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# REVIEW OF THE EFFECTS OF PH ON THE SYNTHESIS OF HETEROPOLY TUNGSTATE ANIONS

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## TABLE OF CONTENTS

1. *Abstract*
2. *Introduction*
3. *Materials & Methods*
4. *Results*
5. *Conclusions*
6. *Acknowledgements*
7. *References*

## 1. ABSTRACT

The reaction of the $WO_4^{2-}$ ion in the pH range 2 to 8 was carried out with the following metal ions individually & in combination: $Mn^{2+}$, $Mn^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Co^{3+}$, $Ni^{2+}$, $Cu^{1+}$, $Cu^{2+}$, $Zn^{2+}$, $Ga^{3+}$, $Mg^{2+}$, $In^{3+}$, $RAsO_3^{2-}$, & $RSbO_3^{2-}$. Some 36 heteropolyanions have been isolated in the crystalline form & characterized fully. The antiviral activity of these anions has been determined against HIV, herpes & respiratory viruses. The redox potentials for these anions have been measured by cyclic voltammetry & documented. At pH 8, the anions adopt a Weakley structure & at pH 7, the Keggin structure is formed. At pH 6 to 7, the distorted Keggin structure, 1:1:11, is formed. Below pH 6, the distorted Dawson structure is formed. Some anions showed good antiviral activity with positive redox potentials and others with negative redox potentials. When the metal ion is attached to an organic group, a ring-type structure is formed: a 2:5, 2:6, and 1:7 heteropolytungstate.

## 2. INTRODUCTION

The reactions of $WO_4^{2-}$ with most of the elements of the periodic table have been covered in the literature.(1 - 6) The Keggin structure (7, 8) (see Figure 1) or structures related to the Keggin structure like the Dawson (9) (see Figure 2) and the Weakley (10) (see Figure 3) are predominant species. The Keggin structure has virtual Td symmetry and is based on an $XO_4$ tetrahedral unit surrounded by twelve $WO_6$ octahedra arranged into four groups of three edge-shared octahedra, $W_3O_{13}$. These groups are linked by shared corners to each other and to the central $XO_4$ tetrahedral unit. The Keggin, Dawson, and Weakley structures each have octahedral $WO_6$ units bonded through shared corners and shared edges. The Dawson structure consists of two $XW_9$ units fused into a cluster of virtual $D_{3h}$ symmetry with two types of W(VI) atoms: six polar and twelve equatorial. The Weakley structure consists of two $XW_9$ units sandwiching a planar array of four $MO_6$ units.(4) The Keggin structure has one tetrahedral site in the center of the structure, the Dawson has two such sites and the Weakley structure has two as well. With a large heteroatom like Ce (IV) the paratungstate, $(Ce(IV)W_{12}O_{42})^{8-}$, is formed (see Figure 4). However, when the reaction is run with $RAsO_3^{2-}$, the predominant species was the 2:6 structure (11) (see Figure 5) a ring of six $WO_6$ octahedra linked by three shared edged, and capped on either side by $RAsO_3$ groups where R is methyl, phenyl, or a phenyl derivative and with P the 2:5 complex is formed (12) (see Figure 6). When the pH was 7.5 – 8 and the metal atom was As (13) the 1:7 structure is formed `where four $WO_6$ octahedra share edges. The other three $WO_6$ share edges among them and corners with the other four. The heteroatom occupies a tetrahedron which shares three corners with the two sets of $WO_6$ octahedra (Figure 8).

In this paper we review the reactions of certain metal ions (from 0.68 to 0.99 Å) individually and in

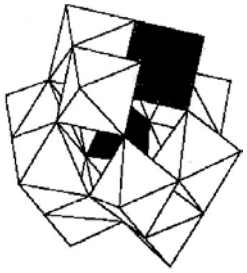

**Figure 1.** Keggin Structure, $(M(m)X(n)W_{11}O_{40})^{(14-m-n)-}$ .

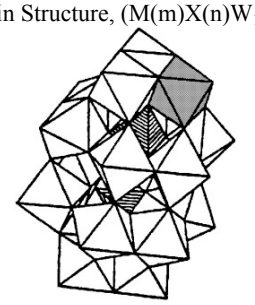

**Figure 2.** Dawson Structure, $(M(m)X(n)_2W_{17}O_{62})^{(22-m-2n)-}$ .

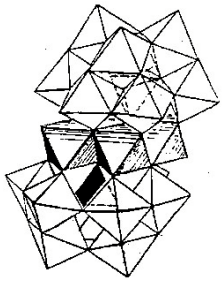

**Figure 3.** Weakley Structure, $(X(n)_2M(n)_4W_{18}O_{70}H_y)^{(32-4m-2n-y)-}$

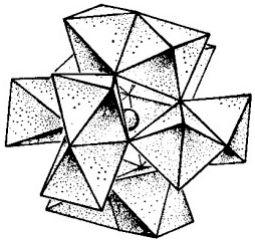

**Figure 4.** The paratungstate structure, $(X(n)W_{12}O_{42})^{(12-n)-}$ .

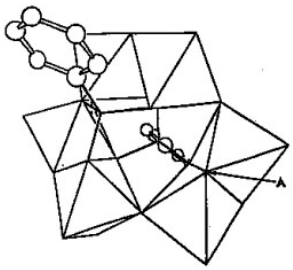


**Figure 5.** The structure of $((PhAs)_2W_6O_{25}H)^{5-}$. Open Circles are Phenyl Carbon Atoms Making up the Phenyl Group.

combination with each other that have been carried out in our lab. Table 1 summarize those reactions in the range pH 2-8. The antiviral activity of 23 anions against HIV, herpes, and respiratory viruses is presented. The redox potentials of these anions have also been determined by cyclic voltammetry and documented and in addition, we report the preparation and characterization of the new heteropolyanion: $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ which has the Weakley structure.

