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SYNTHESIS AND CHARACTERIZATION OF α,β-TRIINDIUM SUBSTITUTED HETEROPOLYTUNGSTATES

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Abstract—The complexes of α,β-$K_aH_bXW_9O_{37}(InH_2O)_3 \cdot xH_2O$ ($X = Si$, Ge; $a+b = 7$) were synthesized from their lacunary precursors α,β-$XW_9O_{34}^{10-}$ ($X = Si$, Ge) and characterized by elemental analysis, ^{183}W NMR, IR and UV spectroscopy and polarography. ^{183}W NMR spectra of the title complexes consist of two lines with intensity ratio 2 : 1, as expected for the C_{3v} structure of trisubstituted Aα- and Aβ-Keggin anions.

After Herve and Teze's work,[1] studies of the heteropolyanion derivatives of α,β-enneatungstosilicates and -germanates have been continued. The trivacant polyanions can act as ligands with numerous metal cations,[2] leading to trinuclear trisubstituted complexes XW_9M_3. These complexes are important for catalytic purposes, particularly for the oxidation of organic substrates.[3] Recently, the high catalytic activity and selectivity of some transition metal trisubstituted heteropolyanions in the epoxidation of alkenes have been demonstrated in our laboratory.[4–6] In order to entirely understand the properties and activities of trisubstituted heteropolyanions, we have also synthesized some trisubstituted complexes containing group 3A elements.[7] This paper gives the results of the preparation and characterization of α,β-$[XW_9O_{37}\{InH_2O\}_3]^{7-}$ ($X = Si$, Ge) heteropolyanions.

EXPERIMENTAL

Reagents and apparatus

All reagents were of analytical or guaranteed quality.

The trivacant heteropoly tungstates α,β-$[SiW_9O_{34}]^{10-}$ and α,β-$[GeW_9O_{34}]^{10-}$ sodium salts (denoted as α,β-SiW_9 and α,β-GeW_9) were prepared following ref. 1 and were identified by polarography.

^{183}W NMR spectra were recorded at 16.64 MHz on a Unity-400 spectrometer using a 10 mm diameter NMR tube at 20°C. Chemical shifts were referenced to 2 M Na_2WO_4 in D_2O. IR spectra were recorded on an Alpha Centaurt FTIR spectrometer (4000–200 cm^{-1} range) as KBr pellets. UV spectra were recorded on a Beckman DU-8B spectrophotometer (solvent H_2O). Polarograms were obtained using a 384B Polarographic Analyser, equipped with 303A type electrodes.

Synthesis of α-$K_aH_b[XW_9O_{37}(InH_2O)_3] \cdot xH_2O$

To an aqueous (100 cm^3) solution of $In(NO_3)_3 \cdot 4\frac{1}{2}H_2O$ (2.3 g, 5.8 mmol) was added 6 N HNO_3 and the pH adjusted to 2.0. α-SiW_9 (5.0 g, 1.8 mmol) or α-GeW_9 (5.2 g, 1.8 mmol) was added in small portions with vigorous stirring. The solution was adjusted to pH 4.5–5.0 with sodium carbonate and followed after stirring for 30 min at 80°C by solid KCl (5 g). The white precipitate was

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filtered and recrystallized from warm water. Found: W, 54.1; Si, 0.9; In, 11.0; K, 8.6; H_2O, 6.9. Calc. for α-$K_7[SiW_9O_{37}(InH_2O)_3]\cdot 8H_2O$ (denoted as α-SiW_9In_3): W, 53.6; Si, 0.9; In, 11.2; K, 8.8; H_2O, 6.4%. Found: W, 53.9; Ge, 2.3; In, 11.2; K, 6.3; H_2O, 7.0. Calc. for α-$K_5H_2[GeW_9O_{37}(InH_2O)_3]\cdot 9H_2O$ (denoted as α-GeW_9In_3): W, 53.8; Ge, 2.3; In, 11.2; K, 6.4; H_2O, 7.0%.

