$, 9.3%. IR: 961, 914, 799 cm^{-1}. Calc. for α-$(Bu_4N)_2H_5[SiW_9Cr_3(OH_2)_3O_{37}] \cdot 5H_2O$: W, 53.9; Cr, 5.1; H_2O, 6.2; $(Bu_4N)_2O$, 16.5. Found: W, 54.2; Cr, 5.0; H_2O, 6.0; $(Bu_4N)_2O$, 16.1%. IR: 969, 919, 799 cm^{-1}.

Synthesis of β-trichromicononatungstosilicates

$Cr(NO_3)_3 \cdot 9H_2O$ (8 g) and β-SiW_9 (10 g) were dissolved in 40 ml HOAc–NaOAc buffer solution (pH 4.7). After standing 24 h or more, the solution was treated with a saturated solution of KCl (20 ml), and then with 1:1 EtOH/H_2O solution (60 ml). The green potassium salt precipitated was purified in HOAc–NaOAc buffer solution with 1:1 EtOH/H_2O. The potassium salt was filtered, washed with EtOH and Et_2O-dried, respectively. *Anal.* Calc. for β-$K_{4.5}H_{2.5}[SiW_9Cr_3(OH_2)_3O_{37}] \cdot 11H_2O$ (noted β-K-SiW_9Cr_3): W, 57.9; Cr, 5.4; Si, 1.0; K, 6.1; H_2O, 9.6. Found: W, 57.8; Cr, 5.4; Si, 0.8; K, 5.9; H_2O, 9.3%. IR: 956, 897, 788 cm^{-1}.

The preparations of the tetraalkylammonium salts were the same as that of the α-salts. *Anal.* Calc. for β-$(Me_4N)_3H_4[SiW_9Cr_3(OH_2)_3O_{37} \cdot 4H_2O$: W, 59.5; Cr, 5.6; H_2O, 5.8; $(Me_4N)_2O$, 8.8. Found: W, 59.8; Cr, 5.5; H_2O, 6.0; $(Me_4N)_2O$, 9.0%. IR: 954, 897, 792 cm^{-1}. Calc. for β$(Et_4N)_3H_4[SiW_9Cr_3(OH_2)_3O_{37}] \cdot 3H_2O$: W, 56,4; Cr, 5.3; H_2O, 4.9; $(Et_4N)_2O$, 14.1. Found: W, 56.9; Cr, 5.3; H_2O, 4.7; $(Et_4N)_2O$, 13.8%. IR: 961, 890, 796 cm^{-1}. Calc. for β-$(Bu_4N)_3H_4$-$[SiW_9Cr_3(OH_2)_3O_{37}] \cdot 2H_2O$: W, 50.8; Cr, 4.8; H_2O, 3.9; $(Bu_4N)_2O$, 23.3. Found: W, 51.4; Cr, 4.7; H_2O, 4.2; $(Bu_4N)_2O$, 23.0%. IR: 961, 902, 805 cm^{-1}.

Results and discussions

IR spectra

The main IR spectral bands are characteristic of the Keggin structure. It was confirmed that the various salts of $SiW_9Cr_3(OH_2)_3O_{37}{}^{7-}$ have an identical Keggin structure.

By analogy with the assignments of Keggin anions [4], the band at ~960 cm^{-1}, the broader band at ~900 cm^{-1}, and the very broad band at ~800 cm^{-1} were assigned to the vibrations of W–O_d, Si–O_a, overlapping of corner-sharing octahedra W–O–W, and edge-sharing octahedra W–O–W, respectively. The main vibrational frequencies increased with the cation-size increase. This regularity could be explained by the electrostatic mode of anion–anion interactions and by the effect arising from water of crystallization [5].

In order to compare the IR spectra of α- and β-$SiW_{12-x}Cr_x$ ($x = 1, 2, 3$) isomers, the main vibrational frequencies are listed in Table 1. On passing from $SiW_{11}Cr$ to SiW_9Cr_3, the ν_{as}(W–O_d) and ν_{as}(Si–O_a) vibrational frequencies become smaller, owing to the more negative charge on these anions (−5, −6, −7, respectively), which leads to lengthening of the W–O and Si–O bonds and a decrease of the stretching frequencies. In addition, a lowering of the ν_{as}(Si–O_a) frequency from α to β isomers was observed, showing a lengthening of the Si–O_a bond. Such a lengthening was also observed in β-SiW_{12} [6].