## 3. MATERIALS AND METHODS

The preparation procedures may be summarized by mixing the heteroatoms with addenda atoms in a 1:3 molar ratio. The mixing is done after heating the $WO_4^{2-}$ to 55°C. After adjusting the pH of the solution to the desired value, by adding HF. Then, the heteroatom or atoms are introduced drop wise in the solution. When the addition of heteroatom is completed, the reaction mixture is covered with a watch glass and boiled for a few minutes. 30 % $H_2O_2$ is usually added as an oxidizing agent whenever it is necessary. Table 1 lists the different combinations of heteroatoms used in the reactions. Below, we list the isolated compounds with their proper pH values. At pH 8, the following anions: $(Fe_3Co_4W_{17}O_{70}H_6)^{10-}$ and $(Cu_2Fe_4W_{18}O_{70}H_6)^{10-}$ are yielded. When the pH drops to the pH 6 - 7 range, this reaction yields: $(CuW_{11}O_{38}F_2H_6)^{4-}$, $(MnW_{11}O_{38}F_2H_6)^{4-}$, $(GaW_{11}O_{40}H_4)^{7-}$, $(CuNiW_{11}O_{38}F_2H_4)^{4-}$, $(NiMnW_{11}O_{38}F_2H_4)^{4-}$,$(CoSiW_{11}O_{40}H_2)^{6-}$, $(K_7FeCoW_{11}O_{40}H_2)^{7-}$, $(Co_2W_{11}O_{39}FH_2)^{7-}$,$(NiCoW_{11}O_{39}FH_2)^{7-}$,and $(CuMn^{2+}W_{11}O_{39}FH_2)^{7-}$. When the pH is 6, $((C_6H_5Sb)_2W_6O_{24})^{4-}$ and $(H_2F_6NaW_{18}O_{56})^{7-}$ form. In the pH range 5 – 6, the following anions were isolated: $(Mn^{3+}W_{17}O_{56}F_6NaH_4)^{8-}$, $(InW_{17}O_{56}F_6NaH_5)^{7-}$, $(CuW_{17}O_{56}F6NaH_4)^{9-}$,$(Mn^{2+}W_{17}O_{56}F_6NaH_4)^{9-}$, $(Fe^{3+}W_{17}O_{56}F_6NaH_4)^{8-}$, $(ZnW_{17}O_{56}F_6NaH_0)^{9-}$, $(MgW_{17}O_{56}F_6NaH_4)^{9-}$, $Cu^{+}W_{17}O_{53}F_9NaH_2)^{9-}$, $(Co^{3+}W_{17}O_{56}F_6NaH_4)^{8-}$, and $(NiW_{17}O_{56}F_6NaH_4)^{9-}$. At pH 5.5 , the following anions form: $(C_6H_5AsW_7O_{27}H)^{7-}$, and $(K_9CoW_{17}O_{56}F_6NaH_4)^{9-}$. Finally, at pH 5 $((C_6H_5Sb)_2W_6O_{24})^{6-}$ forms. The antiviral activity of these anions against different viruses such as HIV, Herpes Type I, Herpes Type II, RSV, Flu A, and Flu B are summarized in Tables 2, 3 and 4 (14).

## 4. RESULTS AND DISCUSSION

The reported compounds were characterized by X-ray diffraction single crystal and powder pattern measurements, elemental analyses, Fourier transform infrared (FTIR) spectroscopy, ultraviolet (UV)- visible (VIS) electronic spectroscopy, cyclic voltammetry, fast atom bombardment mass spectral (FABMS) and magnetic susceptibility measurements were carried out as previously described.(15)

The analyses were performed by Galbraith Laboratories, Inc, and are in good agreement with those calculated from the formulation of $Na_{12}(Fe_2Co_4W_{18}O70H_6)$•39 $H_2O$. Elemental Analysis for $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ (mw 5761) Anal.

