442. *Higher Complex Fluorides of Tungsten.*

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

Work on the complex fluorides of tungsten has been continued; the salts K_2WF_8, K_3WF_8, $RbWF_7$, $CsWF_7$, and $CsWOF_5$ have been obtained and characterised.

WORK with elementary fluorine and molybdenum carbonyl[1] yielded two lower fluorides of molybdenum, the pentafluoride MoF_5 and the tetrafluoride MoF_4. Starting from a parallel investigation with tungsten carbonyl, we have found several compounds in which tungsten apparently exhibits a high co-ordination number with respect to fluorine.

Ruff found that molybdenum and tungsten hexafluorides are absorbed by the alkali fluorides, and Cox, Sharp, and Sharpe[2] obtained definite compounds of the general formulæ M_2MoF_8 and M_2WF_8, although, as Clark and Emeléus[3] showed that dry alkali fluorides do not absorb the hexafluorides we reopened the subject. We now report the preparation of complex fluorides of sexivalent tungsten; these are K_2WF_8, $RbWF_7$, and $CsWF_7$.

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[1] Peacock, *Proc. Chem. Soc.*, 1957, 59.
[2] Cox, Sharp, and Sharpe, *J.*, 1956, 1242.
[3] Clark and Emeléus, *J.*, 1957, 4778.

In addition, $CsWOF_5$ and K_3WF_8 were characterised. We believe we have also solved some earlier problems.

EXPERIMENTAL

Attempted Preparation of Lower Tungsten Fluorides.—(*a*) Fluorine diluted with nitrogen was allowed to interact with resublimed tungsten carbonyl under conditions similar to those described for molybdenum carbonyl.[1] There is no action below 0°; above this temperature intermittent combination takes place and tungsten hexafluoride WF_6 and carbonyl fluoride COF_2 are formed: $W(CO)_6 + 9F_2 \longrightarrow WF_6 + 6COF_2$.

(*b*) Iodine pentafluoride, prepared from the elements and purified by trap-to-trap distillation in a vacuum, was condensed on tungsten carbonyl. Iodine was liberated, carbon monoxide was evolved, and the presence of tungsten hexafluoride was inferred from its physical properties. All the products were easily volatile, and no lower fluorides were found:

$$5W(CO)_6 + 6IF_5 \longrightarrow 5WF_6 + 30CO + 3I_2.$$

Complex Fluorides of Tungsten.—Tungsten carbonyl was sublimed in a high vacuum. Tungsten hexafluoride and iodine pentafluoride were prepared from the elements and sublimed or distilled in a vacuum. The alkali iodides and fluorides were carefully dried, the former at 100° and the latter by heating them to incipient fusion.

(1) *Reaction of Tungsten Carbonyl and Alkali Iodide with Iodine Pentafluoride.*—(a) *Mixture* $W(CO)_6 : KI = 1 : 1$. Warmed together, these produced *dipotassium octafluorotungstate*(VI) K_2WF_8, a white solid readily freed from iodine and excess of iodine pentafluoride by heating it in a vacuum at 150° for 30 min. (Found: W, 44·1; F, 36·3%; equiv., 415. K_2WF_8 requires W, 44·4; F, 36·7%; equiv., 415): $5W(CO)_6 + 10KI + 8IF_5 = 5K_2WF_8 + 9I_2 + 30CO$. It is stable in dry air but decomposes in a moist atmosphere with rapid attack on glass containers. It is completely and easily soluble in water to a solution which smells of hydrofluoric acid. Debye *X*-ray photographs, detailed below, show a cubic unit cell with $a = 10{\cdot}03$ Å.

(b) *Mixture* $W(CO)_6 : CsI = 1 : 1$. Although the white solid from this reaction had similar properties to the above potassium salt, and a composition near to the formula Cs_2WF_8, Debye *X*-ray photographs disclosed a phase isostructural with that[4] of $CsWF_6$ indicating the probable presence of the oxyfluoride $CsWOF_5$ (see below) (Found: W, 30·7; F, 26·9%. Calc. for Cs_2WF_8: W, 30·6; F, 25·3%. Calc. for a mixture of $CsWOF_5 : Cs_2SiF_6 = 2 : 1$: W, 29·1; F, 24·1%).