Synthesis of β-$K_aH_b[XW_9O_{37}(InH_2O)_3]\cdot xH_2O$

To an aqueous (100 cm^3) solution of $In(NO_3)_3\cdot 4\frac{1}{2}H_2O$ (2.4 g, 5.2 mmol) was added β-SiW_9 (5.1 g, 1.8 mmol) or β-GeW_9 (5.4 g, 1.8 mmol) in small portions with vigorous stirring. The solution was adjusted to pH 5.0 with sodium carbonate. It was stirred for 30 min at 70°C. After cooling, KCl (5 g) was added and the resulting white precipitates filtered off and recrystallized from warm water. Found: W, 54.8; Si, 0.9; In, 10.8; K, 7.4; H_2O, 6.9. Calc. for β-$K_6H[SiW_9O_{37}(InH_2O)_3]\cdot 8H_2O$ (denoted as β-SiW_9In_3): W, 54.2; Si, 0.9; In, 11.3; K, 7.7; H_2O, 6.9%. Found: W, 53.3; In, 11.0; Ge, 2.3; K, 6.3; H_2O, 7.0. Calc. for β-K_5H_2 $[GeW_9O_{37}(InH_2O)_3]\cdot 9H_2O$ (denoted as β-GeW_9In_3): W, 53.0; In, 11.1; Ge, 2.3; K, 6.4; H_2O, 7.0%.

Chemical analyses

Tungsten, silica and germanium were determined by ICP-AES spectroscopy. Potassium was determined by atomic absorption spectroscopy. Indium was determined volumetrically. The water content was determined by thermogravimetry.

RESULTS AND DISCUSSION

IR and UV spectra

The observed frequencies and tentative assignments of the main IR and UV bands of the complexes are listed in Table 1.

IR studies on heteropolyanions of Keggin structure have been made previously[8,9] and also on "unsaturated" polyanions.[10] In comparision with XW_{12} anions, the main IR bands of the title complexes are characteristic of the Keggin structure. However, perturbed by the substituted element, the IR spectra of α,β-XW_9In_3 anions are different from that of α,β-XW_{12}. The principal differences are as follows. (1) The ν_{as}(W—Od), which is at 967 ± 2 cm^{-1} in α,β-XW_{12}, decreases to 950 ± 4 cm^{-1}. The asymmetric stretching frequency of the ν_{as}(W—Od) bond vibration of heteropolyanions is an individual stretching mode, which is not affected by change of anion symmetry.[8] Obviously, this decrease of ν_{as}(W—Od) is due to an increase of negative charge on the polyanion; some bond force constants become smaller and vibration frequencies decrease. (2) The decrease of the asymmetric bridge stretching frequency and splitting of W—Oc—W bridge bond vibrations. The ν_{as}(W—Oc—W), which is at about 790 cm^{-1} in α,β-XW_{12}, is separated into 780 ± 6 and 720 ± 6 cm^{-1} in α,β-XW_9In_3. This fact most probably results from the change of anion symmetry, and is similar to the other trisubstituted Keggin anions.[11,12] (3) The bands ν_{as}(Si—Oa) at 920 cm^{-1} and ν_{as}(Ge—Oa) at 830 cm^{-1} in α,β-SiW_9In_3 and α,β-GeW_9In_3 were hidden by the broadened ν_{as}(W—Ob—W) and ν_{as}(W—Oc—W).

The UV spectra of the title complexes reveal two peaks at about 208 ± 2 and 260 ± 4 nm ($\varepsilon_{max} = 10^4$ dm^3 $mol^{-1}cm^{-1}$). Compared with α,β-XW_{12} anions,[13] the UV maxima of the title anions all shift to higher energy. The intense absorption band at *ca* 260 ± 4 nm is a characteristic band of a heteropolytungstate with Keggin structure and should be assigned as an Ob/Oc → W charge transfer band. The band 210 ± 2 nm at higher energy should be assigned to an Od → W charge transfer band. The difference between the characteristic bands of α- and β-isomers is significant. A "red shift" of *ca* 10 nm of β-isomers occurred. This difference should allow one to discriminate between α- and β-isomers.

