

890. *Higher Complex Fluorides of Molybdenum.*

By G. B. HARGREAVES and R. D. PEACOCK.

From the interaction of molybdenum hexafluorides with alkali fluoride the salts K_2MoF_8 , K_3MoF_8 , $RbMoF_7$, $RbMoOF_5$, and $CsMoOF_5$ have been obtained and characterised.

DURING a study of the fluorination of tungsten carbonyl a number of higher complex fluorides of tungsten were isolated.¹ We now show that molybdenum forms similar compounds, K_2MoF_8 , K_3MoF_8 , and $RbMoF_7$. In addition, two complex oxyfluorides, $RbMoOF_5$ and $CsMoOF_5$, have been characterised and we submit X-ray evidence for the existence of $CsMoF_7$ and $NaMoOF_5$.

TABLE I.

Reagents	Solid products	Reagents	Solid products
<i>1. Reactions starting from molybdenum carbonyl and excess of iodine pentafluoride</i>		<i>3. Reactions of rhenium hexafluoride and alkali iodide</i>	
$Mo(CO)_6 + IF_5$	$MoF_6, MoF_4?$	$MI + ReF_6 + IF_5$	$MReF_6 \ddagger$
$MI + Mo(CO)_6 + IF_5$	$MMoF_6^*$	<i>4. Reaction of rhenium hexafluoride and potassium fluoride</i>	
$2KI + Mo(CO)_6 + IF_5$	K_3MoF_8	<i>(a) In iodine pentafluoride</i>	
$2MI + Mo(CO)_6 + IF_5$	$KMoF_6 + MF \ddagger$	$KF + ReF_6 + IF_5$	K_2ReF_8
$CsF + Mo(CO)_6 + IF_5$	$CsMoF_6$	<i>(b) In liquid sulphur dioxide</i>	
<i>2. Reactions of molybdenum hexafluoride and alkali fluoride</i>		$KF + ReF_6 + SO_2$	K_2ReF_8
<i>(a) In iodine pentafluoride</i>		<i>(b) In liquid sulphur dioxide</i>	
$NaF + MoF_6 + IF_5$	NaF	$KF + MoF_6 + SO_2$	K_3MoF_8
$KF + MoF_6 + IF_5$	K_2MoF_8	$RbF + MoF_6 + SO_2$	$RbMoOF_5$
$RbF + MoF_6 + IF_5$	$RbMoF_7$	$CsF + MoF_6 + SO_2$	$CsMoOF_5$
$CsF + MoF_6 + IF_5$	$CsMoF_7$	<i>(c) In arsenic trifluoride</i>	
$RbF + MoF_6 + IF_5 \S$	$RbMoOF_5$	$CsF + MoF_6 + AsF_3$	$CsMoOF_5$
$CsF + MoF_6 + IF_5 \S$	$CsMoOF_5$		

* M = Na, K, Rb, Cs. † M = Na, Rb. ‡ M = K, Rb, Cs. § Slightly moist.

As in the work with tungsten,¹ the chief experimental difficulty was to distinguish true compounds from mixtures. Preparative methods are summarised in Table I, which

¹ Hargreaves and Peacock, *J.*, 1958, 2170.

shows that the products obtained are not always analogous to those from parallel reactions of tungsten. In iodine pentafluoride solution hexavalent molybdenum is more readily reduced to the quinquevalent state than hexavalent tungsten, so that interaction between molybdenum or rhenium hexafluoride and alkali iodides gives fluoromolybdates(v) and fluororhenates(v) (cf. ref. 2). At first we attributed this reduction to dissolved iodine from the alkali iodide, but later work has suggested that the active agent is the tetrafluoroiodate(III) ion, IF_4^- .