(c) *Mixture* $W(CO)_6 : NaI = 1 : 1$. Under rigorously dry conditions tungsten was not found in the product, a result in conformity with the behaviour of tungsten hexafluoride described below. It is difficult to dry sodium iodide thoroughly without slight oxidation or hydrolysis, so products were sometimes obtained with a composition approximately Na_2WF_8, but the Debye *X*-ray photographs showed a phase isostructural with that of $NaWF_6$, which was most probably the oxyfluoride $NaWOF_5$ (Found: W, 49·3; F, 38·1. Calc. for Na_2WF_8: W, 48·2; F, 39·8%. Calc. for a mixture $NaWOF_5 : Na_2SiF_6 = 2 : 1$: W, 44·6; F, 36·9%.

(d) *Mixture* $W(CO)_6 : KI = 2 : 1$. 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 octafluorotungstate*(V) (Found: W, 40·9; F, 38·9%; equiv., 431. K_3WF_8 requires W, 40·6; F, 40·1%; equiv., 453), which is stable in dry air but decomposed by moist air. Its aqueous solution is pale green, unlike the blue or purple solution of potassium hexafluorotungstate(V) KWF_6. Debye *X*-ray photographs show a rhombohedral unit cell with $a = 9{\cdot}75$ Å and $\alpha = 86{\cdot}4°$. (Molybdenum appears to form a similar compound which is still under investigation.)

(e) *Mixture* $W(CO)_6 : NaI = 2 : 1$. Again quinquevalent tungsten was produced, but Debye *X*-ray photographs showed the product to be a mixture containing $NaWF_6$. The material dissolved in water to give the blue colour characteristic of the WF_6^- ion.

(2) *Reaction of Tungsten Hexafluoride and Alkali Fluoride.*—(a) *In absence of solvent.* On rigorously dried material our results agree with those of Clarke and Emeléus, who found there was no combination. With slightly moist potassium fluoride, however, there was rapid reaction in the cold; the impure product contained HF and was not amenable to *X*-ray examination in glass. It had a composition near to K_2WF_8 (Found: W, 39·0; F, 35·3%). Cæsium fluoride, also slightly moist, gave a product containing 24·1% of tungsten; according to the Debye *X*-ray photographs it contained $CsWOF_5$.

(b) *In the presence of iodine pentafluoride.* With dry potassium fluoride dipotassium octafluorotungstate K_2WF_8 was formed (Found: W, 44·4; F, 36·8%), a conclusion supported by Debye *X*-ray photographs. So far we have been unable to dry either rubidium or cæsium fluorides to give a stoicheiometric product. The moist salts yielded complex oxyfluorides, isostructural with $RbWF_6$ and $CsWF_6$, of which the *cæsium oxypentafluorotungstate*(VI), a white solid stable in dry air, was analysed (Found: W, 43·2; F, 23·1%. $CsWOF_5$ requires Cs, 42·0; F, 21·7%). Our preparation attacked glass slowly; we ascribe this to HF or moisture and do not believe it is characteristic of the pure compound. The salt dissolves in water to a colourless solution.

(3) *Reaction of Tungsten Hexafluoride and Alkali Iodide in the Presence of Iodine Pentafluoride.*—Alkali iodides were used because, except for lithium and sodium iodides, they are more easily purified and dried than the fluorides. With potassium iodide, dipotassium octafluorotungstate was formed (Found: W, 44·3; F, 36·6%). Debye *X*-ray photographs supported the conclusion reached from the analysis. Neither rubidium nor cæsium iodides gave a product corresponding in composition to that from potassium iodide, but gave *rubidium heptafluorotungstate*(VI) and *cæsium heptafluorotungstate*(VI) (Found: W, 45·3; F, 33·4%; equiv., 389. $RbWF_7$ requires W, 45·7; F, 33·1%; equiv., 402. Found: W, 40·0; F, 29·5%; equiv., 460. $CsWF_7$ requires W, 40·0; F, 28·9%; equiv., 460). Both heptafluorotungstates resemble K_2WF_8 in appearance and properties: $5WF_6 + 5RbI + IF_5 \longrightarrow 5RbWF_7 + 3I_2$; $5WF_6 + 5CsI + IF_5 \longrightarrow 5CsWF_7 + 3I_2$. Debye *X*-ray photographs, detailed below, show $CsWF_7$ to have a cubic unit cell with $a = 5·49$ Å. The three fluoro-complexes of sexivalent

TABLE 1.

