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# Preparation and Properties of some new 6-Heteropoly–Tellurate Compounds of Tungsten and Molybdenum containing Vanadium

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## Abstract

Methods for preparing the following compounds $(NH_4)_7TeW_5VO_{24}\cdot5H_2O$, $(NH_4)_8TeW_4V_2O_{24}\cdot xH_2O$, $(NH_4)_9TeV_3W_3O_{24}\cdot xH_2O$ and $(NH_4)_7TeMo_5VO_{24}\cdot 8H_2O$ are described. The compounds thus prepared were examined for thermal behavior, IR, Raman, UV, X-ray, NMR and reaction with base.

## Introduction

The 6-heteropolytellurate compounds with Anderson–Evans structure are typical heteropoly compounds and have been studied extensively and are well understood. Having found them acting as catalysts in some organic reactions [1], people are interested in studying their properties further. Although some research of 6-heteropolytellurate compounds has been reported, until now no paper on vanadium substitution of the 6 series heteropoly compounds has appeared in the literature. As we know, when tungsten or molybdenum is replaced by vanadium in 12-heteropoly compounds, their catalytic properties are greatly improved. The same holds for the 6 series compounds.

## Experimental

### *Materials*

The compounds used in the experiments were all commercial A.R. agents, except for telluric acid which was commercial C.P. agent and was purified by G.R. nitric acid. Ammonium tungstate was prepared as previously reported [2].

Instruments Q-Derivatograph (Hungary): PE-783 infrared spectrophotometer (U.S.A.), RAMOUR-HGD laser raman spectrograph (France); UV-240 spectrophotometer (Japan); XD-3 X-ray diffractometer (Japan); FT-80A NMR spectrograph (U.S.A.).

### *Preparation*

#### *(a)* $(NH_4)_7TeW_5VO_{24}\cdot5H_2O$

An aqueous solution of telluric acid and an ammonia solution of vanadium pentoxide were mixed and refluxed for 5 h. A solution of ammonium tungstate was added and the contents were refluxed again for 12 h. The solution was concentrated and allowed to crystallize in the refrigerator until yellowish crystals were obtained. These were recrystallized 3 times from an aqueous solution of acetic acid at pH 4. (The molar ratio of telluric acid, vanadium pentoxide and ammoniun tungstate was 1:2:8.)

#### *(b)* $(NH_4)_8TeW_4V_2O_{24}\cdot xH_2O$ *and* $(NH_4)_9TeW_3V_3O_{24}\cdot xH_2O$

These were prepared *in situ* as already given under (a) and the solutions were allowed to crystallize in the refrigerator. The colour of the crystals was slightly deeper than that of (a). In this case the molar ratio of the original materials should be changed as the output was lower than in (a).

#### *(c)* $(NH_4)_7TeMo_5VO_{24}\cdot 8H_2O$

To 100 ml aqueous solution of 0.034 mol of ammonium metavanadate, 30 ml of 0.017 mol of telluric acid was added with constant stirring at a controlled temperature of 60 ℃. Then 10 min later 0.03 mol of ammonium paramolybdate and 10 ml of aqua ammonia were added. The solution was boiled slowly for 3 h, evaporated to ¼ of its volume and allowed to crystallize at room temperature until yellowish crystals were obtained. These were recrystallized 3 times from an aqueous solution of acetic acid at pH 4.5.

### *Analytical Procedures*

Tellurium was determined gravimetrically by sulfuric dioxide–hydrazine chloride; tungsten was determined gravimetrically by 8-hydroxyquinoline; molybdenum was determined gravimetrically by α-benzoin oxime; ammonium was determined titrametrically by the distillation method; vanadium was determined titrametrically by oxidation–reduction; the amount of water was determined by thermal gravimetric analysis. The results are shown in Table 1.

