

A NOVEL HEXAD CONDENSED CHROMIUM-CONTAINING TUNGSTOSILICATE(I): SYNTHESIS AND CHARACTERIZATION

PENG JUN,* GUO YINHANG and QU LUNYU

Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024,
P.R. China

and

XU YIHUA

Department of Chemistry, Jilin University, Jilin 130022, P.R. China

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Abstract—A novel hexad condensed chromium-containing tungstosilicate, with the formula $K_{20}H[CrSi_6W_{60}O_{210}H_{12}] \cdot nH_2O$, was synthesized and characterized by IR and UV-vis spectroscopy, polarography, X-ray powder diffraction and magnetic susceptibility. It has a molecular weight up to 17,000 and a structure different from those of any known heteropolyanions, such as the Keggin, Dawson and As_4W_{40} structures.

The polyoxometallates with Keggin structure that are based on a central XO_4 tetrahedron surrounded by 12 MO_6 octahedra arranged in four groups of three edge-shared octahedra, M_3O_{13} and the Dawson structure, which consists of two A-type XM_9 units fused into a cluster of virtual D_{3h} symmetry are well known.¹ Thousands of derivatives have been synthesized and studied. Among them, to date, the quadruple condensed compounds of AsW_{10} are maximal molecules whose molecular weights are *ca* 10,000.²

On the basis of a series of studies on the heteropolyanions with the Keggin structure from SiW_9 ,^{3–6} We carried out the synthesis and characterization of a novel hexad condensed chromium-containing tungstosilicate formed by α - SiW_9 with great interest in its structure, which has a molecular weight up to 17,000 and a structure different from those of any known heteropolyanions, such as the Keggin, Dawson and As_4W_{40} structures.

EXPERIMENTAL

Reagents and apparatus

All reagents were of analytical or guaranteed quality. The preparation of α - $Na_9HSiW_9O_{34} \cdot xH_2O$ (denoted as α - SiW_9) was described in ref. 2. The apparatus used was as follows: 5DX FT IR spectrometer with KBr pellets; DU-8B UV spectrophotometer; 384B polarographic analyser with 303A electrodes; MB-2 magnetic balance, at room temperature; P-E 3030 atomic absorption spectrometer; Plasma-Spec(I) (Leeman) ICP emission spectrometer; Hitachi S-570 scanning electron microscope; D/Max III C X-ray diffractometer; TGA 7 derivatograph; AST 386 Computer.

Synthesis of α - $K_{20}H[CrSi_6W_{60}O_{210}H_{12}] \cdot 98H_2O$ [α - $Cr(SiW_{10})_6$]

Na_2WO_4 solution (0.1 mol dm^{-3} , 40 cm^3) was dropped into α - SiW_9 suspension (5.8 g in 20 cm^3 H_2O). After adjusting to pH 4 with HCl, the solution was heated for 1 h on a water bath, $Cr(NO_3)_3$ (0.8 g) was then added. After heating for 30 min,

* Author to whom correspondence should be addressed.

the resulting solution was treated with a saturated solution of KCl (10 cm³) and light green hexahedral pyramidal crystals of the title compound were obtained after some hours.

Elemental analyses

The elements in the compound were determined by the following methods: potassium by atomic absorption spectrophotometry; tungsten, silicon and chromium by plasma emission spectrometry; water by thermal analysis. The analytical data for α -K₂₀H[CrSi₆W₆₀O₂₁₀H₁₂] · 98H₂O [hereafter denoted as α -Cr(SiW₁₀)₆] are as follows. Found (Calc.): W, 67.1 (64.4); Cr, 0.3 (0.3); Si, 1.0 (1.0); K, 4.6 (4.6); H₂O, 10.6 (10.9)%.

RESULTS AND DISCUSSION

The number of cations of " α -Cr(SiW₁₀)₆"

Ion exchange and titration experiments indicated that approximately 20 exchangeable cations existed in " α -Cr(SiW₁₀)₆" and that Cr^{III} was unexchangeable, suggesting that the Cr^{III} is located inside the framework of the anion. There was no measurable H⁺ ion in the unexchanged potassium salt.

IR spectra

The IR spectral data for " α -Cr(SiW₁₀)₆" are listed in Table 1. The IR spectrum of " α -Cr(SiW₁₀)₆" was more similar to that of α -SiW₁₂ than to those of α -SiW_{12-x}Cr_x.⁵ However, there were some differences between " α -Cr(SiW₁₀)₆" and α -SiW₁₂ in the $\nu_{\text{as}}(\text{Si}-\text{O}_a)$ band and in the $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ band. Two split bands of the $\nu_{\text{as}}(\text{Si}-\text{O}_a)$ band and of the $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ band were respectively observed in the SD IR spectrum for " α -Cr(SiW₁₀)₆" but not for α -SiW₁₂. This may support our argument that three groups of SiW₁₀ form one-half of the " α -Cr(SiW₁₀)₆" structure in corner connectivity, so two kinds of Si—O_a bonds and W—O_b—W bonds exist in the compound.

