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Yu. A. Buslaev, R. L. Davidovich

Preparation of Some Complex Fluorides of Molybdenyl and Tungstenyl and Their Properties

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Complex fluorides formed by the "yl" groups MoO_2^{2+} and WO_2^{2+} have been studied very little, especially in comparison with analogous uranyl compounds. Salts of the types $M_2EO_2F_4$ ([1–3]) and MEO_2F_3 ([4,5]), where $M = K, NH_4$ and E = Mo or W, have been described in the literature. Some compounds of more complex composition are also known ([6–8]). Rubidium and cesium salts of fluoromolybdenyl and fluorotungstenyl had not been obtained up to the present time. Delafontaine ([4]) reported the synthesis of rubidium fluoroxomolybdate $RbMoO_2F_3 \cdot H_2O$ by the action of an excess of hydrofluoric acid on a saturated solution of rubidium trimolybdate. However, the composition of this salt has been questioned ([9]). The present communication is devoted to the synthesis of complex fluorides of molybdenyl MoO_2^{2+} and tungstenyl WO_2^{2+} containing K, Rb, or Cs in the outer sphere. The compounds were obtained by interaction, in solution, of fluoroxyacids of molybdenyl and tungstenyl with alkali-metal fluorides taken in various molar ratios.

Molybdic and tungstic acids were dissolved in twice-distilled hydrofluoric acid in such a way that the ratio $HF : MoO_3$ was equal to $2 : 1$ ([10]) and $4 : 1$, while for the tungstic acid solution the ratio $HF : WO_3 = 4$. An alkali-metal fluoride was introduced into the acid solutions, the solutions were evaporated until crystallization began, and then cooled. The crystals that separated were suction-filtered on a platinum funnel, washed with methyl alcohol, and dried in air. All operations were carried out in platinum vessels. The compounds obtained were analyzed, and the contents of the alkali metal as well as of molybdenum or tungsten were found. The fluorine content was determined by the pyrohydrolysis method ([11]). Complex fluorides of molybdenyl were decomposed by water vapor at 500°. Pyrohydrolysis of tungsten compounds was carried out at 700–800°. The contents of molybdenum and tungsten were found by both volumetric and gravimetric methods. In complex tungstenyl compounds the alkali metal was determined in the form of sulfate after removal of fluorine with sulfuric acid and precipitation of tungsten as WO_3. In oxofluoromolybdates, determination of the alkali metal as sulfate was carried out after separation of Mo by the sulfide method ([12]). The results of analyses of the synthesized compounds are

presented in Table 1.

$K_2MoO_2F_4 \cdot H_2O$ crystallizes in the form of lustrous plates after evaporation of a solution of MoO_3 in hydrofluoric acid ($HF : MoO_3 = 2 : 1$), to which a dilute solution of KF had been added at a ratio $KF : MoO_2F_2$ from 1 : 1 to 2 : 1. Rubidium and cesium tetrafluoromolybdenylates crystallize anhydrous, in the form of large prisms, upon evaporation of solutions of MoO_3 in HF to which an excess amount of alkali-metal fluoride has been added (∼ 3 : 1). Salts of the type $M_3Mo_2O_4F_7$ ($M = K, Rb, Cs$) were obtained from solutions with a molar ratio $HF : MoO_3$ equal to 4 : 1, when a stoichiometric amount of alkali-metal fluoride was added to them.

$K_2MoO_2F_4 \cdot H_2O$ dissolves readily in hydrofluoric acid. After evaporation and cooling of the solution, a crystalline substance separates in the form of needles. The chemical composition of this compound corresponds to the formula $K_{10}Mo_6O_{11}F_{24}$. Marchetti ([2]) also obtained, upon recrystallization of $K_2MoO_2F_4 \cdot H_2O$ from hydrofluoric acid, a salt in the form of needles, but assigned to it the formula $K_2MoO_2F_4$. The solubility of alkali-metal tetrafluoromolybdenylates in hydrofluoric acid decreases on going from the potassium salt to the cesium salt. The latter dissolves with difficulty even on heating. After slight-