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TABLE I. Analysis of Compounds

| Compounds | Found | | | | Calculated | | | |
|---|---|---|---|---|---|---|---|---|
| | %$NH_4^+$ | %Te | %$WO_3$($MoO_3$) | %V | %$NH_4$ | %Te | %$WO_3$($MoO_3$) | %V |
| 1: $(NH_4)_7TeW_5VO_{24}\cdot 5H_2O$ | 7.40 | 7.53 | 68.30 | 2.99 | 7.22 | 7.56 | 68.28 | 3 |
| 2: $(NH_4)_8TeW_4V_2O_{24}\cdot H_2O$ | 9.09 | 8.04 | 58.59 | 6.42 | | | | |
| 3: $(NH_4)_9TeW_3V_3O_{24}\cdot H_2O$ | 11.02 | 8.67 | 47.40 | 10.43 | | | | |
| 4: $(NH_4)_7TeMo_5VO_{24}\cdot H_2O$ | 9.59 | 9.70 | 54.86 | 3.88 | 9.6 | 9.72 | 54.84 | |

TABLE II. Thermal Behavior of $TeW_5V$ and $TeMo_5V$

| Compound | Endotherms (℃) | Exotherms (℃) |
|---|---|---|
| $(NH_4)_7TeW_5VO_{24}\cdot 5H_2O$ | 146 | 580 |
| $(NH_4)_7TeMo_5VO_{24}\cdot 8H_2O$ | 132, 305, 360 | 325, 405 |

## Results and Discussion

### *Thermal Behavior*

The data for the thermal analysis of (a) and (c) are shown in Table II. It has been reported [3] that when ammonium compounds of molybdenum or vanadium are decomposed by heating, ammonia is oxidised on the surface of the molybdenum or vanadium oxide and, at the same time, the oxide catalyses the oxidation process. This also happened in the thermal decomposition of $(NH_4)_7TeMo_5VO_{24}\cdot 8H_2O$. It began to lose weight at 80 ℃ up to 132 ℃ when there was an endothermal peak on the curve of DTA. Five molecules of water were lost. After that weight continued to be lost up to 305 ℃ when there was another endothermal peak, corresponding to loss of some ammonium and water. The compound had decomposed slightly; the oxidation of the ammonium, lost as ammonia, took place on the surface of the vanadium and molybdenum oxides, so there was an exothermal peak on the DTA curve at 325 ℃. However ammonium and water were not lost completely and the loss of weight continued according to the endothermal peak at 360 ℃. Finally the compound was decomposed completely and one exothermal peak appeared on the curve of DTA at 405 ℃. The combined catalysis action of the oxides of vanadium and molybdenum probably cuased the exothermal peak between the two endothermal peaks. It also accelerated the decomposition of the compound and lowered its thermal stability.

### *Ultraviolet Spectrum*

These compounds are coloured and have absorption in the range of 190–400 nm $TeW_5V$: 204.4 nm, $TeMo_5V$: 207 nm.

The absorption belongs to charge transfer absorption and $p\pi$–$d\pi$ transition between metal and oxygen atoms.

### *NMR Spectrum*

$^{51}V$ NMR of the aqueous solution of $TeW_5V$ was determined. There was only a single sharp peak $\delta = 114.74$ ppm. It showed the purity of the compound and no isomer.

### *IR and Raman Spectrum*

The data are shown in Table III. The results given in ref. [4] were helpful in assigning vibration models to the compounds prepared in this paper. The data show that when vanadium is substituted for the molybdenum or tungsten atom, there is no effect on the bond between the centre and ligand atoms. However there is a strong effect on the terminal and bridge bonds on the planar annulus skeleton formed by $MO_6$ octahedra sharing edges, especially on the symmetric stretching vibration of the bridge bond and the antisymmetric stretching vibration of the terminal bond as shown in Fig. 1.

As can be seen in Fig.1, repalcement of molybdenum and tungsten by vanadium results in a shift of the vibration energy levels of the bridge and terminal bonds of the ligand and an increase in the reaction activity because the shift is to a low frequency area. The terminal bond vibration energy levels of two and three vanadium substitutions are reduced to the same level as that of $TeMo_5V$. This shows that when solid 6-heteropoly compounds act as a catalyst, the catalytic reaction takes place on the planar annulus molecular skeleton with the substituted vanadium as the active centre.