**Table 1.** Heteropolyoxotungstates and Heteropolyoxofluorotungstate Anions

| No. | Formula | References | No. | Formula | References |
|---|---|---|---|---|---|
| 1 | $(CN_3H_6)_6(C_6H_5Sb)_2W_6O_{24}•XH_2O$ | 25 | 24 | $(CN_3H_6)_7H_2F_6NaW_{18}O_{56}•10H_2O$ | 28 |
| 2 | $(CN_3H_6)_7C_6H_5AsW_7O_{27}H•XH_2O$ | 13 | 25 | $(NH_4)_9NiW_{17}O_{56}F_6NaH_4•9H_2O$ | 28 |
| 3 | $Na_{10}Fe_3Co_4W_{17}O_{70}H_6•29H_2O$ | 20 | 26 | $(NH_4)_4CuNiW_{11}O_{38}F_2H_4•3H_2O$ | 34 |
| 4 | $Na_{10}Cu_2Fe_4W_{18}O_{70}H_6•29H_2O$ | 28 | 27 | $(NH_4)_4NiMnW_{11}O_{38}F_2H_4•3H_2O$ | 34 |
| 5 | $K_9CoW_{17}O_{56}F_6NaH_4•9H_2O$ | 30 | 28 | $(N(CH_3)_4)_4CuW_{11}O_{38}F_2H_6•10H_2O$ | 35 |
| 6 | $K_7FeCo^{2+}W_{11}O_{40}H_2•5H_2O$ | 27 | 29 | $(N(CH_3)_4)_4MnW_{11}O_{38}F_2H_6•10H_2O$ | 35 |
| 7 | $K_7Co^{2+}FeW_{11}O_{40}H_2•5H_2O$ | 27 | 30 | $(NH_4)_7GaW_{11}O_{40}H_4•5H_2O$ | 26 |
| 8 | $K_6FeCo^{3+}W_{11}O_{40}H_2•5H_2O$ | 27 | 31 | $(NH_4)_7InW_{17}O_{56}F_6NaH_5•9H2O$ | 37 |
| 9 | $K_6Co^{3+}FeW_{11}O_{40}H_2•5H_2O$ | 27 | 32 | $(NH_4)_6(CoW_{11}O_{38}F_2H_4)•4H_2O$ | 37 |
| 10 | $(CN_3H_6)_4(C_6H_5Sb)_2W_6O_{24}•XH_2O$ | 27 | 33 | $(NH_4)_7(Mn^{2+}ZnW_{11}O_{39}FH_2)•19H_2O$ | 27 |
| 11 | $(NH_4)_9Mn^{2+}W_{17}O_{56}F_6NaH_4•9H_2O$ | 27 | 34 | $(NH_4)_6(Mn^{3+}ZnW_{11}O_{38}F_2H_2)•19H_2O$ | 27 |
| 12 | $(NH_4)_8Fe^{3+}W_{17}O_{56}F_6NaH_4•8H_2O$ | 30 | 35 | $(NH_4)_8((H_2O)CuO_5ZnO_4W_{11}O_{28}F_2)•18H_2O$ | 38 |
| 13 | $(NH_4)_8Mn^{3+}W_{17}O_{56}F_6NaH_4•8H_2O$ | 46 | 36 | $(NH_4)_6(Fe^{3+}ZnW^{6+}{}_{10}W^{5+}O_{36}F_4)•17H_2O$ | 15 |
| 14 | $(NH_4)_9CuW_{17}O_{56}F_6NaH_4•9H_2O$ | 31 | 37 | $Na_{12}(Co_6W_{18}O_{70}H_8)•29\ H_2O$ | 16 |
| 15 | $(NH_4)_7NiCoW_{11}O_{39}FH_2•XH_2O$ | 32 | 38 | $Na_{12}(Fe_6W_{18}O_{70}H_8)•20\ H_2O$ | 16 |
| 16 | $(NH_4)_7CuMn^{2+}W_{11}O_{39}FH_2•XH_2O$ | 32 | 39 | $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)•20\ H_2O$ | 44 |
| 17 | $(NH_4)_9ZnW_{17}O_{56}F_6NaH_4•9H_2O$ | 47 | 40 | $(CN_3H_6)_4((RP)_2W_5O_{21})$ | 12 |
| 18 | $(NH_4)_9MgW_{17}O_{56}F_6NaH_4•XH_2O$ | 33 | 41 | $(CN_3H_6)_5((RAs)_2W_6O_{24}H)$ | 11 |
| 19 | $(NH_4)_9Cu^{+}W_{17}O_{53}F_9NaH_2•12H_2O$ | 33 | 42 | $(CN_3H_6)_4((RAs)_2W_6O_{25}H_2)$ | 11 |
| 20 | $(NH_4)_8(Fe^{+3}W^{+5}W^{+6}{}_{16}O_{55}F_7NaH_4)$ | 33 | 43 | $(CN_3H_6)_7(CH_3AsW_7O_{27}H)$ | 11 |
| 21 | $(NH_4)_8Co^{3+}W_{17}O_{56}F_6NaH_4•8H_2O$ | 32 | 44 | $(NH_4)_6(NaCoW_{11}O_{43}FH_2)$ | 40 |
| 22 | $(NH_4)_6(NiMn^{3+}W_{10}O_{37}F_3H_6)$ | 46 | 45 | $(NH_4)_6(NaNiW_{11}O_{43}FH_2)$ | 40 |
| 23 | $(NH_4)_7(Mn^{3+}W_{11}O_{37}F_3H)$ | 36 | 46 | $(NH_4)_9CuW_{17}O_{56}F_5NaH_5$ | 31 |

**Table 2.** The Redox Potentials for Some Heteropoly Compounds That Have Been In-Vitro Tested Against HIV

| Compound | $E_{pk}$(Cathode)/$E_{pk}$(Anode)<br>GCE vs. Ag/AgCl Reference Electrode 0.9-M $Na_2SO_4$ (V) | Therapeutic Index (TI)<br>TI = $IC_{50}/EC_{50}$ |
|---|---|---|
| $Na_{10}Cu_2Fe_4W_{18}O_{70}H_6•29H_2O$ | -0.225/-0.037; -0.773/-0.397 | 35.6 |
| $(NH_4)_7CuMn^{+2}W_{11}O_{39}FH_2•XH_2O$ | 0.631/0.950;-0.171/-0.082; -0.334/-0.550 | 9.6 |
| $K_6CoSiW_{11}O_{40}H_2•XH_2O$ | 0.715/0.905;-1.275/-1.053 | 2.2 |
| $(NH_4)_4CuNiW_{11}O_{38}F_2H_4•3H_2O$ | -0.304/-0.149;-0.426/-0.369;-0.750/-0.870 | IA |
| $(NH_4)_4NiMnW_{11}O_{38}F_2H_4•3H_2O$ | 0.488/0.877;-0.272/-0.197;-0.758/-0.755 | IA |
| $(N(CH_3)_4)_4CuW_{11}O_{38}F_2H_6•10H_2O$ | -0.720/-0.029 (pH5.0) | IA |
| $(N(CH_3)_4)_4MnW_{11}O_{38}F_2H_6•10H_2O$ | 0.686/0.419;-1.195/-0.535 (pH5.0) | IA |
| $(NH_4)_7GaW_{11}O_{40}H_4•5H_2O$ | 0.308/--;-1.337/--;-1.521/-- | IA |
| $(NH_4)_7InW_{17}O_{56}F_6NaH_5•9H_2O$ | -0.673/-0.513;-1.185/-1.229 | IA |
| $K_9CoW_{17}O_{56}F_6NaH_4•9H_2O$ | -0.896/-0.625;-1.332/-0.890; | IA |
| $(NH_4)_9Mn^{+2}W_{17}O_{56}F_6NaH_4•9H_2O$ | 0.519/0.815;0.321/--;-0.952/-0.554; -1.235/-0.817 | 17 |
| $(NH_4)_8Fe^{+3}W_{17}O_{56}F_6NaH_4•8H_2O$ | -0.336/-0.105;-0.858/-0.571; -1.177/-0.761 | 30 |
| $(NH_4)_8Mn^{+3}W_{17}O_{56}F_6NaH_4•8H_2O$ | 0.948/0.722;-0.342/-0.299; -0.921/-0.622;-1.177/-0.821 | 7.3 |
| $(NH_4)_9CuW_{17}O_{56}F_6NaH_4•9H_2O$ | -0.169/-0.025;-0.638/-0.633;-0.864/-0.699 | 4.9 |
| $(NH_4)_9ZnW_{17}O_{56}F_6NaH_4•9H_2O$ | -0.656/-0.505;-1.242/-1.118;-1.510/-1.461 | >130/26 |
| $(NH_4)_9MgW_{17}O_{56}F_6NaH_4•XH_2O$ | 0.903/0.823;-0.826/-0.518 | 21 |
| $(NH_4)_9Cu^{+}W_{17}O_{53}F_9NaH_2•12H_2O$ | -0.157/-0.086;-0.672/-0.420; -0.863/-0.665; -1.260/-1.153 | IA |
| $(CN_3H_6)_7H_2F_6NaW_{18}O_{56}•10H_2O$ | -0.305/-0.203;-0.409/-0.341; -0.769/-0.689;-1.025/-0.929 | 10 |
| $(NH_4)_9NiW_{17}O_{56}F_6NaH_4•9H_2O$ | -0.897/-0.769;-1.168/-1.010;-1.450/-1.363 | 18 |