		K_2WF_8			$RbWF_7$		
N	Indices	Intensity	$\sin^2\theta \times 10^4$ found	$\sin^2\theta \times 10^4$ calc.	Intensity	$\sin^2\theta \times 10^4$ found	$\sin^2\theta \times 10^4$ calc.
4	200	s	332	318	s	312	304
5	210	w	414	397	ms	393	380
8	220	vs	671	635	vs	621	608
9	300 221	vw	727	714	ms	698	684
10	310	vvw	829	794	—	—	—
12	222	vw	969	953	vw	923	911
13	320	vvw	1055	1032	vw	1006	987
14	321	vw	1135	1112	vw	1068	1063
16	400	ms	1296	1270	ms	1227	1215
17	410 322	w	1373	1350	vw	1302	1291
20	420	w	1617	1588	—	—	—
21	421	s	1690	1667	ms	1609	1595
24	422	vs	1928	1906	vs	1840	1823
25	430 500	w	1988	1985	vw	1918	1899
26	511 431	vw	2085	2064	vw	1994	1975
29	520 432	ms	2325	2303	w	2222	2203
30	521	vw	2409	2382	vw	2292	2279
32	440	w	2566	2541	w	2445	2430
33	522 441	w	2648	2620	vw	2525	2506
36	600 442	w	2877	2858	vw	2755	2734
37	610	w	2963	2938	vw	2829	2810
40	620	ms	3203	3176	ms	3052	3038
41	443 621 540	vs	3281	3255	ms	3130	3114
42	541	w	3369	3335	vw	3215	3190
45	630 542	w	3601	3573	w	3433	3418
46	631	vw	3683	3652	vw	3514	3494
48	444	—	—	—	vw	3658	3646
49	700 632	w	3917	3891	w	3745	3722

TABLE 1. (*Continued.*)

		K_2WF_8			$RbWF_7$		
N	Indices	Intensity	$\sin^2\theta \times 10^4$ found	$\sin^2\theta \times 10^4$ calc.	Intensity	$\sin^2\theta \times 10^4$ found	$\sin^2\theta \times 10^4$ calc.
50	543 710 550	vw	4015	3970	vvw	3814	3798
53	720 641	w	4235	4208	w	4065	4025
54	552 721 633	vw	4320	4288	vw	4134	4101
56	642	ms	4465	4446	s	4275	4253
61	650 643	w	4862	4843	vw	4641	4633
62	732 651	w	4955	4923	vw	4735	4709
65	810 740	ms	5183	5160	w	4948	4937
66	811 741	w	5281	5240	vw	5050	5013
69	821 742	ms	5499	5479	w	5259	5241
70	653	vw	5586	5558	vw	5338	5317
73	830 661	w	5817	5796	—	—	—
74	743 831 750	vw	5908	5875	—	—	—
77	832 654	ms	6142	6114	w	5861	5848
81	744 900 663 841	ms	7456	6431	vw	6193	6152
84	842	—	—	—	w	6380	6380
86	655 921 761	ms	6859	6828	—	—	—
89	843 922 762 850	w	7084	7067	—	—	—
90	754 930 851	ms	7168	7146	—	—	—
93	852	vvw	7403	7384	—	—	—
94	932 763	vw	7485	7464	—	—	—
98	770 941 853	w	7794	7781	—	—	—
101	10·10 861 942 764	s	8041	8019	w	7674	7670
105	10·21 854	s	8357	8337	—	—	—
109	10·30 863	ms	8664	8654	—	—	—
110	10·31 952 765	ms	8735	8734	—	—	—
113	10·32 944 870	ms	8968	8972	—	—	—
115	953	ms	9096	9131			
117	10·41 960 872	ms	9296 9315	9290	vw	8810	8810

		$CsWF_7$		
N	Indices	Intensity	$\sin^2\theta \times 10^4$ found	$\sin^2\theta \times 10^4$ calc.
1	100	w	279	273
2	110	vs	559	546
4	200	w	1105	1091
6	211	s	1654	1637
8	220	w	2205	2182
10	310	ms	2758	2728
12	222	vw	3306	3274
14	321	s	3846	3819
16	400	vvw	4393	4365

		$CsWF_7$		
N	Indices	Intensity	$\sin^2\theta \times 10^4$ found	$\sin^2\theta \times 10^4$ calc.
18	411 330	w	4932	4910
20	420	vw	5486	5456
22	332	vvw	6027	6002
26	431 500	w	7108	7093
30	521	vw	8209	8184
34	530	vvw	9276	9275

tungsten, and the complex oxyfluoride, are all slightly paramagnetic ($\mu_{\text{eff}} \sim 0{\cdot}2$ B.M.) at room temperature.

