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Preparation and Properties of Potassium Pentafluorodioxo-Tungstate (VI) $K_3WO_2F_5$ and Potassium Octafluoropentaoxo-Ditungstate (VI) $K_6W_2O_5F_8$

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SUMMARY

The potassium salts of two new hepta coordinated oxyfluoro anions of tungsten (VI) are reported in this paper. The monomer, $K_3WO_2F_5$ was obtained from the aqueous solution while the dimer, $K_6W_2O_5F_8$ was isolated from alchohol. The absorption peak of $K_6W_2O_5F_8$ at 830 cm^{-1} has been attributed to W-O-W link. The W-O-W angle is found to be 155° and the force constant is 4.44 mdyn/A° . The d values obtained from x-ray powder diffraction studies are given.

INTRODUCTION

The known oxyfluoro anions formed by hexavalent tungsten are as follows: $WO_2F_3^-$, $WO_2F_4^{2-}$, $WO_3F_3^{3-}$ and WOF_5^-. A relatively stable peroxyfluorotungstate anion, $WO(O_2)F_4^{2-}$ may also be added to this list.{1} In recent years thorough investigations have not been done to isolate salts of other oxyfluoro anions of tungsten from aqueous solutions. In the ions reported above the coordination number of tungsten does not exceed six. Both tungsten as well as molybdenum form K_3WF_8 and K_3MoF_8 respectively, but the coordination number of the metal atoms are not exactly known in these compounds.{2} Examples of 7 and 9 coordinate complexes of tungsten are $RbWF_7$, $WOCl_4\cdot$ (diars), $NOWF_7$ and $WH_6(Me_2PhP)_3$ {3,4}. Niobium and tantalum form heptacoordinate complex fluoro as well

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as oxyfluoro anions. Hepta coordinate oxyfluoro anions of hexavalent tungsten are for the first time being reported in this paper. The salt that was isolated in our laboratory, we feel, agrees with the molecular formula $K_3WO_2F_5$.

A few binuclear fluorooxo anions of transition metals have been reported from our laboratory. {5,6} These binuclear compounds could not be isolated from aqueous medium The M-O-M bond undergoes hydrolysis producing two M-OH groups and in the presence of excess fluoride ion, substition of OH^- by F^- takes place. Thus all of the reported compounds, usually isolated from aqueous solution in the presence of excess fluoride ion are monomeric. Dimeric oxygen bridged compounds of tungsten (VI) are known. The peroxo compound $K_2(O_2)_2(H_2O)(O)W\text{-}O\text{-}W(O)(H_2O)(O_2)_2$ contains two terminal W-O links and one bent oxygen bridge. In this laboratory the binuclear compound $K_6W_2O_5F_8$ has been isolated and the solid state IR spectra of the compound strongly suggests the existence of W-O-W link. The existence of a fluorine bridge in compounds such as $MoOF_4$, $ReOF_4$ etc. has been shown by x-ray studies.{7,8} The structure of WOF_4 resemble that of NbF_5. Each unit contains four molecules with cis bridging fluorine atoms.{9} In the solid state the lone pair on fluorine acts as a good donor. Because of this, the crystalline coordination number of fluoro and fluorooxy anions of metals may under go some revision in the near future. So, tungsten may be eight coordinate through a fluorine bridge in the ion $WO_2F_5^{3-}$. Similarly the dimer, $W_2O_5F_8^{6-}$ with four terminal W-O links and one W-O-W link may also be eight coordinate through a fluorine bridge. It may be mentioned here that the compound formulated previously as $K_2[W(OH)Cl_5]$ has been shown to be the salt of μ-Oxo-decachloroditungstate (III, V) $K_4[Cl_5WOWCl_5]$ and in this compound a bent W-O-W group exists with small interaction between tungsten atoms. {10}

