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Solid State Chemistry of Polytungstic Acids and Their Salts

II. Synthesis, Properties, and Structure of Noncrystalline Hydrogen–Sodium Metatungstate and Powdered Crystalline Cesium Metatungstate

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A noncrystalline hydrogen–sodium metatungstate and a powdered crystalline cesium metatungstate have been prepared by a cation-exchange membrane electrolytic method and examined with UV and IR photoacoustic, thermal, conductance, and X-ray diffraction techniques. The results show that the formulas of the hydrogen–sodium metatungstate and the cesium metatungstate are $Na_4H_2[H_2(W_3O_{10})_4] \cdot 10H_2O$ and $Cs_6[H_2(W_3O_{10})_4] \cdot 9H_2O$, respectively. The ionic conductivity of inner-sphere hydrogen of the complex anion $[H_2(W_3O_{10})_4]^{6-}$ is far smaller than that of the hydrogen in the outer sphere of solid state metatungstate. A single crystal of cesium metatungstate has also been prepared; it belongs to a triclinic system. © 1987 Academic Press, Inc.

1. Introduction

Metatungstic acid and its normal salts from sodium, potassium, and lithium in solution are well-known compounds; the hydrogen and cesium salts of metatungstic acid are little known, and the chemistry of their noncrystalline state is nearly unknown. This paper relates the preparation of noncrystalline hydrogen–sodium metatungstate (HSMT) and powdered crystalline cesium metatungstate (CMT) with a cation-exchange membrane electrolytic method (CEMEM) (*1*) and the determination of their solid state properties and structure.

2. Experimental

2.1. *Preparation*

2.1.1. Noncrystalline state HSMT. The samples should be prepared with great care since the preparation conditions have a strong influence on the experimental results. The preparation method was as described in Ref. (*1*), except that a highly concentrated (almost saturated) Na_2WO_4 solution was used as electrolyte, electrolysis was carried out to a pH = 1.0–1.7 in the anode solution at ±1°C, and a transparent plate of the noncrystalline state HSMT was obtained by cold-drying under vacuum.

2.1.2. CMT. Addition of a CsCl solution to a HSMT solution readily yielded a white precipitate CMT. Its single crystal was prepared by a solution method.

2.2. *Instruments*

The instruments used were as described in Ref. (*1*). Solid state or solution proper-

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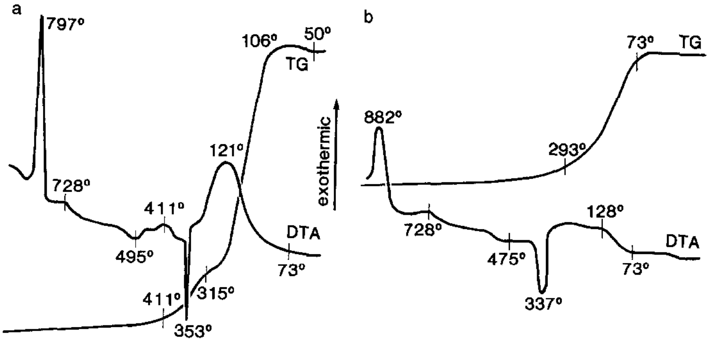

FIG. 1. The TG and DTA curves of the HSMT (a) and CMT (b).

ties were measured by the absorption spectra with a photoacoustic spectrum technique, and the CMT structure was determined with a four-circle diffractometer (Enraf-Nonius, Holland) and a single crystal.

3. Results and Discussion

3.1. Composition Analysis of HSMT and CMT

Na concentrations of 2.8–2.9% in the HSMT and 10^{-5}–10^{-6} in the CMT were detected using a flame spectrophotometer and an atomic absorption spectrophotometer, respectively. The metal-atom ratio of CMT was Cs: W = 6.00 : 12.12; this value should be compared with the theoretical value Cs : W = 6.00 : 12.00 for the CMT $Cs_6[H_2(W_3O_{10})_4]$. CMT is a member of the 12-tungstate family.

3.2. Thermogravimetric (TG) and Differential Thermal Analyses (DTA) of HSMT and CMT

The TG and DTA curves (Fig. 1) for HSMT and CMT indicated the following results:

3.2.1. Decomposition. The anhydrous HSMT and CMT began to decompose at 315 and 293°C, respectively.

3.2.2. Formulas. One mole of anhydrous HSMT dehydrated one mole of water more than one mole of anhydrous CMT, indicating that a mole of anhydrous HSMT contains two hydrogens more than a mole of anhydrous CMT.