The three salts K_2MoF_8 , RbMoF_7 , and CsMoF_7 have similar properties to their tungsten analogues. They are stable to 150° in a vacuum and remain unchanged in a dry atmosphere. When exposed to moist air, however, they soon attack glass containers and turn blue; solid molybdenum hexafluoride behaves in a similar way. They are slightly paramagnetic ($\mu_{\text{eff.}}$ 0.2 B.M.) at room temperature, like the corresponding tungsten salts. Debye X-ray photographs show that the higher complex fluorides K_2MoF_8 , RbMoF_7 , and CsMoF_7 are structurally related to the higher fluorotungstates (Table 2); the densities indicate that the unit-cells of K_2MoF_8 and RbMoF_7 each contain 48 fluorine atoms.

The oxypentafluorides MMoOF_5 ($\text{M} = \text{Na, Rb, Cs}$) are isostructural with the hexafluoromolybdates MMoF_6 , and in fact the unit-cell sizes of corresponding compounds are practically the same. As with tungsten, there is no potassium salt; perhaps the tetragonal

TABLE 2.

	Unit-cell size * (Å)	Density		Fluorine atoms per unit cell	Unit-cell size (Å)
		(obs.)	(calc.)		
K_2MoF_8	10.01 C	3.19	3.23	48	NaMoOF_5 8.19 C
RbMoF_7	10.25 C	3.46	3.33	48	RbMoOF_5 5.12 (96.5°) R
CsMoF_7	5.36 C	—	—	—	CsMoOF_5 ... 5.29 (96.0°) R
K_2MoF_8	14.1 C	—	—	—	

* C = cubic; R = rhombohedral.

KMoF_6 structure which, like the KNbF_6 structure recently described³ must contain two shorter Mo-F bonds in each MoF_6^- octahedron, is not sufficiently flexible to allow the easy replacement of fluorine by oxygen.

The quinquevalent complex K_3MoF_8 has a cubic unit-cell. Only potassium salts of the series $\text{M}_3\text{Mo}^{\text{V}}\text{F}_8$ and $\text{M}_3\text{W}^{\text{V}}\text{F}_8$ have been made; this is perhaps a measure of the stability of the several MMoF_6 and MWF_6 lattice structures. Tripotassium octafluoromolybdate is hydrolysed immediately by water; the first effect is the formation of a deep reddish brown solution quite different in appearance from the blue solution given by potassium hexafluoromolybdate(v) KMoF_6 , but similar to that given by the mixture " Rb_3MoF_8 ," so that the only reliable way of distinguishing $\text{MMoF}_6 + 2\text{MF}$ from M_3MoF_8 is by Debye X-ray photographs.

In view of the existence of complexes between the alkali fluorides and the hexafluorides of molybdenum and tungsten, it will be interesting to know whether ReF_6 , OsF_6 , OsF_8 , IrF_6 , the recently discovered PtF_6 , UF_6 , and the hexafluorides of the actinides behave similarly. We have good reason to believe from preliminary experiments that ReF_6 does form such compounds; with the platinum-metal fluorides it may be difficult to find a suitable solvent to promote combination. So far as other hexafluorides are concerned, fluorotellurates(vi) such as Cs_2TeF_8 have recently been isolated;^{4, 5} SF_6 and SeF_6 are probably too inert to combine with alkali fluorides.

EXPERIMENTAL

1. *Reactions starting from Molybdenum Carbonyl and Iodine Pentafluoride.*—(a) $\text{Mo}(\text{CO})_6$ alone. In the cold with excess of IF_5 , molybdenum hexafluoride was formed which was

² Hargreaves and Peacock, *J.*, 1957, 4212.

³ Bode and Döhren, *Acta Cryst.*, 1958, **11**, 80.

⁴ Muetterties, *J. Amer. Chem. Soc.*, 1957, **71**, 1004.

⁵ Muetterties and Phillips, *J. Amer. Chem. Soc.*, 1957, **71**, 2975.

identified by its physical properties. With excess of $\text{Mo}(\text{CO})_6$ impure molybdenum tetrafluoride remained as a reddish brown solid (Found: Mo, 59.6; F, 41.2%. Calc. for an equivalent mixture of MoF_3 and MoF_4 : Mo, 59.1; F, 40.9%), magnetic moment $\mu_{\text{eff.}} = 2.45$ B.M. at 25° ($\mu_{\text{eff.}} \text{MoF}_4 = 2.3$ B.M.).

