844. *Some Fluoromolybdates*(V) *and Fluorotungstates*(V).

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Complex fluorides of quinquevalent molybdenum and tungsten involving the MoF_6^- and WF_6^- ions have been obtained from the action of the hexafluorides on the alkali iodides in liquid sulphur dioxide. Their hydrolysis is described.

ALTHOUGH oxyhalide complexes of quinquevalent molybdenum and tungsten such as $K_2Mo^VOCl_5$ and $K_2W^VOCl_5$ have been known for a long time there are no references in the literature to oxygen-free complex halides in this oxidation state. Recent work by one of us has shown that in the presence of a suitable solvent, such as liquid sulphur dioxide, rhenium hexafluoride is reduced by potassium iodide to the quinquevalent state with the formation of a complex fluoride $KReF_6$.[1] We have now discovered that this behaviour towards potassium iodide is paralleled by that of molybdenum and tungsten hexafluorides, thus enabling us to prepare fluoromolybdates(V) and fluorotungstates(V), $MMoF_6$ and MWF_6, where M is an alkali metal.

[1] Peacock, *J.*, 1957, 467.

When solutions of the reactants are brought together iodine is immediately liberated even at −60°, and the complex fluoride is precipitated. If excess of hexafluoride is present, all the alkali iodide is used and the complex salt can be obtained pure merely by

$$2MoF_6 + 2MI \longrightarrow I_2 + 2MMoF_6\downarrow$$
$$2WF_6 + 2MI \longrightarrow I_2 + 2MWF_6\downarrow$$

gradually warming it to 200° in a good vacuum to remove volatile materials. In this way the sodium, potassium, rubidium, and cæsium compounds have been isolated for each of the elements.

The fluoromolybdates(v) are all white crystals, but some specimens of the fluorotungstates(v) tend to be brown. All are stable to 250°, but above this temperature they start to attack glass. Like the corresponding rhenium compounds the salts are very sensitive to traces of moisture and rapidly become blue when exposed to the atmosphere. Water vigorously decomposes them; the fluoromolybdates(v) give a dark blue solution which slowly fades to red-brown and deposits brownish hydrated oxide MoO_2,nH_2O; the fluorotungstates(v) give an intensely blue stable solution. In neither case is there any indication of the formation of quadrivalent complex fluorides such as occurs with fluoro-osmates(v),[2] fluororuthenates(v),[3] and to a less extent with fluororhenates(v). Presumably 6-co-ordinated complexes of quadrivalent molybdenum and tungsten would possess an unoccupied *d* orbital providing a ready point of attack for water molecules, a mechanism not available with rhenium or the platinum metals. Hence they would not be formed from aqueous solution, and it is interesting to note that quadrivalent chloromolybdates and chlorotungstates are also unknown.

The unit-cell sizes of both series of salts have been found from *X*-ray data and, as expected, lie close to those of the rhenium compounds (Table). Like potassium hexafluororhenate, potassium hexafluoro-molybdate and -tungstate have a slight tetragonal modification of the cubic cæsium chloride structures adopted by potassium hexafluoroniobate and -tantalate.[4] Magnetic moments at 25° have been measured for two of the salts, for $KMoF_6$ $\mu_{\text{eff}} = 1{\cdot}24$ B.M. and for $NaWF_6$ $\mu_{\text{eff}} = 0{\cdot}51$ B.M., where the spin-only value for one unpaired electron would be $\mu = 1{\cdot}78$ B.M. These low values are to be expected for Mo^{5+} and W^{5+} at ordinary temperature because of spin-orbit coupling.

Niobium and tantalum form seven- and even sometimes eight-co-ordinated complex ions, such as K_2NbF_7 and Na_3TaF_8, with fluorine, and it might be supposed that analogous molybdenum and tungsten compounds exist. We have made several attempts to isolate such complex salts, *e.g.* by fusing potassium hexafluoro-molybdate and -tungstate with potassium hydrogen difluoride and extracting the cold melt with acetone–water to remove soluble salts. While we have been able to make a new complex oxyfluoride, K_2MoOF_5, during these experiments there has been no indication of 7- and 8-co-ordinate complexes, and it must be concluded that these are too unstable towards water to be isolated in this way. The complex oxyfluoride K_2MoOF_5 itself appears to hydrolyse readily; it is a pale green crystalline solid.