Replacement by vanadium makes the symmetry of the 6-heteropoly compound lower than that of

TABLE III. The Data of IR and RA Spectra

| Compounds | Peak ($cm^{-1}$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (a) IR | | | | | | | | | | | | | | |
| 1: $(NH_4)_6TeMo_6O_{24}\cdot H_2O$ | 463 | 495 | 545 | 620 | 675 | 885 | | 932 | 1410 | 1680 | 3030 | 3160 | 3440 (4) | |
| 2: $(NH_4)_7TeW_5VO_{24}\cdot 5H_2O$ | 460 | 490 | 560 | 625 | 670 | 890 | | 945 | 1395 | 1600 | 3020 | 3140 | 3540 | |
| 3: $(NH_4)_8TeW_4V_2O_{24}\cdot 5H_2O$ | 460 | | 570 | 620 | 690 | 890 | | 920 | 1400 | 1620 | 3150 | | 3510 | |
| 4: $(NH_4)_9TeW_3V_3O_{24}\cdot H_2O$ | 460 | | 570 | 620 | 690 | 890 | | 920 | 1400 | 1600 | 3140 | | 3500 | |
| 5: $(NH_4)_7TeMo_5VO_{24}\cdot H_2O$ | 460 | 490 | 545 | 610 | 665 | 860 | 885 | 920 | 1400 | 1640 | 3020 | 3140 | 3520 | |
| | Va<br>Vs | M–O–M<br>$\mathrm{Te{-}O}{<}^{\mathrm{M}}_{\mathrm{M}}$ | | Va<br>Vs | $\mathrm{O}{<}^{\mathrm{M}}_{\mathrm{M}}$ | Va<br>Vs | O–M | | $NH_4$ | $H_2O$ | $NH_4$ | | $H_2O$ | |
| (b) Raman | | | | | | | | | | | | | | |
| $(NH_4)_6TeMo_6O_{24}\cdot 7H_2O$ | 946 | 894 | 743 | 704 | 632 | 573 | 550 | 448 | 390 | 349 | 307 | 221 | 150 | 108 |
| $(NH_4)_7TeW_5VO_{24}\cdot 5H_2O$ | 950 | 920 | 874 | 720 | 662 | 550 | 456 | 324 | 332 | 346 | 296 | 274 | 212 | 128 |
| $(NH_4)_7TeMo_5VO_{24}\cdot 8H_2O$ | 990 | 938 | 798 | 660 | 474 | 374 | 333 | 278 | 234 | 207 | 192 | 142 | 120 | 108 |

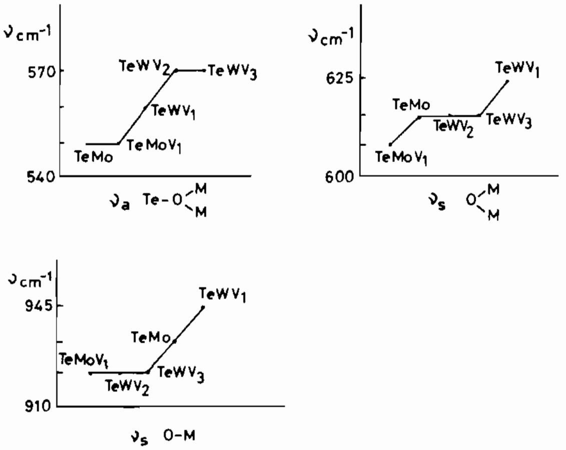

Fig. 1. Comparison of absorption bands.

the compound formed by the same ligands and the same absorption band split, such as the stretching vibration of ammonium telluromolybdate at 885 $cm^{-1}$ which becomes 865 and 880 $cm^{-1}$ in the absorption of ammonium telluromolybdovanadate. When the number of vanadium atoms is increased, the vibration of

$$\mathrm{Te{-}O}{<}^{\mathrm{M}}_{\mathrm{M}}$$

and

$$\mathrm{O}{<}^{\mathrm{M}}_{\mathrm{M}}$$

become respectively several vibrations, such as

$$\mathrm{Te{-}O}{<}^{\mathrm{M}}_{\mathrm{W}} \quad \mathrm{Te{-}O}{<}^{\mathrm{W}}_{\mathrm{V}} \quad \mathrm{Te{-}O}{<}^{\mathrm{V}}_{\mathrm{V}}$$