EXPERIMENTAL

Preparation of compounds and elemental analysis

Reagent grade chemicals were used for the preparation of these compounds. The starting material, $K_3WO_2F_5$ was prepared by dissolving tungstic acid in 40% aqueous hydrofluoric acid followed by the addition of excess of KHF_2. The solution was heated for a short time and then filtered hot. Pale yellow crystals were obtained when the filtrate cooled. Approximately 25g. of this starting material was isolated. The analysis of the compound gave the following results.** Found: W, 39.86%, F, 20.59%, calculated for $K_3WO_2F_52H_2O$: W, 39.61% F, 20.47%. The compound was found to loose approximately 4% of its original weight when kept at 120°C for twelve hours. If the decrease in weight is attributed solely to the loss of water molecules it should be concluded that only one of the two water molecules left the crystal lattice at this temperature. The loss of weight at higher temperatures was not determined. This is because at higher temperatures HF is also expected to escape with H_2O molecules. The partly dehydrated compound was analysed. Found: K, 27.29%; $K_3WO_2F_5\cdot H_2O$ requires K, 26.29%; and $K_3WO_2F_5$ requires K, 27.40%.

The starting material was then treated with an equivalent amount of KOH dissolved in ethanol. The presence of excess water or CO_2 was found to have harmful effects on the purity of the final product. The temperature was kept at 60°C and approximately 200 ml. of alcohol was used for the preparation of 2-3g. of the final compound. The solution was stirred and refluxed for 24 hours. The pH of the solution dropped with time and the final product which was almost white, was washed with cold water to remove potassium fluoride obtained as a by product of the reaction.

$$2K_3WO_2F_5\cdot H_2O + 2KOH. \rightleftarrows K_6W_2O_5F_8 + 2KF + 2H_2O$$

The final product was analyzed. Found: K, 28.17%; W, 44.22%; F, 18/29%. Calculated for $K_6W_2O_5F_8$: K, 28.10%; W, 44.12%; F, 18.23%.

** The chemical analyses reported in this paper were all done by Galbraith Laboratories, Knoxville, Tennessee, U.S.A. 37921. The fluorine analysis of $K_3WO_2F_5$ was checked in our laboratory and the result agreed with the value reported by Galbraith Laboratories.

I.R. and Raman Spectra

The I.R. and Raman spectra of the compounds were taken in the solid state. The results are given in Table I.

TABLE I

Absorption Frequency In cm^{-1} And Intensity Of The Peaks

I.R.				Raman			
$K_3WO_2F_52H_2O$		$K_6W_2O_5F_8$		$K_3WO_2F_52H_2O$		$K_6W_2O_5F_8$	
cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
970	s	960	s	952	s	952	s
915	v.s.	905	s	905	m	915	s with a shoulder at 905
750	v.w.	830	s	803	s	817	m
585	m.s.			705	m.s.	370	m.s.
560	m.s.	570	m.	375	m.w.	305	m
470	s	560	s	307	m	255(?)	w
440	s	460	s	265	w		

Two sets of peaks were exhibited by both the compounds - one set in the region of 1200 cm^{-1} and the other at 1600 cm^{-1}. These later were considered overtones. In addition, $K_3WO_2F_5\cdot 2H_2O$ showed the characteristic absorption for water in the 3400 cm^{-1} region. The dimer, however, had no peak at this region indicating that the compound does not contain an OH group.