Based on the above analysis (including the composition analysis) and the results that follow, the formulas for HSMT and CMT are $Na_4H_2[H_2(W_3O_{10})_4] \cdot 10H_2O$ and $Cs_6[H_2(W_3O_{10})_4] \cdot 9H_2O$, respectively.

3.2.3. Heat effect. Both HSMT and CMT underwent the following heat effects: endothermic peaks of a dehydration of crystalline water, exothermic peaks of a crystallization of amorphous anhydrous HSMT and CMT, an exothermic peak of a crystallization of amorphous WO_3, and two endothermic peaks making solid state structural phase transitions corresponding to the following reactions:

$$WO_3\ (\text{monoclinic}) \xrightarrow{728^\circ C} WO_3\ (\text{rhombic})$$

$$WO_3(\text{rhombic}) \xrightarrow[882^\circ C\ (\text{for CMT})]{797^\circ C\ (\text{for HSMT})} WO_3(\text{tetragonal})$$

The structural phase transitions of WO_3 are in good accord with Ref. (*2*). In addition to the above reaction temperatures, the other characteristic temperatures of HSMT and CMT were 121 and 128°C, 353 and 337°C, and 495 and 475°C. Dehydration of the compositional water, which causes the de-

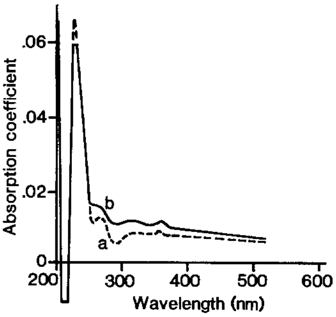

FIG. 2. The solution UV spectra of HSMT (a) and CMT (b).

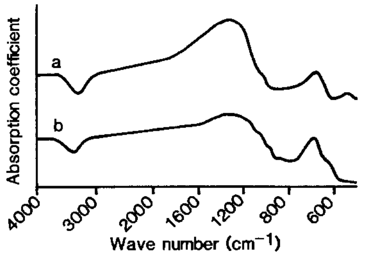

FIG. 3. The solid state IR spectra of HSMT (a) and CMT (b).

composition of anhydrous HSMT and CMT not only progressed slowly but also exhibited a weak endothermic effect; crystallization of amorphous anhydrous HSMT and CMT produces a strong exothermic effect before a dehydration of the compositional water is complete. The exothermic effect of the latter, with only one exothermic peak (357°C for HSMT, or 337°C for CMT), appears between about 250 and 400°C on the DTA curve of the HSMT or CMT. (A weak endothermic effect in HSMT at 410°C may represent loss of the second compositional water.)

3.3. Absorption Spectra of HSMT and CMT and Transparency of Noncrystalline HSMT

3.3.1. UV and IR spectra. The UV spectra (Fig. 2) of the HSMT and the CMT in solution are very similar to each other and to those of tungstosilicic acid and tungstophosphoric acid (*1*). For example, each of these spectra has two strong absorption peaks (225 and 260 nm). The solid state IR spectra (Fig. 3) of HSMT and CMT are also alike, as are those for tungstosilicic acid and tungstophosphoric acid (*1*).

The four compounds contain the polyanions $[H_2(W_3O_{10})_4]^{6-}$, $[P(W_3O_{10})_4]^{3-}$, and $[Si(W_3O_{10})_4]^{-4}$. We believe that the UV spectra show the $(W_3O_{10})_4^{8-}$ shell of these polyanions, whereas the solid state IR spectra reveal the differences between the cationic cores. This work has demonstrated that more detailed structural information is available from solid state IR spectra than from solution UV spectra.

3.3.2. Photoacoustic spectra and transparency noncrystalline HSMT. Figure 4 shows the photoacoustic spectrum of a transparent disk of a noncrystalline HSMT; its absorption peaks are like those of the UV spectrum of HSMT in solution. Figure 5 shows the transparency of the noncrystalline HSMT disk for which the photoacoustic spectrum is shown in Fig. 4. The problem associated with its nonradiative transitions will be discussed in another paper.

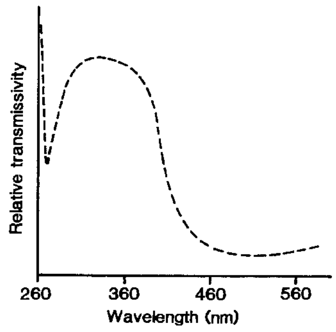

FIG. 4. The photoacoustic spectra of a transparent disk of noncrystalline HSMT.