Unit-cell dimensions (*lengths in* Å, *with* α_0 *in parentheses*) *of some* ABF_6 *compounds*; *for others, see also refs.* 1 *and* 4.

	MoF_6^-	WF_6^-	ReF_6^-
Na	8·20	8·18	8·18
K	$a_0 = 10{\cdot}17$, $c_0 = 9{\cdot}97$	$a_0 = 10{\cdot}21$, $c_0 = 10{\cdot}09$	$a_0 = 10{\cdot}26$, $c_0 = 10{\cdot}01$
Rb	$a_0 = 5{\cdot}11$ (96·5)	$a_0 = 5{\cdot}14$ (97·3)	$a_0 = 5{\cdot}11$ (96·7)
Cs	$a_0 = 5{\cdot}29$ (96·0)	$a_0 = 5{\cdot}31$ (95·3)	$a_0 = 5{\cdot}28$ (95·9)

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[2] Hepworth, Robinson, and Westland, *J.*, 1954, 4268.

[3] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.

[4] Cox, *J.*, 1956, 876.

EXPERIMENTAL

Preparation of Quinquevalent Fluoromolybdates and Fluorotungstates.—Molybdenum and tungsten fluorides were prepared from the elements. Sulphur dioxide was dried over phosphoric acid and fractionated, and alkali iodides were dried at 100° in a vacuum before use.

The preparative method was the same as for rhenium hexafluoride, and similar rigorously dry conditions were required to obtain pure quinquevalent *fluoromolybdates* and *fluorotungstates* [Found: Mo, 38·7; F, 45·8. $KMoF_6$ requires Mo, 38·5; H, 45·8%. Found: Mo, 32·9; F, 40·2. $RbMoF_6$ requires Mo, 32·5; F, 38·6%. Found: Mo, 27·9; F, 36·4. $CsMoF_6$ requires Mo, 28·0; F, 33·3%. Found: Mo, 41·2; F, 48·9. $NaMoF_6$ requires Mo, 41·2; F, 48·4%. Found: W, 53·5; F, 33·8. KWF_6 requires W, 54·6; F, 33·8%. Found: W, 48·0; F, 28·6. $RbWF_6$ requires W, 48·0; F, 29·7%. Found: W, 42·3; F, 26·5. $CsWF_6$ requires W, 42·7; F, 27·5%. Found: W, 56·7; F, 36·5. $NaWF_6$ requires W, 57·3; F, 35·5%].

Preparation of the Complex Oxyfluoride K_2MoOF_5.—Potassium hexafluoromolybdate(V) (about 0·5 g.) was fused with a large excess of anhydrous potassium hydrogen fluoride in an atmosphere of carbon dioxide. The temperature of the melt was raised to drive off hydrogen fluoride, and, after cooling, the resulting solid was leached with acetone containing a little water until all the potassium fluoride had been dissolved out. Pale green *potassium oxypentafluoromolybdate*(V) remained (Found: Mo, 32·0; F, 32·8. K_2MoOF_5 requires Mo, 33·6; F, 33·3%).

Analysis.—The salts were always decomposed by a large excess of water, and molybdenum and tungsten oxidised to the sexavalent state with a little concentrated nitric acid. Molybdenum was estimated as the oxine derivative; tungsten was precipitated as the tannin–cinchonine complex and ignited to trioxide. In the molybdenum experiments fluorine was estimated gravimetrically as lead chlorofluoride; in the tungsten experiments fluorine was estimated volumetrically after distillation and subsequent precipitation as lead chlorofluoride. Magnetic measurements were made at the ordinary temperature, a permanent magnet being used. *X*-Ray photographs were taken on 9-cm. cameras, filtered Co-$K\alpha$ radiation being used; specimens were made up in Pyrex-glass capillaries.

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