# SYNTHESIS OF A COBALT(III) TUNGSTATE

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INTRODUCTION

Polyoxoanions

The formation of polyoxoanions is quite common and yet may be unfamiliar except for a few species. In every case, the polyoxoanion has two or more metal ions (or a nonmetal or metalloid in a high oxidation state) surrounded by oxide ions and joined by sharing one or more oxygens. The most familiar polyoxoanion is probably the dichromate ion, $Cr_2O_7^{2-}$, where each chromium(VI) is at the center of a tetrahedron of oxide ions and the two tetrahedra are joined by a single common oxygen.
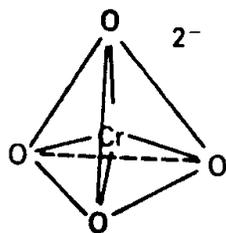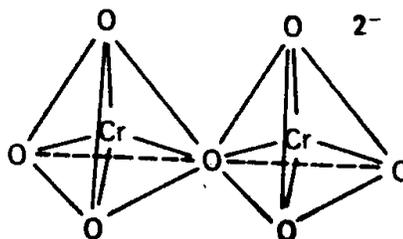
CrO_4^{2-} $\qquad\qquad\qquad\qquad\qquad$ $Cr_2O_7^{2-}$

The tetrahedra are said to be joined by corner sharing and this is the common way polysilicates and polyphosphates form.

Surprisingly, molybdenum and tungsten (which are in the same periodic group as chromium) form much more complex polyoxoanions. In these cases, the metal is at the center of an octahedron of oxygens and the octahedra are joined by sharing two oxygens on an edge. If an $Mo_2O_{10}^{8-}$ ion were to form this way, it would have the structure shown, analogous to that of $I_2(OH)_2O_8^{2-}$.
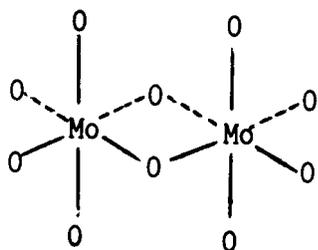
hypothetical $Mo_2O_{10}^{8-}$ $\qquad\qquad$ $I_2(OH)_2O_8^{2-}$ $\qquad\qquad$ $Mo_7O_{24}^{6-}$
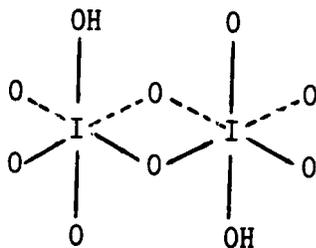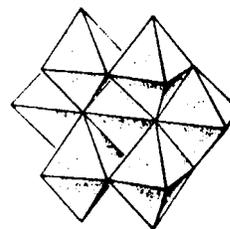
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A typical isopolymolybdate is $Mo_7O_{24}^{6-}$ with the structure shown. These three examples are called isopoly anions because there is only one type of metal ion.

Other polyoxoanions have structures such that another ion can be incorporated into them due to the presence of a cavity with oxygens situated at the edges of the cavity in the proper orientation for bonding. It is this type of polyanion that is prepared in this experiment with the basic structure composed of tungsten and oxygen atoms and a cobalt ion in the cavity. The structure of $CoW_{12}O_{40}^{5-}$ is shown. While it may be difficult to see from the figure, there are 4 oxygens in the cavity at the corners of a tetrahedron which means the cobalt is in a tetrahedral environment.
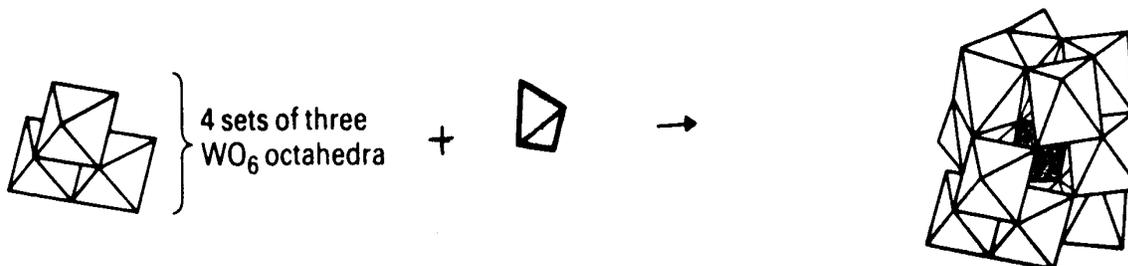
The charge on the ion is dependent on the oxidation state of the cobalt. If the cobalt is +2 (prepared prior to the final product and then oxidized), the ion is $CoW_{12}O_{40}^{6-}$ (W is +6, O is -2). If the cobalt is +3, which is the final compound prepared, the ion is $CoW_{12}O_{40}^{5-}$. In the solid compound prepared, the cation is K^+ and there are twenty waters of hydration giving $K_5CoW_{12}O_{40} \cdot 20\ H_2O$.