TABLE I

THE CONTRIBUTION OF INNER- AND OUTER-SPHERE HYDROGEN IONS TO CONDUCTIVITY

Anhydrous solid materials		Hydrogen ions (No.)		Conductivity (ohm^{-1} cm^{-1})
Name	Formula	Inner	Outer	
Eu^{3+}-activated zinc, aluminum, and lanthanum oxide	ZnO, Al_2O_3, La_2O_3: Eu^{3+}	0	0	$(3 \pm 2) \times 10^{-7}$
Cesium metatungstate	$Cs_6[H_2(W_3O_{10})_4]$	2	0	$(6 \pm 3) \times 10^{-7}$
Hydrogen–sodium metatungstate	$Na_4H_2[H_2(W_3O_{10})_4]$	2	2	$(4 \pm 2) \times 10^{-5}$
Tungstophosphoric acid	$H_3[P(W_3O_{10})_4]$	0	3	$(2 \pm 1) \times 10^{-4}$
Tungstosilicic acid	$H_4[Si(W_3O_{10})_4]$	2	4	$(3 \pm 1) \times 10^{-3}$

3.4. Hydrogen Ionic Conductivity of the Solid State HSMT and CMT

Table I shows the hydrogen-ion conductivity of some anhydrous solid materials. It can be seen that the inner-sphere hydrogen ions make nearly no contribution to conductivity. Since these inner-sphere ions lie within the tetrahedron made up of four tungstoxide groups, $W_3O_{10}^{3-}$ (Fig. 6), or in the so-called tungsten cage (*3*), any transfer of these hydrogen ions to the outside of a polyanion is very slow, so their contribution may be overlooked. It can be seen clearly from Table I that if no more hydrogen is added to the outer sphere in the complex ion $[Z^{n+}(W_3O_{10})_4]^{n-8}$ (Z = H_2, Si, P, etc., n = chemical valance of the core cation(s) Z), its conductivity increases by approximately one order of magnitude.

The conductivity of the noncrystalline hydrous HSMT was also observed. It is well known that the hydrous heteropoly molybdic and tungstic acids are super protonic conductors (*4*).

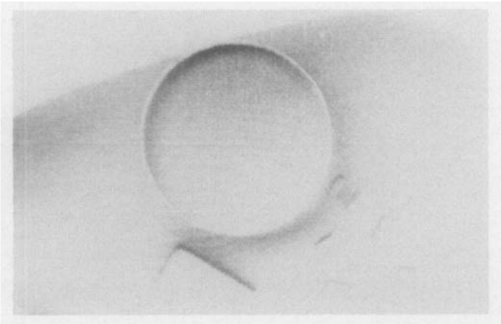

FIG. 5. Photograph of a noncrystalline HSMT transparent disk (2.3 × 13.3 mm) on a hand. The lines of the hand are seen clearly.

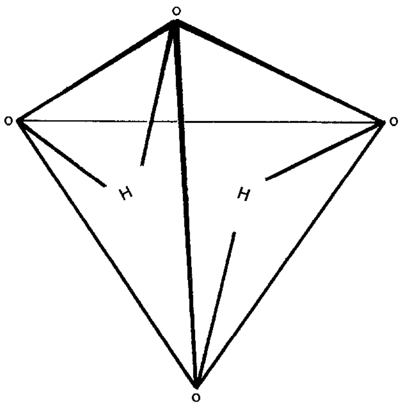

FIG. 6. Tetrahedral coordination of the complex ion $[H_2W_3O_{10})_4]^{6-}$; a small circle represents a tungstoxide group $(W_3O_{10})^{2-}$ of edge-shared octahedra; each octahedral corner shares an oxygen with an octahedral $(W_3O_{10})^{2-}$ group.

3.5. X-Ray Diffraction Structure Analysis of HSMT and CMT

X-ray diffraction showed that as prepared the HSMT and CMT samples were a noncrystalline and a powdery crystalline solid, respectively. A single crystal of CMT was measured with a four-circle diffractometer; its cell parameters were

$$a = 7.6830\ \text{Å}, b = 8.728\ \text{Å}. c = 20.354\ \text{Å}$$

$$a = 78.60\text{Å},\ \beta = 81.29\text{Å},\ r = 38.67\text{Å}.$$

Hence, CMT appears to be triclinic. Its crystalline system is different from that of tungstophosphoric acid (*5*).

Acknowledgments

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