IA = inactive

**Table 3.** Redox Potentials for Some Heteropoly Compounds That Have Been In-Vitro Tested Against Some Herpes Viruses

| Compound | $E_{pk}$(Cathode)/$E_{pk}$(Anode) GCE vs. Ag/AgCl Reference Electrode 0.9-M $Na_2SO_4$ (V) | Selective Index (SI) SI = $IC_{50}/EC_{50}$ | |
|---|---|---|---|
| | | HSV1 | HSV2 |
| $(NH_4)_7CuMn^{+2}W_{11}O_{39}FH_2$•$XH_2O$ | 0.631/0.950;-0.171/-0.082; -0.334/-0.550 | >91 | >100 |
| $K_6CoSiW_{11}O_{40}H_2$·$XH_2O$ | 0.715/0.905; -1.275/-1.053 | >15.6 | IA |
| $(NH_4)_4CuNiW_{11}O_{38}F_2H_4$•$3H_2O$ | -0.304/-0.149;-0.426/-0.369;-0.750/-0.870 | IA | IA |
| $(NH_4)_4NiMnW_{11}O_{38}F_2H_4$•$3H_2O$ | 0.488/0.877;-0.272/-0.197;-0.758/-0.755 | IA | IA |
| $(N(CH_3)_4)_4CuW_{11}O_{38}F_2H_6$•$10H_2O$ | -0.720/-0.029 (pH5.0) | IA | IA |
| $(N(CH_3)_4)_4MnW_{11}O_{38}F_2H_6$•$10H_2O$ | 0.686/0.419;-1.195/-0.535 (pH5.0) | IA | IA |
| $(NH_4)_7GaW_{11}O_{40}H_4$•$5H_2O$ | 0.308/--;-1.337/--;-1.521/-- | >556 | >1667 |
| $Na_{10}Cu_2Fe_4W_{18}O_{70}H_6$•$29H_2O$ | -0.225/-0.037; -0.773/-0.397 | 11.4 | 9.8 |
| $K_9CoW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.896/-0.625; -1.332/-0.890; | >250 | >131 |
| $(NH_4)_9Mn^{+2}W_{17}O_{56}F_6NaH_4$•$9H_2O$ | 0.519/0.815;0.321/--;-0.952/-0.554;-1.235/-0.817 | 94.4 | 185 |
| $(NH_4)_8Fe^{+3}W_{17}O_{56}F_6NaH_4$•$8H_2O$ | -0.336/-0.105; -0.858/-0.571; -1.177/-0.761 | 194 | 4280 |
| $(NH_4)_8Mn^{+3}W_{17}O_{56}F_6NaH_4$•$8H_2O$ | 0.948/0.722;-0.342/-0.299;-0.921/-0.622;-1.177/-0.821 | IA | IA |
| $(NH_4)_9CuW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.169/-0.025;-0.638/-0.633;-0.864/-0.699 | IA | IA |
| $(NH_4)_9ZnW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.656/-0.505;-1.242/-1.118;-1.510/-1.461 | >10.3 | >6.2 |
| $(NH_4)_9MgW_{17}O_{56}F_6NaH_4$•$XH_2O$ | 0.903/0.823; -0.826/-0.518 | >21.7 | >27.8 |
| $(NH_4)_9Cu^{+}W_{17}O_{53}F_9NaH_2$•$12H_2O$ | -0.157/-0.086;-0.672/-0.420; -0.863/-0.665;-1.260/-1.153 | >151.5 | >62.5 |
| $(CN_3H_6)_7H_2F_6NaW_{18}O_{56}$•$10H_2O$ | -0.305/-0.203;-0.409/-0.341;-0.769/-0.689;-1.025/-0.929 | >333 | >164 |
| $(NH_4)_9NiW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.897/-0.769;-1.168/-1.010;-1.450/-1.363 | >159 | >59 |
| $(NH_4)_7InW_{17}O_{56}F_6NaH_5$•$9H_2O$ | -0.673/-0.513; -1.185/-1.229 | >41.7 | >31.2 |