(b) *Mixture* $\text{Mo}(\text{CO})_6$:MI = 1:1. When warmed with excess of iodine pentafluoride this produced white quinquevalent hexafluoromolybdates, which were readily freed from excess of iodine at 150° (Found: Mo, 40.7; F, 48.5. Calc. for NaMoF_6 : Mo, 41.2; F, 48.4. Found: Mo, 38.7; F, 45.4. Calc. for KMoF_6 : Mo, 38.5; F, 45.8. Found: Mo, 32.3; F, 37.3. Calc. for RbMoF_6 : Mo, 32.5; F, 38.6. Found: Mo, 28.0; F, 34.0. Calc. for CsMoF_6 : Mo, 28.0; F, 33.3%).

(c) *Mixture* $\text{Mo}(\text{CO})_6$:KI = 1:2. Treatment of this mixture with iodine pentafluoride yielded a white solid which could be freed from iodine and iodine pentafluoride by heating it in a vacuum at 150° for 30 min. This was *tripotassium octafluoromolybdate(v)* (Found: Mo, 26.0; F, 40.8. K_3MoF_8 requires Mo, 26.3; F, 41.6%) which is stable, like K_3WF_8 , to dry air, but decomposed by moist air. Its aqueous solution is reddish brown. Debye X-ray powder photographs show a cubic unit-cell with $a_0 = 14.07$ Å, and the magnetic moment is $\mu_{\text{eff.}} = 1.23$ B.M. at room temperature.

(d) *Mixture* $\text{Mo}(\text{CO})_6$:NaI = 1:2. Quinquevalent molybdenum was produced in the reaction of this mixture with iodine pentafluoride, but although the product analysed to Na_2MoF_7 (Found: Mo, 34.9; F, 47.3. Calc. for Na_2MoF_7 : Mo, 34.9; F, 48.4%), Debye X-ray photographs showed the presence of NaMoF_6 only, so that the product was a mixture.

(e) *Mixture* $\text{Mo}(\text{CO})_6$:RbI = 1:2. The material produced when these reagents interacted with iodine pentafluoride was again a mixture, but of the composition Rb_3MoF_8 (Found: Mo, 19.8; F, 32.7. Calc. for Rb_3MoF_8 : Mo, 19.1; F, 30.1%). Like the compound K_3MoF_8 this gives a reddish brown aqueous solution, but Debye X-ray photographs showed only the presence of RbMoF_6 .

(f) *Mixture* $\text{Mo}(\text{CO})_6$:CsF = 1:1. This mixture was used in an attempt to obtain CsMoF_7 after it had been realised that sexivalent molybdenum is not formed in iodine pentafluoride solution in the presence of iodide. However, the behaviour of the product towards water showed it to contain Mo^{5+} , and Debye X-ray photographs confirmed the presence of CsMoF_6 .

(2). *Reactions of Molybdenum Hexafluoride and Alkali Fluoride.*—(a) *In the presence of iodine pentafluoride.* A mixture of iodine pentafluoride and excess of molybdenum hexafluoride was condensed on the finely ground dried alkali fluoride. After sufficient time (about 30 min.) had been allowed to complete the reaction, the excess of volatile fluorides was removed at 150° in a vacuum. In each case white residues remained. Sodium fluoride was recovered unchanged but, with potassium fluoride, *dipotassium octafluoromolybdate(vi)* was formed (Found: Mo, 29.7; F, 44.0. K_2MoF_8 requires Mo, 29.4; F, 46.6%). Rubidium fluoride gave *rubidium heptafluoromolybdate(vi)* (Found: Mo, 29.0; F, 40.3. RbMoF_7 requires Mo, 30.5; F, 42.3%). With caesium fluoride the take-up of molybdenum hexafluoride was incomplete (Found: Mo, 21.0%. Calc. for CsMoF_7 : Mo, 26.5%). Debye X-ray photographs confirmed that the principal phase was CsMoF_7 . Slightly moist rubidium and caesium fluorides yielded the *oxypentafluoromolybdates(vi)* (Found: Mo, 32.3; F, 34.1. RbMoOF_5 requires Mo, 32.8; F, 32.5. Found: Mo, 29.1; F, 28.2. CsMoOF_5 requires Mo, 28.3; F, 28.0%). These conclusions were supported by Debye X-ray photographs. Slightly moist sodium fluoride yielded an impure residue which contained some Mo^{6+} . Debye X-ray photographs showed the presence of NaMoOF_5 and NaF.