In addition, no characteristic vibration of H₃O⁺

was observed around the 1700 cm⁻¹ region,⁷ providing evidence for the proposed formula for the compound.

UV and visible spectra

Intense absorption bands at 263 and 204 nm for " α -Cr(SiW₁₀)₆" were observed, indicating that it still maintained the structural characteristics of the Keggin framework. In the visible region, similar to other chromium(III)-containing tungstosilicates, a broad band in the 630 nm region was observed for " α -Cr(SiW₁₀)₆". It was assigned as a ⁴A_{2g} → ⁴T_{2g}(O_h) transition arising from the d³ configuration. This suggests that the Cr^{III} is located in an octahedral field which is weaker than that of Cr(H₂O)₆³⁺.

Magnetic measurement

The magnetic susceptibility of Cr^{III} in " α -Cr(SiW₁₀)₆" was determined ($\chi_g = 0.0342 \times 10^{-6}$ e.m.u. g⁻¹), and β -SiW₉ was used for diamagnetic correction ($\chi_g = -0.2761 \times 10^{-6}$ e.m.u. g⁻¹). The effective magnetic moment calculated (3.55 B.M.) is very close to the value of the pure electron spin magnetic moment of Cr^{III} (3.87 B.M.). This also supports the formula of the title compound.

X-ray powder diffraction

X-ray powder diffraction data were collected with Cu-K_α radiation by step scanning from 4.00 to 80.00° in steps of 0.02° and successfully indexed by the TREOR Program, leading to the cell parameters $a = 19.09(3)$ and $c = 37.71(8)$ Å; unit cell volume = 11,908.30 Å³; hexagonal system. This was supported by the SEM photograph of crystals of the title compound. Part of the indexed data are listed in Table 2. The measured density agrees with the calculated one ($D_{\text{calc}} = 4.78$, $D_{\text{obs}} = 4.76$ g cm⁻³) for $Z = 2$.

Table 1. IR and second derivative IR bands of α -Cr(SiW₁₀)₆ (cm⁻¹)

| | $\nu_{\text{as}}(\text{W}-\text{O}_d)$ | $\nu_{\text{as}}(\text{Si}-\text{O}_a)$ | $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ | $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ |
|-------|--|---|---|---|
| IR | 980.3 | 925.2 | 879.0 | 784.8 |
| SD IR | 981.0 | 943.6 924.0 | 877.5 892.6 | 824.7 780.0 |

Table 2. The indexed X-ray powder diffraction data for α -Cr(SiW₁₀)₆

| <i>h</i> | <i>k</i> | <i>l</i> | <i>D</i> _{obs} | <i>D</i> _{calc} | <i>I</i> / <i>I</i> ₀ | <i>h</i> | <i>k</i> | <i>l</i> | <i>D</i> _{obs} | <i>D</i> _{calc} | <i>I</i> / <i>I</i> ₀ |
|----------|----------|----------|-------------------------|--------------------------|----------------------------------|----------|----------|----------|-------------------------|--------------------------|----------------------------------|
| 1 | 0 | 0 | 16.53(3) | 16.53(5) | 100 | 3 | 2 | 6 | 3.24(8) | 3.24(8) | 52 |
| 1 | 0 | 3 | 10.01(5) | 10.00(8) | 75 | 3 | 3 | 0 | 3.18(2) | 3.18(2) | 15 |
| 1 | 1 | 0 | 9.54(6) | 9.54(7) | 18 | 4 | 1 | 6 | 3.12(9) | 3.12(9) | 42 |
| 0 | 0 | 4 | 9.42(3) | 9.42(9) | 15 | 3 | 1 | 9 | 3.09(3) | 3.09(4) | 19 |
| 2 | 0 | 0 | 8.27(5) | 8.26(8) | 38 | 4 | 0 | 9 | 2.94(4) | 2.94(3) | 10 |
| 2 | 0 | 2 | 7.60(1) | 7.57(2) | 12 | 4 | 2 | 6 | 2.79(8) | 2.79(8) | 31 |
| 2 | 1 | 0 | 6.25(9) | 6.25(0) | 7 | 6 | 0 | 1 | 2.75(1) | 2.74(9) | 10 |
| 1 | 0 | 6 | 5.87(8) | 5.87(6) | 10 | 4 | 1 | 9 | 2.73(5) | 2.73(4) | 19 |
| 2 | 1 | 3 | 5.58(7) | 5.59(6) | 6 | 4 | 3 | 0 | 2.71(9) | 2.71(8) | 11 |
| 1 | 1 | 6 | 5.25(4) | 5.25(0) | 17 | 5 | 1 | 6 | 2.68(7) | 2.68(5) | 14 |
| 3 | 0 | 3 | 5.05(2) | 5.04(8) | 20 | 4 | 3 | 3 | 2.65(6) | 2.65(7) | 6 |
| 2 | 2 | 0 | 4.77(7) | 4.77(3) | 41 | 4 | 3 | 4 | 2.61(7) | 2.61(2) | 4 |
| 0 | 0 | 8 | 4.71(1) | 4.71(5) | 6 | 6 | 0 | 5 | 2.58(9) | 2.58(9) | 19 |
| 3 | 1 | 0 | 4.58(6) | 4.58(6) | 9 | 6 | 0 | 6 | 2.53(4) | 2.52(4) | 21 |
| 3 | 1 | 3 | 4.31(2) | 4.30(8) | 16 | 6 | 1 | 0 | 2.52(1) | 2.52(2) | 11 |
| 4 | 0 | 0 | 4.13(7) | 4.13(4) | 45 | 4 | 2 | 9 | 2.50(5) | 2.50(5) | 13 |
| 2 | 2 | 6 | 3.80(5) | 3.80(2) | 17 | 4 | 1 | 11 | 2.48(5) | 2.48(6) | 15 |
| 2 | 0 | 9 | 3.73(9) | 3.73(8) | 13 | 3 | 3 | 10 | 2.43(0) | 2.43(2) | 3 |
| 3 | 1 | 6 | 3.70(5) | 3.70(5) | 26 | 3 | 0 | 14 | 2.42(1) | 2.42(0) | 3 |
| 3 | 2 | 3 | 3.63(6) | 3.63(2) | 4 | 7 | 0 | 0 | 2.36(1) | 2.36(2) | 30 |
| 2 | 1 | 9 | 3.47(7) | 3.48(1) | 26 | 7 | 0 | 2 | 2.34(4) | 2.34(4) | 5 |
| 4 | 0 | 6 | 3.45(6) | 3.45(4) | 19 | 6 | 2 | 0 | 2.29(3) | 2.29(3) | 3 |
| 3 | 0 | 9 | 3.33(9) | 3.33(6) | 15 | 3 | 1 | 15 | 2.20(4) | 2.20(5) | 4 |
| 5 | 0 | 0 | 3.30(9) | 3.30(7) | 32 | 7 | 1 | 0 | 2.18(9) | 2.19(0) | 7 |