IA = inactive

**Table 4.** Redox Potentials for Some Heteropoly Compounds that have been Tested In-Vitro Against Some Respiratory Viruses

| Compound | $E_{pk}$(Cathode)/$E_{pk}$(Anode) GCE vs. Ag/AgCl Reference Electrode 0.9-M $Na_2SO_4$ (V) | Selective Index (SI) SI = $IC_{50}/EC_{50}$ | | |
|---|---|---|---|---|
| | | RSV | Flu A | Flu B |
| $Na_{10}Cu_2Fe_4W_{18}O_{70}H_6$•$29H_2O$ | -0.225/-0.037; -0.773/-0.397 | IA | IA | IA |
| $K_9CoW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.896/-0.625; -1.332/-0.890; | IA | 16-31 | 16 |
| $(NH_4)_9Mn^{+2}W_{17}O_{56}F_6NaH_4$•$9H_2O$ | 0.519/0.815;0.321/--;-0.952/-0.554;-1.235/-0.817 | 62 | IA | IA |
| $(NH_4)_8Fe^{+3}W_{17}O_{56}F_6NaH_4$•$8H_2O$ | -0.336/-0.105; -0.858/-0.571; -1.177/-0.761 | IA | IA | IA |
| $(NH_4)_8Mn^{+3}W_{17}O_{56}F_6NaH_4$•$8H_2O$ | 0.948/0.722;-0.342/-0.299;-0.921/-0.622;-1.177/-0.821 | IA | IA | IA |
| $(NH_4)_9CuW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.169/-0.025;-0.638/-0.633;-0.864/-0.699 | IA | IA | IA |
| $(NH_4)_9ZnW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.656/-0.505;-1.242/-1.118;-1.510/-1.461 | IA | IA | IA |
| $(NH_4)_9MgW_{17}O_{56}F_6NaH_4$•$XH_2O$ | 0.903/0.823; -0.826/-0.518 | 21 | 15 | 4 |
| $(NH_4)_9Cu^{+}W_{17}O_{53}F_9NaH_2$•$12H_2O$ | -0.157/-0.086;-0.672/-0.420; -0.863/-0.665;-1.260/-1.153 | >12 | 4 | 2 |
| $(CN_3H_6)_7H_2F_6NaW_{18}O_{56}$•$10H_2O$ | -0.305/-0.203;-0.409/-0.341;-0.769/-0.689;-1.025/-0.929 | IA | 7.6 | 20 |
| $(NH_4)_9NiW_{17}O_{56}F_6NaH_4$•$9H_2O$ | -0.897/-0.769;-1.168/-1.010;-1.450/-1.363 | IA | IA | IA |
| $(NH_4)_7CuMn^{+2}W_{11}O_{39}FH_2$•$XH_2O$ | 0.631/0.950;-0.171/-0.082; -0.334/-0.550 | IA | IA | IA |
| $K_6CoSiW_{11}O_{40}H_2$•$XH_2O$ | 0.715/0.905;-1.275/-1.053 | 23 | >8 | >3 |
| $(NH_4)_4CuNiW_{11}O_{38}F_2H_4$•$3H_2O$ | -0.304/-0.149;-0.426/-0.369;-0.750/-0.870 | 10 | 3.1 | 9.6 |
| $(NH_4)_4NiMnW_{11}O_{38}F_2H_4$•$3H_2O$ | 0.488/0.877;-0.272/-0.197;-0.758/-0.755 | 39 | 4.9 | 8.2 |
| $(N(CH_3)_4)_4CuW_{11}O_{38}F_2H_6$•$10H_2O$ | -0.720/-0.029 (pH5.0) | 2 | 0.9 | 15 |
| $(N(CH_3)_4)_4MnW_{11}O_{38}F_2H_6$•$10H_2O$ | 0.686/0.419; -1.195/-0.535 (pH5.0) | 1 | 2.8 | 8.3 |
| (NH4)7GaW11O40H4•5H2O | 0.308/--;-1.337/--;-1.521/-- | 2 | >20 | 0.5 |
| $(NH_4)_7InW_{17}O_{56}F_6NaH_5$•$9H_2O$ | -0.673/-0.513; -1.185/-1.229 | >10 | >18 | 1.8 |

IA = inactive

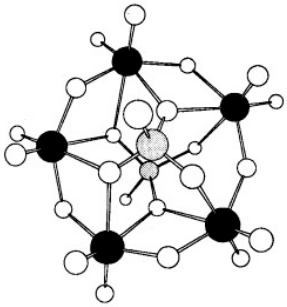

**Figure 6.** Structure of $((RP)_2W_5O_{21})^{4-}$.

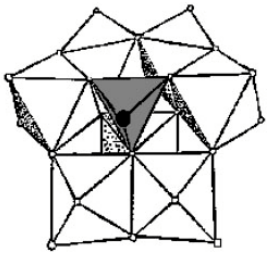

**Figure 7.** Structure of $((MeAs)W_7O_{27}H)^{7-}$, the Black Circle is a Methyl Carbon.

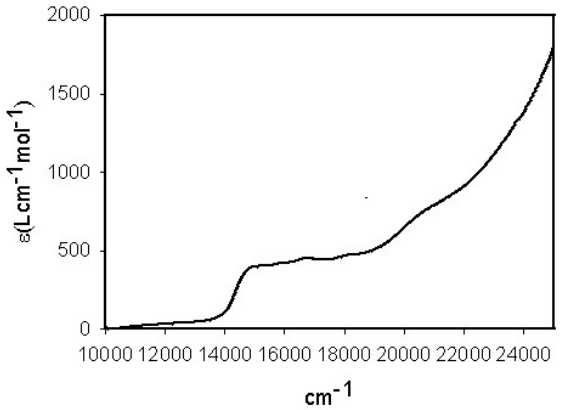


**Figure 8.** Visible Spectrum of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$.

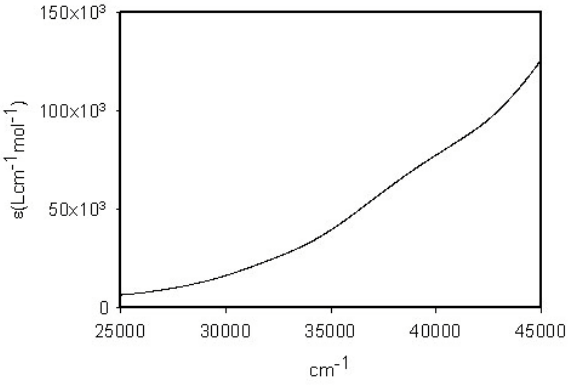


**Figure 9.** Ultraviolet Spectrum of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$.

Found: Na, 5.34%; Co, 3.91%; Fe 2.49%; W, 59.59% Calc.: Na, 4.79%; Co, 4.09%; Fe, 1.94%; W, 57.44%. H2O Analysis: Found: 14.16 % Calc.: 12.2 %.