and

TABLE IV. The Data of X-ray Powder Diffraction

| Te–W$_5$–V | | Te–Mo$_5$–V | |
|---|---|---|---|
| $I/I_0$ | $d$ (A) | $I/I_0$ | $d$ (A) |
| 100 | 8.345 | 100 | 8.345 |
| 60 | 7.225 | 85.6 | 7.254 |
| 100 | 6.417 | 69.1 | 7.138 |
| 51.2 | 5.836 | 100 | 6.501 |
| 43.2 | 5.062 | 65 | 5.848 |
| 17.5 | 4.848 | 41.1 | 5.644 |
| 18.2 | 4.450 | 63.3 | 5.091 |
| 18.0 | 4.291 | 43.3 | 4.874 |
| 16.8 | 4.171 | 33.3 | 3.880 |
| 32.2 | 3.850 | 46.7 | 3.302 |
| 13.0 | 3.720 | 72.2 | 3.232 |
| 59 | 3.290 | 48.3 | 3.203 |
| 58.2 | 3.209 | 38.3 | 3.116 |
| 18 | 3.110 | 33.9 | 3.003 |
| 22.2 | 2.993 | 27.8 | 2.745 |
| 15 | 2.917 | 34.4 | 2.652 |
| 13 | 2.823 | 53.9 | 2.605 |
| 14.5 | 2.737 | 36.7 | 2.71 |
| 22 | 2.640 | 34.4 | 2.501 |
| 37.8 | 2.592 | 46.7 | 2.368 |
| 15 | 2.530 | | |
| 25 | 2.480 | | |
| 13 | 2.436 | | |
| 16 | 2.383 | | |
| 16 | 2.362 | | |
| 12.5 | 2.244 | | |

$$\mathrm{O}{<}^{\mathrm{W}}_{\mathrm{W}} \quad \mathrm{O}{<}^{\mathrm{W}}_{\mathrm{V}} \quad \mathrm{O}{<}^{\mathrm{V}}_{\mathrm{V}}$$

so it makes the bands slightly wider.

### *X-ray Powder Diffraction*

As shown in Table IV, the result is the same as that of the other physical determinations: substitutions of vanadium have the same structure as ammonium telluromolybdate, *i.e.* Anderson–Evans structure. Substitutions of tungsten and molybdenum have not only the same ionic structure, but also the same crystal structure. If we take eight strong diffraction rays this is very clear. As follows: $TeMo_6$: 8.44, 6.506, 7.31, 5.894, 3.3186, 3.2048, 3.2395, 3.25(6); $TeW_5V$: 6.417, 8.345, 7.225, 3.29, 3.209, 5.36, 5.062, 2.592; $TeMo_5V$: 6.501, 8.345, 7.254, 3.232, 7.13 5.848, 5.091, 2.605.

The distance of the crystallographic plane of the substitutions is smaller because the ion radius of vanadium is smaller than that of tungsten and molybdenum.

*Reaction with Base*

The reaction with base of the solutions of $TeW_5V$ and $TeMo_5V$ has been determined. It was carried out titrametrically using standard sodium hydroxide in aqueous solution. There were two leap peaks on the titration curves for $TeW_5V$ and $TeMo_5V$: $TeW_5V$, pH = 7.8–8.7. pH = 9.0–12.1; $TeMo_5V$, pH = 8.5–9.4. pH = 9.4–12.1. The first leap showed the process of the hydroxide decomposition of the compounds. The second showed the conversion between the two different kinds of vanadate ions. During titration the colours of the solutions disappeared in the second leap. $TeW_5V$ at pH 9.42 $TeMo_5V$ at pH 10.2. The reaction with base can be expressed:

$$TeW_5VO_{24}^{7-} + 10\,OH^- = TeO_6^{6-} + 5WO_4^{2-} + VO_3^- + 5H_2O$$

$$TeMo_5VO_{24}^{7-} + 10\,OH^- = TeO_6^{6-} + 5MoO_4^{2-} + VO_3^- + 5H_2O$$

$$VO_3^- + OH^- = HVO_4^{2-}$$

Ripan reported [5] that $TeMo_6O_{24}^{6-}$ in aqueous solution was stable in the range of pH 2–8 but was decomposed completely at pH 8. The result of tiration for our compound shows that replacement of $TeMo_6O_{24}^{6-}$ by vanadium increases stability in the aqueous solution because the leap point of hydroxide decomposition appears later.

## Conclusion

We prepared four new 6 series heteropoly compounds containing vanadium. The results show they have Anderson–Evans structures in which the tellurium atom is the centre atom and the ligand atoms form a planar annulus skeleton. Replacement by vanadium increases stability in aqueous solution, increases reaction activity but decreases thermal stability.

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