Table 1

Results of chemical analysis of complex molybdenyl and wolframyl fluorides

Compound	K, %	Mo (W), %	F, %	H_2O, %	Compound	Rb, %	Mo (W), %	F, %	H_2O, %	Compound	Cs, %	Mo (W), %	F, %	H_2O, %
$KMoO_2F_3$	[illegible]	[illegible]	[illegible]	25,45	$RbMoO_2F_3$	[illegible]	[illegible]	[illegible]	21,08	$CsMoO_2F_3$	[illegible]	[illegible]	[illegible]	17,93
$K_3Mo_2O_4F_7$	[illegible]	[illegible]	[illegible]	26,27	$Rb_3Mo_2O_4F_7$	[illegible]	[illegible]	[illegible]	20,61	$Cs_3Mo_2O_4F_7$	[illegible]	[illegible]	[illegible]	16,89
$K_2MoO_2F_4 \cdot H_2O$	[illegible]	[illegible]	[illegible]	[illegible]	$Rb_2MoO_2F_4$	[illegible]	[illegible]	[illegible]	20,27	$Cs_2MoO_2F_4$	[illegible]	[illegible]	[illegible]	16,17
$K_{10}Mo_6O_{11}F_{24}$	[illegible]	[illegible]	[illegible]	28,52	$Rb_3W_2O_4F_7$	[illegible]	[illegible]	[illegible]	16,20	$Cs_3W_2O_4F_7$	[illegible]	[illegible]	[illegible]	13,80
$K_2WO_2F_4 \cdot H_2O$	[illegible]	[illegible]	[illegible]	[illegible]	$Rb_2WO_2F_4$	[illegible]	[illegible]	[illegible]	16,43	$Cs_2WO_2F_4$	[illegible]	[illegible]	[illegible]	13,60
$K_2WO_2F_4$	[illegible]	[illegible]	[illegible]	20,53	$Rb_{10}W_6O_{11}F_{24}$	[illegible]	[illegible]	[illegible]	17,60	$Cs_{10}W_6O_{11}F_{24}$	[illegible]	[illegible]	[illegible]	14,88
					$Rb_2W_3O_9F_2 \cdot H_2O$	[illegible]	[illegible]	[illegible]	[illegible]	$CsW_3O_9F \cdot H_2O$	[illegible]	[illegible]	[illegible]	[illegible]

* Above the line are analytical data; below the line, values calculated from the formula.

after considerable evaporation from the solution, crystals of rhombic form precipitate. Chemical analysis of the compound obtained showed that its composition corresponds to the formula $CsMoO_2F_3$. Cesium trifluoromolybdenylate was also isolated from a solution of molybdenyl fluoride containing an excess of hydrofluoric acid, upon addition to it of a stoichiometric amount of CsF. $CsMoO_2F_3$,

synthesized by this method, was identical with $CsMoO_2F_3$ obtained by recrystallization of $Cs_2MoO_2F_4$ from 40% HF. In the same way, $RbMoO_2F_3$ was also synthesized both by recrystallization of $Rb_2MoO_2F_4$ from 40% HF and by direct interaction of RbF and MoO_2F_2 in an excess of hydrofluoric acid.

$KMoO_2F_3$ was obtained by recrystallization of $K_2MoO_2F_4 \cdot H_2O$ from a 70% solution of hydrogen fluoride. The compound was isolated in the form of crystals having the shape of bipyramids. It was not possible to obtain potassium trifluoromolybdenylate by direct interaction of KF with MoO_2F_2 in solutions of hydrofluoric acid.

Complex molybdenyl fluorides behave differently toward water. Whereas $K_2MoO_2F_4 \cdot H_2O$ and $Cs_3Mo_2O_4F_7$ recrystallize from an aqueous solution without decomposition, rubidium and cesium tetrafluoromolybdenylates, as well as $K_{10}Mo_6O_{11}F_{24}$ and $K_3Mo_2O_4F_7$, dissolve in water incongruently. The relation of alkali-metal tetrafluoromolybdenylates to water and solutions is illustrated by the following scheme:

Fig. 1. X-ray stick diagrams:
a –$RbMoO_2F_3$;
b –$CsMoO_2F_3$;
v –$Cs_3Mo_2O_4F_7$;
g –$Cs_3W_2O_4F_7$;
d –$Rb_2MoO_2F_4$;
e –$Rb_2WO_2F_4$;
zh –$Rb_{10}W_6O_{11}F_{24}$;
z –$Cs_{10}W_6O_{11}F_{24}$;
i –$Rb_2W_3O_9F_2 \cdot H_2O$;
k –$CsW_3O_9F \cdot H_2O$.