(b) *In the presence of liquid sulphur dioxide.* The experimental technique was identical with that used in the preparation of the hexafluororhenates(v). With sodium fluoride no combination took place, but with potassium fluoride Debye X-ray photographs confirmed the formation of K_2MoF_8 . Rubidium and caesium fluorides gave complex oxyfluorides (Found: Mo, 32.5; F, 34.0. Calc. for RbMoOF_5 : Mo, 32.5; F, 32.5. Found: Mo, 29.1; F, 32.4. Calc. for CsMoOF_5 : Mo, 28.3; F, 28.0%).

(c) *In the presence of arsenic trifluoride.* Arsenic trifluoride was dried over anhydrous sodium fluoride before use. Caesium fluoride again gave only the oxypentafluoromolybdate, a conclusion supported by Debye X-ray photographs (Found: Mo, 30.6; F, 28.3%). Long exposure of molybdenum hexafluoride to either sulphur dioxide or arsenic trifluoride resulted in the formation of some Mo^{5+} as shown by the appearance of blue colours on the surface of the Pyrex apparatus.

3. *Reaction of Rhenium Hexafluoride and Alkali Iodide in Iodine Pentafluoride.*—Rubidium iodide gave rubidium hexafluororhenate(v) as a white powder (Found: Re, 49.9; F, 28.3. Calc. for RbReF_6 : Re, 48.3; F, 29.5%). This conclusion was confirmed by Debye *X*-ray photographs, as was the formation of the corresponding salts from potassium and caesium iodide.

4. *Reaction of Rhenium Hexafluoride and Potassium Fluoride.*—In the absence of a solvent, no combination takes place, but in the presence of iodine pentafluoride, impure dipotassium octafluororhenate(vi) is formed (Found: K equiv., 270. Calc. for K_2ReF_8 : 416.5). Debye *X*-ray photographs showed the presence of potassium fluoride in the product. Combination was also incomplete in the presence of liquid sulphur dioxide as solvent. Potassium octafluororhenate(vi) is a green solid which dissolves in water to give a green solution which hydrolyses on long standing or on boiling.

Analysis.—Molybdenum. The complexes were dissolved in water (quinquevalent molybdenum if present was oxidised with hydrogen peroxide) and fluorine was removed by evaporating the solutions to dryness with a few ml. of perchloric acid. Molybdenum trioxide was redissolved in dilute alkali and the molybdenum estimated either as the oxine complex or as silver molybdate.

Rhenium. The complexes were broken down by mixing them with a large excess of moist fusion mixture and heating gradually in air to incipient redness. Rhenium was determined as nitron per-rhenate.

Fluorine. The compound was heated with dilute sulphuric acid and fluorine determined in the fluorosilicic acid distillate by precipitation as lead chlorofluoride and estimation of the chloride equivalent by the Volhard method.

X-Ray Photography and Densities.—The methods used were similar to those described for tungsten. The results appear in Table 2.

We thank Mining and Chemical Products Ltd. for a gift of caesium salts, Imperial Chemical Industries Limited, General Chemicals Division, for the use of a fluorine cell, the University of London for silica apparatus, and the Department of Scientific and Industrial Research for a maintenance grant (to G. B. H.).