^{183}W *NMR spectra*

The title complexes gave clean ^{183}W NMR spectra (Fig. 1). The ^{183}W NMR spectra of each compound

Table 1. IR data (cm^{-1}) and UV maxima (nm, $C = 1.0\times10^{-5}M$)

Anions	ν_{as} (W—Od)	ν_{as} (X—Oa)	ν_{as} (W—Ob—W)	ν_{as} (W—Oc—W)	λ_{max}
α-SiW_9In_3	951		886	786 726	255 207
β-SiW_9In_3	954		878	791 728	262 208
α-GeW_9In_3	946		885	790 720	256 210
β-GeW_9In_3	945		861	786 718	264 207

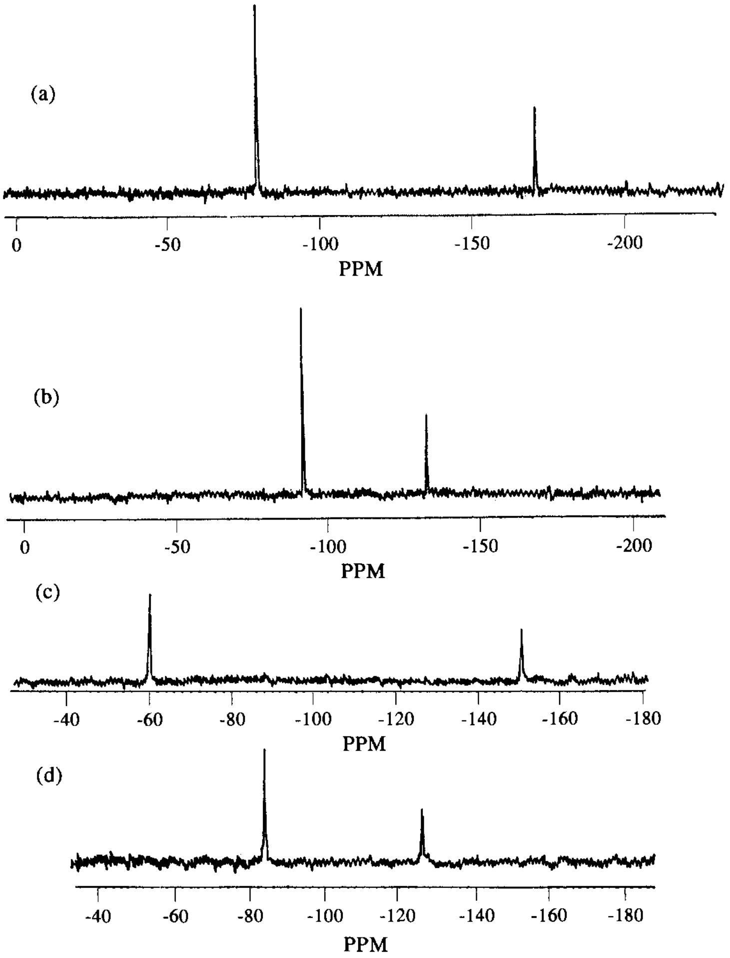
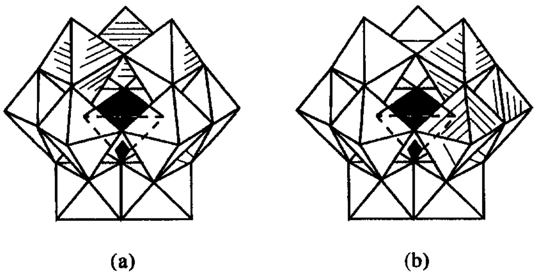


Fig. 1. ^{183}W NMR spectra of potassium salts of α (a), β (b) -SiW$_9$In$_3$; α (c), β (d) -GeW$_9$In$_3$ [in pH6 H_2O/D_2O solution at 20°C, chemical shifts: (a) −78.9, −171.0; (b) −95.5, −136.3; (c) −68.3, −158.9; (d) −84.0, −126.3 ppm].

consist of two lines with intensity ratio 2:1, indicating that there are two non-equivalent tungsten environments in the heteropolyanion and the number ratio of the two kinds of tungsten atoms is 2:1. This fact supports the stoichiometry of the new heteropolyanions and the probable retention of the A-XW$_9$ unit. The three substituted atoms occupy the vacant sites in a triad of corner-sharing InO$_6$ octahedra (see Fig. 2a).[14]



(a) (b)

Fig. 2. Polyhedral representation of (a) A-β-SiW$_9$(InH$_2$O)$_3$O$_{37}^{7-}$ and (b) B-β-SiW$_9$(InH$_2$O)$_3$O$_{37}^{7-}$ with the three indiums represented by the shaded octahedra.