The I.R. and Raman Spectra of different oxyhalo compounds of tungsten have been reported in the literature. The peaks in the region of 800 to 1000 cm^{-1} are attribute to W=O terminal group. In the vapor phase WOF_4 and $WOCl_4$ give sharp W=O peaks at 1050 cm^{-1} and 1030 cm^{-1} respectively.{11,12} In the crystalline state the same peak is observed in the 880 cm^{-1} region. The peaks above 900 cm^{-1} in Table I are attribute to terminal W=O links. The strong peak at 830 cm^{-1} shown by $K_6W_2O_5F_8$ is possibly due to W-O-W. The monomer does not exhibit a peak in this region, indicating that crystall coordination through an oxygen bridge is not common in oxyfluoro compounds of tungsten This is in keeping with the observations made by other investigators. If in the crystalline state $WO_2F_5^{3-}$ exhibits a coordination number higher than seven, fluorine and not oxygen will serve as the bridging atom. It may be mentioned here that the absorption peak of $Mo0_2F_2$ at 781 cm^{-1} has been tentatively assigned for Mo-0-Mo bridge. In solid $WOCl_4$ there is a linear chain of W-0-W and the angle is 180°. In this compound the lone pairs of oxygen are acting as perfect donors. In the ideal case $W_20_5F_8^{6-}$ will have a C_{2v} symmetry, therefore the W-0-W band angle will not be 180°C. The observed peak at 830 cm^{-1} agrees for a bent W-0-W link. The force constant and the W-0-W angle in $K_4W_2OCl_{10}$ has been calculated by Konig {10} using Cotton and Wing's method. {13} Following the same procedure the W-0-W angle in $K_6W_20_5F_8$ has been found to be 155° and the force constant is 4.44 mdyn/A°.

Three factors contribute to the shift to lower energies of the infrared absorption band due to the W-F link. These are: a) the amount of charge on the anion. b) change to hepta coordinated structure from 0_h symmetry. {3} and c) the presence of oxygen atoms replacing other ligands. {13,14} These changes are shown in Table II.

TABLE II

Infrared Absorption Frequencies Of W-F Links

Compound	Absorption Frequency in cm^{-1}	Reference
WF_6	712	15,16
Now $WF_7 \cdot RbWF_7$	620	3,17
$K_3W0_2F_5$	585	Present comments
$K_6W_20_5F_8$	570	

The absorption of WOF_4 at 550 cm^{-1} is attributed to a fluorine bridge. If 560 cm^{-1} in $W0_2F_5^{3-}$ and 570 cm^{-1} in $W_20_5F_8^{6-}$ are interpreted as F-W-F stretches then the compounds in the crystalline states should be considered as eight coordinate.

X-Ray Diffraction and DTA Study

The powder x-ray diffraction spectra of both the compounds were taken using a diffractometer fitted with an x-y recorder. The d-I match shows that the dimeric compound is not a mixture of potassium fluoride and the monomer. The cell constants have not been determined but the d values of the more intense peaks are given in Table III. Most of the d values of $K_6W_2O_5F_8$ agree well with a tetragonal structure.

TABLE III

Powder X-Ray Diffraction Lines Of $K_3WO_2F_52H_2O$ and $K_6W_2O_5F_8$ Compound

$K_3WO_2F_52H_2O$		$K_6W_2O_5F_8$	
d	Intensity	d	Intensity
5.26	W	4.95	W
4.89	W	4.29	W
4.75	W	3.69	M.S.
4.42	S	3.36	M
3.41	W	3.30	S
3.35	W	3.05	M.S.
3.09	M	2.87	M.S.
2.97	W	2.60	W
2.47	M	2.48	M.S.
2.23	S	2.38	W
2.17	M	2.30	S
1.98	W	2.24	S
1.79	M	2.15	W
1.67	W	2.09	S
1.49	W	1.95	S
		1.88	W
		1.76	S
		1.65	W

The DTA Study of $K_6W_2O_5F_8$ revealed that the compound is fairly stable at least up to 350°C and no phase change in the solid state could be detected.

In conclusion it may be stated that the aqueous chemistry of the salts of oxyfluoro anion of tungsten (VI) have not been studied recently. Usually, oxyfluoro anions do not carry more negative charge than the number of oxygen atoms. However, exceptions are known e.g. VOF_5^{3-}. {18} Detailed x-ray diffraction analysis as has been carried out for $WOCl_4$ may in the future describe the structure of the salts of fluoro and oxyfluoro anions of tungsten. Attempts were made to isolate a similar dimer starting from the oxyfluoro anion of molybdenum. Unfortunately, the final products showed the characteristic OH peak in the IR. This is unusual. Molygdenum, particularly at lower oxidation state forms either linear or non linear Mo-O-Mo bridges relatively easily.

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