Once formed, the anion is quite stable toward decomposition except in basic solution. Since the cobalt ion is buried within the polytungstate framework, it does not undergo substitution reactions but it has been shown that the oxidation-reduction of the Co^{2+}-Co^{3+} is as easily carried out as in normal complexes.[2]

PROCEDURE

Synthesis Overview

The synthesis of the potassium salt of $CoW_{12}O_{40}^{5-}$ is adapted from that given by Baker.[3] The mixing of WO_4^{2-} and Co^{2+} in 6 to 1 proportions at a pH of 6.5 - 7.5 with heating (the formation of polytungstates is slow at room temperature) does not give the Co(II) containing ion $CoW_{12}O_{40}^{6-}$. Instead the product is $H_2Co_2W_{11}O_{40}^{8-}$ or $CoW_{11}Co(OH_2)O_{39}^{8-}$ where one cobalt(II) is inside the framework - a framework not of twelve tungstens with oxygens but eleven tungstens, one cobalt and oxygens; the second cobalt replaces one of the tungstens in the framework. Addition of KCl provides a high concentration of K^+ and the potassium salt of $CoW_{11}Co(OH_2)O_{39}^{8-}$ precipitates and is isolated by filtration.

When dissolved in 2 M H_2SO_4, this salt is converted to $CoW_{12}O_{40}^{6-}$. Some Co^{2+} (aq) will form and WO_3 (s) may also form from this reaction; any solid WO_3 can be removed by filtration.

To obtain the cobalt(III) form, the cobalt(II) is oxidized with $K_2S_2O_8$, potassium peroxodisulfate (commonly called potassium persulfate). The $K_2S_2O_8$ also provides excess K^+ to reduce the solubility of the salt and aid in its precipitation.

Synthesis

Using a 250 mL beaker, dissolve 19.8 g (0.060 mol) of $Na_2WO_4 \cdot 2\ H_2O$ in 40 mL of water. When the solid is completely dissolved, add 3 to 3.5 mL of glacial acetic acid [CAUTION: skin irritant]. **IMPORTANT:** Check the pH carefully with pHydrion paper to be sure it is in the range 6.5 - 7.5.

In a small beaker, dissolve 2.5 g (0.01 mol) of $Co(C_2H_3O_2)_2 \cdot 4\ H_2O$ in 12 - 13 mL of water to which 2 drops of glacial acetic acid has been added.

On a hot plate, heat the Na_2WO_4 solution to near boiling and add the $Co(C_2H_3O_2)_2$ solution to it all at once with stirring. Boil the resulting mixture gently for about 15 minutes; don't boil vigorously to cause splattering. Replace any water that evaporates during the heating. Then add 13.0 g of KCl to the boiling solution; stir the mixture well. Cool to room temperature (you may use an ice bath to speed the cooling) and separate the precipitate by filtration on a Buchner funnel; use a clean filter flask. Use some of the filtrate to wash the remaining solid from the beaker onto the filter. Allow to air dry for a short time on filter paper.

In a 150 or 250 mL beaker, add about 25 g of the solid just prepared to 40 mL of 2 M H_2SO_4 and heat gently for a few minutes. Filter the solution by gravity filtration into a 250 mL beaker to remove any undissolved solid. Save the solution. This solution should contain the $CoW_{12}O_{40}^{6-}$ ion.

Heat the $CoW_{12}O_{40}^{6-}$ solution to near boiling and add, with stirring, solid $K_2S_2O_8$ in about 0.5 g increments. Add the $K_2S_2O_8$ until the solution changes to a dark gold color. This color change will occur rather rapidly, almost like a titration. The amount of $K_2S_2O_8$ required for this will be about 10 g. Once the solution has become gold in color, continue heating gently for about 5 minutes to decompose the excess $K_2S_2O_8$. Cool the solution in an ice bath and filter the precipitate using a Buchner funnel.

If the crystals are not a light yellow, recrystallize the crude product from water. Not all the solid may dissolve so do not use more than 60 mL of hot water. If there is some insoluble material, remove it by filtration (or decantation) of the hot solution. When cooled in an ice bath the solution will yield crystals of $K_5CoW_{12}O_{40} \cdot 20\ H_2O$. If crystals do not form, evaporate the solution to about two-thirds of its original volume followed by cooling in an ice bath. Allow the crystals to dry in air. Store the crystals in a sample

bottle.

Calculations

Calculate the theoretical yield of $K_5CoW_{12}O_{40} \cdot 20\ H_2O$ assuming that the sodium tungstate is the limiting reagent.

References

1. Walmsley, F. *J. Chem. Educ.*, **1992**, *69*, 936.
2. Rasmussen, P.G.; Brubaker, C.H. Jr. *Inorg. Chem.* **1964**, *3*, 977.
3. Baker, L.C.W.; McCutchean, T.P. *J. Am. Chem. Soc*. **1956**, *78*, 4503.