The visible and ultraviolet spectra of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ in Figure 9 and 10 show peaks at ($cm^{-1}$) ( extinction coefficient ($Lcm^{-1}mol^{-1}$)): 12,800 (42.9); 15,200 (402); 16,000 (422); 16,800 (452); 18,100 (472); 21,100 (805). Listed in Table 5 are the maxima of the absorption bands of several model compounds with octahedral and tetrahedral coordinated Co(II) along with that of $Na_{12}(Co_6W_{18}O_{70}H_8)$•39 $H_2O$. The electronic spectrum of this compound is consistent with Co(II) ions in tetrahedral geometry. The two tetrahedral sites in the Weakley structure are occupied by two Co(II) ions while the remaining four Co(II) ions occupy the sandwiched octahedral sites. Visible spectra of tetrahedral Co(II) usually are five times as intense as that of octahedral Co(II). As a result, only the spectra due to tetrahedral cobalt will be observed. The visible spectrum of a 10-3 M aqueous solution of $Na_{12}(Co_6W_{18}O_{70}H_8)$•39 $H_2O$ (15,500 $cm^{-1}$ (extinction coefficient 559 $cm^{-1}mol^{-1}$); 16,400 $cm^{-1}$ (extinction coefficient 622 $cm^{-1}mol^{-1}$); 17,600 cm-1 (extinction coefficient 466 $cm^{-1}mol^{-1}$); 20,200 $cm^{-1}$ (extinction coefficient 478 $cm^{-1}M^{-1}$)) (16) is very similar to that of $(Co(II)W_{12}O_{40})^{6-}$ which includes two relatively intense, very broad multi-component bands with centers of gravity at approximately 8,000 $cm^{-1}$ and 17,090 $cm^{-1}$ and $(CoO_6CoO_4W_{11}O_{30}H_2)^{8-}$ which has bands at 15,700 $cm^{-1}$ (extinction coefficient 250 $cm^{-1}mol^{-1}$), 16,600 $cm^{-1}$ (extinction coefficient 260 $cm^{-1}mol^{-1}$), 17,700 $cm^{-1}$ (extinction coefficient 162 $cm^{-1}mol^{-1}$), and 20,200 $cm^{-1}$ (extinction coefficient 61 $cm^{-1}mol^{-1}$). All the spectra are similar with respect to the major features: a relatively intense (extinction coefficient 40–400 $cm^{-1}$ $mol^{-1}$) broad multi-component band with center of gravity at 5500-8500 $cm^{-1}$ and a second more intense (e 150-2200 $cm^{-1}mol^{-1}$) multi-component band with center of gravity at 14,000-17,000 $cm^{-1}$. The general band assignment suggested by Orgel (17) and Ballhausen and Jorgensen (18) on the basis of limited experimental evidence has been confirmed since by all subsequent experimental and analytical work. The lower frequency of the two intense bands is assigned as n2 corresponding to the transition from the $^4A_2$ ground state to the $^4T_1(4F)$ level. The higher frequency band is then attributed largely to n3, corresponding to the $^4A_2(4F)$ $>^4T_1(4P)$ transition. The broadness of n2 is presumed to derive mainly from the effects of spin orbit coupling. The usual failure to observe a band corresponding to n1 has been explained on the grounds that in a tetrahedral point group, the electric dipole transition $A_2 > T_2$ is formally forbidden.(19-24) The electrochemical properties of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ studied were examined by recording cyclic voltammograms in various buffers (pH 2-pH 8). The same solutions were used first to record cyclic voltammograms, then to record visible spectra. These voltammograms were recorded using a glass-carbon working electrode, a Ag/AgCl reference electrode, and a platinum wire as the counter electrode. Generally, the compound is very stable in a variety of pH buffers except pH 8. It slightly changed in the first hour then gives

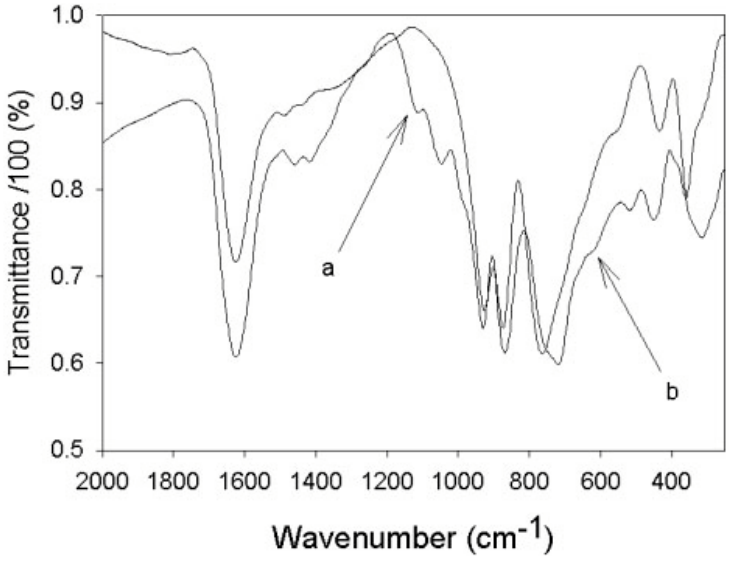


**Figure 10.** Infrared Spectrum of a. $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ and b. $Na_{10}Cu_2Fe_4W_{18}O_{70}H_6$•29$H_2O$.