$$K_2MoO_2F_4 \cdot H_2O \begin{cases} \xrightarrow{H_2O} & K_2MoO_2F_4 \cdot H_2O \\ \xrightarrow{HF(40\%)} & K_{10}Mo_6O_{11}F_{24} \\ \xrightarrow{HF(70\%)} & KMoO_2F_3 \end{cases}$$

$$Rb_2MoO_2F_4 \begin{cases} \xrightarrow{H_2O} & (9RbF : 5MoO_2F_2) \\ \xrightarrow{HF(40\%)} & RbMoO_2F_3 \end{cases}$$

$$Cs_2MoO_2F_4 \begin{cases} \xrightarrow{H_2O} & Cs_3Mo_2O_4F_7 \\ \xrightarrow{HF(40\%)} & CsMoO_2F_3 \end{cases}$$

The ease of cleavage of the alkali-metal fluoride increases from the potassium salt to the cesium salt. Apparently, this is explained by the ability of alkali-metal fluorides to form acid salts, which changes in the same sequence. Thus,

the dependence established by G. S. Savchenko and I. V. Tananaev ([13]) of the stability of complex fluoride salts $M^I\ ^VF_7$, where M^I = K, Rb, Cs and = Nb, Ta, in solution on the radius of M^I

confirmed by the example of complex molybdenyl and wolframyl fluorides, whose degree of decomposition in water and in hydrofluoric acid increases on going from potassium salts to cesium salts.

Complex compounds of wolframyl fluoride with alkali-metal fluorides are less varied in composition than the molybdenyl compounds. Possibly this is explained by the low stability of wolframyl fluoride in aqueous solution ([14]). When potassium fluoride is introduced into a concentrated solution of WO_3 in hydrofluoric acid (molar ratio KF : WO_3 from 1 : 1 to 2 : 1), crystals separate in the form of plates, of composition $K_2WO_2F_4 \cdot H_2O$.

Rubidium and cesium tetrafluorowolframylates, like the corresponding molybdenylates, crystallize in an anhydrous form. They are obtained as large prisms from hydrofluoric-acid solutions of WO_3 to which a stoichiometric amount of an alkali-metal fluoride is added. Rubidium and cesium heptafluorodivolframylates of composition $M_3W_2O_4F_7$ were obtained in the same way as the corresponding heptafluorodimolybdenylates. These salts also separated from solutions at an MF : WO_3 ratio equal to 1 : 1. Compounds of the type MWO_2F_3 (M –K, Rb, Cs) were not obtained by mixing solutions of MF and WO_3 in hydrofluoric acid in ratios from 0.5 to 2.5.

$K_2WO_2F_4 \cdot H_2O$ dissolves in water without decomposition. Its aqueous solution is stable on boiling for a long time, whereas $Cs_2WO_2F_4$ decomposes in aqueous solution. The hydrolysis product is $CsW_3O_9F \cdot H_2O$–a white precipitate, insoluble in water but soluble in hydrofluoric acid. $Rb_2WO_2F_4$ is more stable in water than $Cs_2WO_2F_4$. However, on prolonged boiling a yellow substance precipitates, whose composition corresponds to the formula $Rb_2W_3O_9F_2 \cdot H_2O$.

Tetrafluorowolframylates behave differently toward hydrofluoric acid. On recrystallization of $K_2WO_2F_4 \cdot H_2O$ from hydrofluoric acid, anhydrous $K_2WO_2F_4$ is formed, which agrees with the data of ([2]). The rubidium and cesium salts form complex compounds of composition $Rb_{10}W_6O_{11}F_{24}$ and $Cs_{10}W_6O_{11}F_{24}$. The behavior of fluorowolframylates in water and in hydrofluoric acid is illustrated by the scheme:

$$K_2WO_2F_4 \cdot H_2O \begin{cases} \xrightarrow{H_2O} K_2WO_2F_4 \cdot H_2O \\ \xrightarrow{HF(40\%)} K_2WO_2F_4 \end{cases}$$

$$Rb_2WO_2F_4 \begin{cases} \xrightarrow{H_2O} Rb_2W_3O_9F_2 \cdot H_2O \\ \xrightarrow{HF(40\%)} Rb_{10}W_6O_{11}F_{24} \end{cases}$$

$$Cs_2WO_2F_4 \begin{cases} \xrightarrow{H_2O} CsW_3O_9F \cdot H_2O \\ \xrightarrow{HF(40\%)} Cs_{10}W_6O_{11}F_{24} \end{cases}$$

All the compounds studied were subjected to X-ray phase analysis (Cu radiation with a nickel filter). Figure 1 gives the powder X-ray patterns of some of the compounds obtained. Indexing of the Debyegrams confirmed that the synthesized complex salts are individual chemical compounds.

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Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Far Eastern Branch named after V. L. Komarov
Siberian Division of the Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.