Thermal gravimetric analysis

The TGA experiment for " α -Cr(SiW₁₀)₆" was carried out in air. The TGA curve exhibited two distinct steps. The first step, below 478°C, corresponds to the loss of water of crystallization. The second step, from 478 to 678°C, corresponds to the loss of six molecules of the structural water (gravimetric change = 0.7%), providing further evidence of the formula of " α -Cr(SiW₁₀)₆".

Cyclic voltammogram measurement

Cyclic voltammogram and electrochemical parameters of " α -Cr(SiW₁₀)₆" are given in Fig. 1 and Table 3, respectively. Four reduction steps of W^{VI} → W^V for α -Cr(SiW₁₀)₆ were observed, which are different from the two W^{VI} → W^V reduction steps of α -SiW_{12-x}Cr_x.

It is worth noting that the third reduction wave disappeared, and the electrochemical behaviour was the same as that of the SiW₁₂ anion when " α -Cr(SiW₁₀)₆" was subjected to rapid recrystallization. A probable reason is that α -SiW₁₂ anions came out of recrystallization as its dissociative substance.

Another interesting point is that the same compound, " α -Cr(SiW₁₀)₆", can also be synthesized

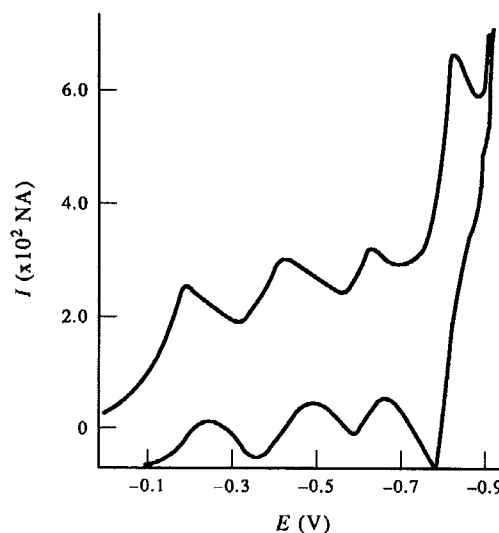


Fig. 1. Cyclic voltammogram of " α -Cr(SiW₁₀)₆".

from β -SiW₉. We suggest that some stereo effect leads to restorations of the rotated W₃O₁₃ groups in β -SiW₉ subunits in the process of polymerization of the β -SiW₉ precursor. So, instead of β -Cr(SiW₁₀)₆, " α -Cr(SiW₁₀)₆" is formed.

Table 3. Electrochemical parameters obtained from polarogram and cyclic voltammogram of α -Cr(SiW₁₀)₆

| | E_{pc} (V) | E_{pa} (V) | ΔE_p (mV) | $E_{1/2}$ (V) |
|-----|--------------|--------------|-------------------|---------------|
| I | -0.204 | | | -0.200 |
| II | -0.428 | -0.366 | 60 | -0.444 |
| III | -0.630 | -0.596 | 36 | -0.708 |
| IV | -0.826 | -0.778 | 48 | -0.900 |

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