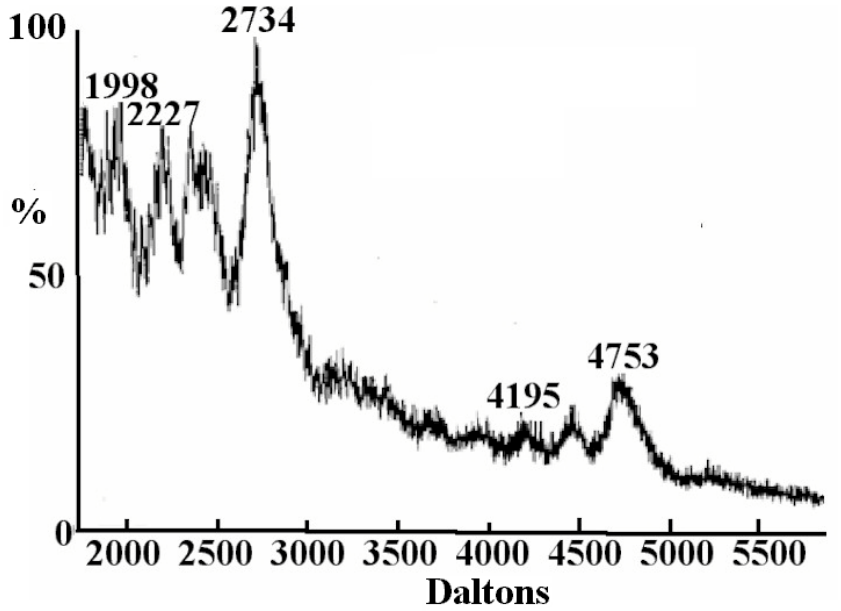


**Figure 11.** FABMS of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$.

identical peak-to-peak potential and the same peak-to-peak current. All samples were initially scanned over the entire available range of voltage. The working electrode was cleaned thoroughly prior to recording each final voltammogram. The redox potentials of solutions of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ and the two model compounds $Na_{12}(Co_6W_{18}O_{70}H_8)$•39 $H_2O$ and $Na_{12}(Fe_6W_{18}O_{70}H_2)$•26 H2O are presented in Table 6.

The infrared spectrum of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ is compared with that of $Na_{10}(Cu_2Fe_4W_{18}O_{70}H_6)$•29$H_2O$, a heteropolyanion with a known Weakley structure (4), in Figure 11. In addition, it is compared with the infrared spectrum of the two model compounds, $Na_{12}(Co_6W_{18}O_{70}H_8)$•39 $H_2O$ and $Na_{12}(Fe_6W_{18}O_{70}H_2)$•26 $H_2O$ in Table 7. The similarities support the Weakley structure for the subject compound. The single crystals were not of high enough quality to do a single crystal x-ray diffraction.

The magnetic susceptibility per gram sample at room temperature, cg,. of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ is 5.41 X $10^{-6}$ cgs units. This value indicates strong antiferromagnetic interaction between the paramagnetic

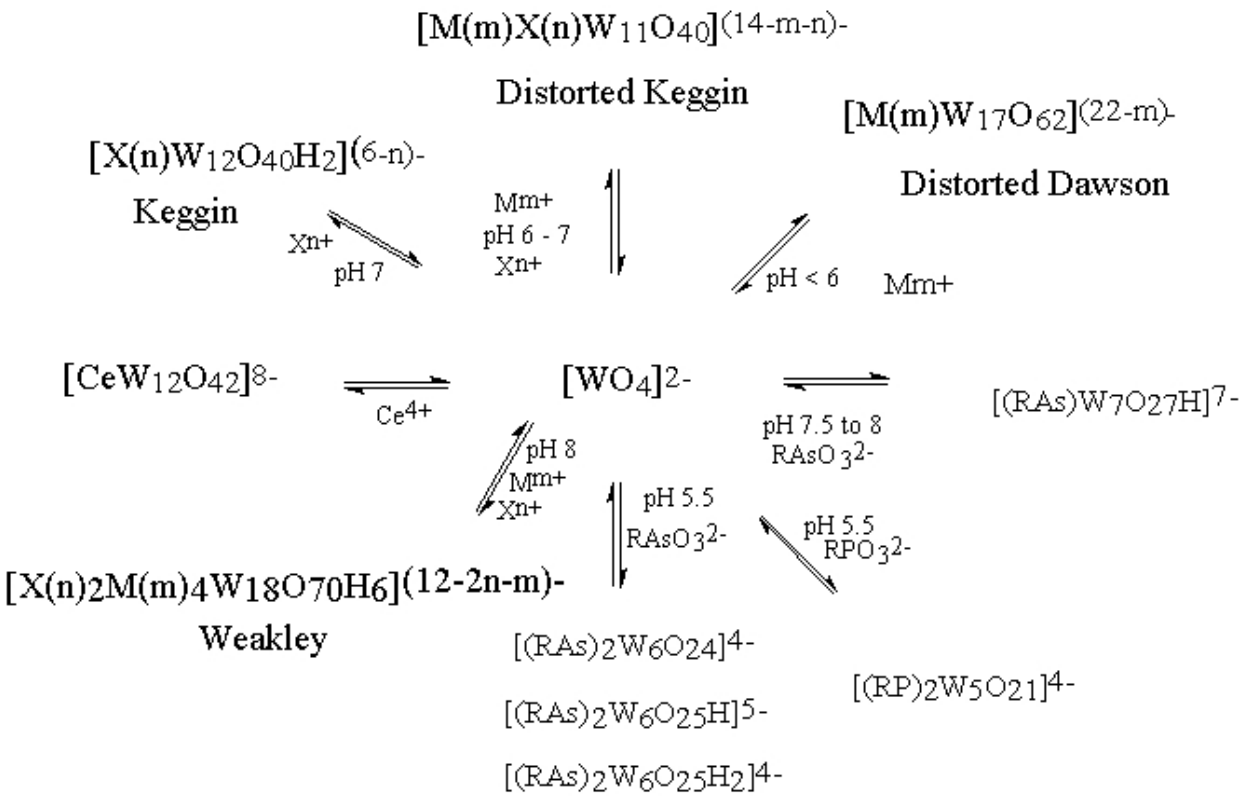


**Figure 12.** Aqueous Heteropolyoxotungstate Polymerization from Tungstate and Heteroatoms.

**Table 5.** Electronic Spectra of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ and Model Octahedral and Tetrahedral Co(II) Heteropolyanions