Analysis.—Tungsten. The complexes were dissolved in water (quinquevalent tungsten if present was oxidised with nitric acid) and the tungsten was precipitated by the cinchonine–tannin method and weighed as WO_3 after ignition of the precipitate at 800°.

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

X-*Ray Photography.*—Since the compounds were too hygroscopic for transference in a dry-box, the thin-walled Pyrex capillary of about 0·5 mm. diameter was sealed to the preparation line. The compound was powdered by shaking it with a number of glass beads, and was then shaken into the capillary. A 9-cm. camera and Co-$K\alpha$ radiation in conjunction with an iron filter were used. A 19-cm. camera gave no better photographs. For results, see Table 1.

Densities.—Carbon tetrachloride was carefully dried by distillation over phosphoric oxide. A 2 ml. density bottle with a stopper was used. About 1 g. of material was required for each determination. The results are presented in Table 2.

DISCUSSION

The results show the necessity of thoroughly drying the reactants and emphasise the diagnostic value of X-ray photography. The earlier failure to prepare complex rubidium and cæsium fluorotungstates(VI) from the carbonyl reaction may well be due to the difficulty of freeing iodine pentafluoride from HF and SiF_4. Complex oxyfluorides are clearly formed preferentially with even small quantities of moisture or hydrogen fluoride present, except perhaps when the alkali metal is potassium.

If sufficient alkali iodide is present when tungsten carbonyl interacts with iodine pentafluoride, quinquevalent complex fluorides are formed. We do not know why this is so, but only suggest that with large amounts of free iodine the increase in "basicity" is sufficient to stabilise W^{5+} in iodine pentafluoride. It is noteworthy that whereas sodium iodide gives a hexafluorotungstate(V) under these conditions,[cf. 4] potassium iodide gives an octafluorotungstate(V) K_3WF_8.

Sexivalent complex fluorides of tungsten are best prepared by the addition of excess of tungsten hexafluoride to alkali iodide in presence of iodine pentafluoride. We agree with Clark and Emeléus that rigorously dried alkali-metal fluorides do not combine appreciably with tungsten hexafluoride and our work also indicates that a solvent such as iodine pentafluoride is necessary to promote the reaction.

TABLE 2.

	Unit cell size (Å)	Density (g./ml.)	Formula units per unit cell	Density calc. from unit cell (g./ml.)
K_2WF_8	$a_0 = 10{\cdot}03$ (Cubic)	4·10	6	4·09
$RbWF_7$	$a_0 = 10{\cdot}27$,,	4·14	(6·76)	(4·14)
$CsWF_7$	$a_0 = 5{\cdot}49$,,	4·54	1	4·61
$NaWOF_5$	$a_0 = 8{\cdot}17$,,	—	—	—
$CsWOF_5$	$a_0 = 5{\cdot}31$; $\alpha = 95{\cdot}5°$ (Rhombohedral)	—	—	—
K_3WF_8	$a_0 = 9{\cdot}75$; $\alpha = 86{\cdot}4°$,,	—	—	—

Debye X-ray photographs show that the three sexivalent complex fluorides have simple cubic symmetry, but that whereas K_2WF_8 and $RbWF_7$ seem to be closely related in structure $CsWF_7$ stands by itself. Density measurements indicate that the unit cell of K_2WF_8 contains 6 formula units, and that of $RbWF_7$ about 6·8 formula units (Table 2). In each case, therefore, the unit cell probably contains 48 fluorine atoms. Without a complete set of intensity measurements we cannot be specific about their structures, but it is reasonable to imagine the 48 fluorine atoms to be divided into 8 octahedrally arranged sets of 6 with statistical distributions of tungsten and alkali-metal atoms between them. $CsWF_7$ contains only one formula unit in the unit cell and the absent reflections suggest

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[4] Hargreaves and Peacock, *J.*, 1957, 4212.

a cæsium chloride arrangement of cæsium and tungsten atoms; nothing can be said about the positions of the fluorine atoms. Since the structures of the salts depend markedly on the size of the alkali-metal atom, the absence of a stable sodium fluorotungstate(VI) is scarcely surprising.

The chief interest in the complex sexivalent fluorotungstates lies in the covalency of the tungsten atom. Octacovalent tungsten is well known in the quadrivalent octacyanotungstates $M_4W(CN)_8$ and osmium, which lies in the same period of the Periodic Table, forms an octafluoride OsF_8. Whether tungsten has a covalency greater than six in our compounds is uncertain, although in the cæsium salt a covalency of seven seems likely.

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IMPERIAL COLLEGE, LONDON, S.W.7.

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