Table 2. Polarographic half-wave data (V) of the title anions

	$E_{1/2}$ (electron)	
Anions	$In^{III} \rightarrow In^{I}$	$W^{VI} \rightarrow W^{V}$
α-SiW$_9$In$_3$	−0.68	−0.78(4)
β-SiW$_9$In$_3$	−0.68	−0.78(2) −0.88(2)
α-GeW$_9$In$_3$	−0.68	−0.87(4)
β-GeW$_9$In$_3$	−0.68	−0.80(2) −0.90(2)

When three indium atoms occupy the three vacant sites of α,β-enneatungstosilicates and -germanates, there are two possibilities, i.e. the A arrangement of a triad of corner-sharing InO$_6$ octahedra, which exhibits two non-equivalent tungsten environments (Fig. 2a), and the B arrangement of a triad of edge-

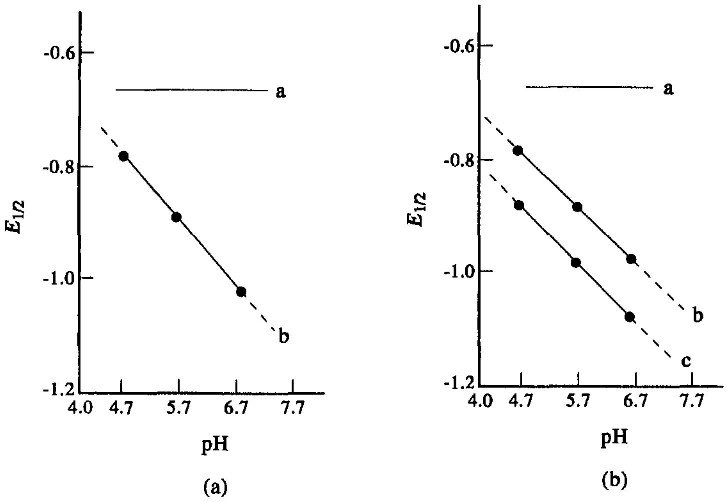


Fig. 3. Polarographic half-wave potential (V, vs SCE) vs pH diagram of α (a) and β-SiW_9In_3 (b). a, b, c represent the reduction of In^{III} and W^{VI} respectively.

sharing octahedra, which has five non-equivalent tungsten environments (Fig. 2b). The above two-line ^{183}W NMR spectra confirmed that the title complexes have A-type α,β-Keggin structures.

The above ^{183}W NMR data also show that the chemical shifts are affected by the centre atoms silicon or germanium. When the centre atom changes from silicon to germanium, all chemical shifts of each peak shift 11 ± 1 ppm to lower magnetic field; because silicon or germanium has the same electric charge, this effect most probably results from the different ionic radii of silicon and germanium.

Polarography

At 298 K and pH 4.70 in a 0.5 mol cm^{-3} acetate buffer solution with saturated calomel and dropping mercury electrodes, the $E_{1/2}$ values were determined as follows.

(1) The reduction processes of α,β-XW_9In_3 anions involved the reduction of indium and tungsten, as shown in Table 2 and Fig. 3. The first peak at -0.68 V is assigned to the reduction of In^{III} to In^{I}, and it does not change with different pH, indicating that there is no protonation accompanying this reduction. (2) The reduction of W^{VI} of α,β-XW_9In_3 is similar to those of their parent compounds α,β-SiW_9, showing one-step four-electron (α) or two-step two-electron (β) pH-dependent reduction peaks, implying that the reduction of W^{VI} is accompanied by protonation. (3) The reduction of W^{VI} of α,β-GeW_9In_3 is different from that of the parent compound α,β-GeW_9. Perturbed by the reduction of In^{III} to In^{I}, the two-step reduction of W^{VI} in α-GeW_9 changes to a one-step broadened four-electron reduction process in the α-GeW_9In_3 anion, and the two-step two-electron reduction process of W^{VI} in β-GeW_9 is partly overlapped in the β-GeW_9In_3 anion. (4) Straight lines can be obtained by plotting $E_{1/2}$ of each peak versus pH, and from the slope of $E_{1/2}$ versus pH plots it can be calculated that two or four protons must be added to gain two or four electrons while the heteropolyanions are reduced.

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