| Compound | Transition | υ ($cm^{-1}$) | ε ($cm^{-1}$ $M^{-1}$) | References |
|---|---|---|---|---|
| $(Co^{2+}W_{11}O_{38}F_2H_4)^{6-}$ | Charge Transfer | 39,500 | 45,000 | 36 |
| | $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | 19,900 | 46 | |
| | | 19,000 | 53 | |
| | $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | 18,100 | 59 | |
| | | 15,400 | 18 | |
| $(Co^{2+}O_5SiW_{11}O_{35}H_2)^{6-}$ | Charge Transfer | 38,100 | 30,500 | 46 |
| | | 19,600 | 40 | |
| | | 18,200 | 60 | |
| $(Co^{2+}O_5P_2W_{17}O_{57}H_2)^{8-}$ | Charge Transfer | 37,000 | 36,900 | 46 |
| | | 20,000 | 90 | |
| | | 18,200 | 98 | |
| $(Co^{2+}O_5P_2W_{17}O_{57}H_2)^{8-}$ | $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | 19,800 | 113 | 36 |
| | $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | 18,300 | 114 | |
| | $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ | 7,600 | 0.812 | |
| $(CoO_6CoO_4W_{11}O_{30}H_2)^{8-}$ | | 20,200 | 61 | 45 |
| | | 17,700 | 162 | |
| | | 16,600 | 260 | |
| | | 15,700 | 250 | |
| $(Fe_2Co_4W_{18}O_{70}H_6)^{12-}$ | | 21,100. | 805 | 43 |
| | | 18,100 | 472 | |
| | | 16,800 | 452 | |
| | | 16,000 | 422 | |
| | | 15,200 | 402 | |
| | | 12,800 | 42.9 | |
| $(Co_6W_{18}O_{70}H_8)^{12-}$ | | 20,200 | 478 | 16 |
| | | 17,600 | 466 | |
| | | 16,400 | 622 | |
| | | 15,500 | 559 | |

**Table 6.** Cyclic Voltammetry of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ and Model Compounds

| Compound | pH | $E_{pk}$(cathode)/$E_{pk}$(anode) : (V/V) | References |
|---|---|---|---|
| $Na_{12}(Co_6W_{18}O_{70}H_8)$•39 $H_2O$ | 2 | .82/.91;-.37/-.30; -.55/-.50;-.70/-.76. | 16 |
| | 3 | .82/.92; -.38/-.29;-.54/--; -.65/--. | |
| | 4 | .84/.84; -.46/-.35;.61/--; .50/--. | |
| | 5.5 | .75/.82; .55/.50; -.20/.27;--/-.40. | |
| | 7 | .72/.88; -.60/-.69;-.50/.21; --/-.44. | |
| | 8 | -.19/.04. | |
| $Na_{12}(Fe_6W_{18}O_{70}H_2)$•26 $H_2O$ | 2 | .36/.45; -.39/-.49;-.52/--; -.62/--;-.93/--. | |
| | 3 | .24/-.43;-.40/.47; -.56/.62 | 16 |
| | 4 | -.42/.47; -.63/-.48; .20/--. | |
| | 5.5 | -.33/.30; -.50/-.50;-.73/-.77; -.80. | |
| | 7 | -.145/.29; -.59/-.42; --/-.02 | |
| | 8 | -.11/-.10; -.81/.33 | |
| $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ | 2 | -0.75/-0.371; -0.100/0.300; 0.550/0.800 | 44 |
| | 3 | -0.547/-0.393; -0.397/0.457; -/-0.697; -/0.807 | |
| | 4 | -0.437/-0.349; -/-0.371 | |
| | 5.5 | -0.300/-0.475; 0/0.170; 0.500/- | |
| | 7 | 0.460/0.630; -0.180/0.110; -0.880/- | |
| | 8 | -0.180/-0.340; -/-0.060 | |

**Table 7.** Comparison of the Infrared Spectrum of $Na_{12}[Fe_2Co_4W_{18}O_{70}H_6]$•39 $H_2O$ with two Model Compounds

| $Na_{12}[Co_6W_{18}O_{70}H_8]$•29 $H_2O$ | $Na_{12}[Fe_6W_{18}O_{70}H_8]$•20 $H_2O$ | $Na_{12}[Fe_2Co_4W_{18}O_{70}H_6]$•20 $H_2O$ | Assignment[46] |
|---|---|---|---|
| 3537 (s) | 3504 (m) | 3450 (s) | |
| 1626 (s) | 1629 (s) | 1632 (m) | |
| 1505 (w, sh) | | | |
| 1457 (w, sh) | | | |
| 927 (m) | 939 (s) | 930 (m) | $W=O_d$ symmetric stretch |
| 874 (m) | 874 (s) | 866 (s) | $W\text{-}O_b\text{-}W$ asymmetric stretch |
| 764 (s) | 729 (m) | 738 (s) | $W\text{-}O_c\text{-}W$ asymmetric stretch |
| 656 (w, sh) | | 625 (w) | |
| 433 (m) | 441 (m) | 437 (m) | |
| 314 (m) | 348 (w) | 357 (m) | |
| 243 (w) | 295 (m) | | |
| 16 | 16 | | Reference |

centers at room temperature. Shown in Figure 12 is the FABMS of $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$. Based on a formula weight of 5761, when $Na_{12}(Fe_2Co_4W_{18}O_{70}H_6)$•39 $H_2O$ loses 39 $H_2O$, 12 Na+, 6 H+, and 3 $O_2$- ions (total mass loss of 1032), the calculated mass of the anion is 4729 is in excellent agreement with the measured mass of 4754 da.

Shown in Figure 12 is the schematic diagram representing the reactions and products of the tungstate with selected metal ions. That diagram summarizes those reactions that are covered in this paper.

## 5. CONCLUSIONS

We have shown that the reactions between metal ions and $WO_4^{2-}$ below pH 6 result in the formation of the distorted Dawson structure. Between pH 6 – 7, the distorted Keggin structure, above pH 7, and close to pH 8, the Weakley structure is formed. Some compounds of the Keggin, Dawson, and Weakley structure have shown antiviral activity.

## 6. ACKNOWLEDGMENT

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