Electroanalysis

Cyclic voltammograms and the electrochemical parameters of α- and β-$SiW_{12-x}Cr_x$ ($x = 2, 3$) are

TABLE 1. Main IR bands for α- and β-$SiW_{12-x}Cr_x$ potassium salts (cm^{-1})

	α-$SiW_{11}Cr$ [8]	α-$SiW_{10}Cr_2$ [5]	α-SiW_9Cr_3	β$SiW_{11}Cr$ [8]	β-$SiW_{10}Cr_2$ [5]	β-SiW_9Cr_3
ν_{as} (W–O_d)	962	960	958	970	962	956
ν_{as} (Si–O_a)	925	914	914	925	908	897
	880 (w)	877 (sh)	884 (sh)			
ν_{as} (W–O_c–W)	790	782	785	800	779	788

TABLE 2. Electrochemical parameters obtained from polarograms and cyclic voltammograms of α- and β-$SiW_{12-x}Cr_x$ ($x = 2, 3$)[a]

Compound	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	$-59/n$ (mV)
α-SiW_9Cr_3	I −0.890	I −0.858	32	−0.898	
	II −0.960	II −0.920	40	−0.956	
α-$SiW_{10}Cr_2$	I −0.872	I −0.832	40	−0.866	29
	II −0.964	II −0.926	38	−0.960	27
β-SiW_9Cr_3	I −0.846				
	II −0.952				
β-$SiW_{10}Cr_2$	I −0.856				
	II −0.962				

[a] 1 M HOAc–NaOAc + 0.1 M KCl solutions; V vs. Ag–AgCl electrode; sweep rates 50 mV/s; ±5 mV.

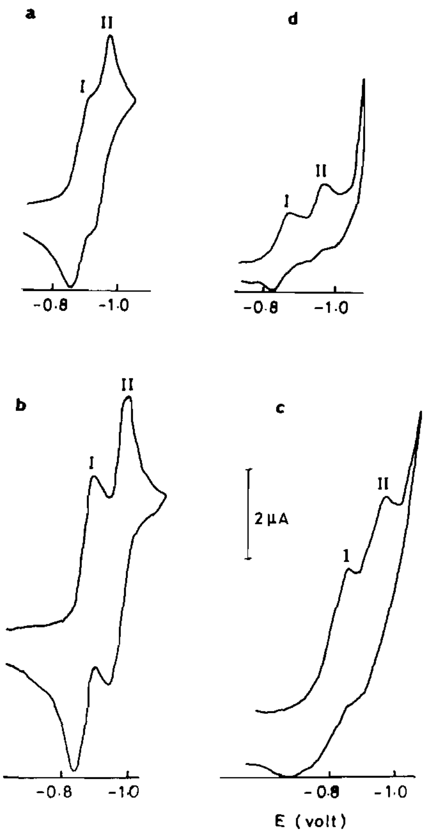

Fig. 2. Cyclic voltammograms of α- and β-$SiW_{12-x}Cr_x$ ($x = 2, 3$): a, α-SiW_9Cr_3; b, α-$SiW_{10}Cr_2$; c, β-SiW_9Cr_3; d, β-$SiW_{10}Cr_2$.

given in Fig. 2 and Table 2. Two reduction steps for α-$SiW_{12-x}Cr_x$, which are different from the one four-electron reduction step of W(VI) of the precursor α-SiW_9 [7], were observed. Two reduction steps for β-$SiW_{12-x}Cr_x$, which are similar to the two reduction steps of W(VI) of the precursor β-SiW_9, were observed. The cyclic voltammograms of α-$SiW_{12-x}Cr_x$ showed two reversible reduction peaks, but those of β-$SiW_{12-x}Cr_x$ exhibited two irreversible reduction peaks. In the polarogram of α-$SiW_{10}Cr_2$, the slopes ($-59/n$ mV) given by logarithmic analysis of the polarogram indicated that both waves were reversible bielectronic waves. In the polarogram of α-SiW_9Cr_3, the separation between the first wave and the second wave was so small that the two waves must be identified by the differential pulse polarogram. But the ΔE_p data in the cyclic voltammogram of α-SiW_9Cr_3 were an indication of reversible bielectronic waves. Generally, chromium(III) in a substituted heteropolyanion is less reducible than molybdenum(VI) or tungsten(VI), so it is reasonable to assign the reversible waves of α-$SiW_{12-x}Cr_x$ as the reduction of W(VI) to W(V) [1]. The difference in the redox behavior between α and β isomers is of great importance for distinguishing the isomers. Since α and β isomers only differ by the way in which the W_3O_{13} groups are linked together, the dramatic differences in reversibility among the voltammograms must be related to the rotated W_3O_{13} group. The reduction of the α isomer must be accompanied by only minor structural changes, but larger structural changes may occur in the reduction of the β isomer.

UV and visible spectra

Intense absorption bands at 256 and 198 nm for α-K-SiW$_9$Cr$_3$ and at 260 and 204 nm for β-K-SiW$_9$Cr$_3$ were observed. The UV spectra were characteristic of 12-heteropoly tungstosilicate anions with Keggin structure and were assigned to $O_b \rightarrow W$ or $O_c \rightarrow W$ charge-transfer bands. In the visible region, unlike SiW$_{11}$Cr [8], only a broad band was observed at 624 nm for α-K-SiW$_9$Cr$_3$ or at 608 nm for β-K-SiW$_9$Cr$_3$. It was assigned as d–d transition arising from the d^3 configuration in a near-octahedral crystal field. The visible spectra of the complexes display a bathochromic shift against that of $Cr(H_2O)_6{}^{3+}$ ($\lambda_{max} = 574$ nm). With the assignment of the band to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h), it is seen that $10Dq$ of the complexes is smaller than that of $Cr(H_2O)_6{}^{3+}$. This suggests that the Cr(III) in the heteropolyanion is located in a weaker octahedral field.

ESCA

The $W_{4d\,5/2}$ and $O_{1s\,1/2}$ binding energies in SiW$_9$Cr$_3$ polyanions are, on average, 0.4 eV higher than those in SiW$_9$ polyanions. The $O_{1s\,1/2}$ and $Cr_{2p\,5/2}$ binding energies in SiW$_9$Cr$_3$ are lower by 2 and 0.7 eV, respectively, than those in $Cr(NO_3)_3$. In contrast with SiW$_9$Fe$_3$ polyanions [2], no $Cr \rightarrow O$ donation was found in SiW$_9$Cr$_3$.

Magnetic measurement

The magnetic susceptibilities of the Cr(III) in the heteropoly complexes were determined (298 K) and the effective magnetic moments were calculated (Table 3). The observed values of the magnetic moments are very close to the value of the pure electron spin magnetic moment (3.87 BM). These are in good agreement with the interpretation of the ligand field theory for the d^3 configuration.

TABLE 3. Magnetic measurements

Compound	$10^{-6} \times \chi_g$ (e.m.u./g)	$10^{-5} \times \chi_m$ (e.m.u./m)	μ_{eff}(BM)
α-K-SiW$_9$Cr$_3$	6.086	1726	3.69
β-K-SiW$_9$Cr$_3$	5.281	1511	3.45

Thermal gravimetric analysis

TG and DTA experiments for α- and β-SiW$_9$Cr$_3$ isomers were carried out in air. TG curves exhibited three distinct steps (except the potassium salts). The first step, below 200 °C, corresponds to the loss of crystal water (endotherms). The second step, at 200–500 °C, corresponds to the loss of organic ammonium (exotherms), which was provided by the disappearance of the $\nu_{(C-H)}$ and $\nu_{(C-N)}$ vibrational frequencies in the IR spectra of those compounds when they were heated at 550 °C. The third, above 600 °C, corresponds to the loss of the constitutional water (endotherms) with the complete destruction of Keggin structure.

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