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Abstract

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NEW COMPLEX COMPOUNDS OF THE HEXAFLUORIDES OF MOLYBDENUM, TUNGSTEN, AND URANIUM WITH CESIUM AND AMMONIUM FLUORIDES

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The interaction of the hexafluorides of tungsten, molybdenum, and uranium with fluorides of the alkali metals and with ammonia was first reported by O. Ruff et al. ([1]-[3]). However, the authors did not describe the double compounds formed in this process, indicating only that interaction with gaseous ammonia reduces uranium to the tetravalent state. Martin, Albers, Dust, and others ([4]-[7]) synthesized a series of complex compounds formed by uranium hexafluoride with the fluorides of potassium, sodium, rubidium, and silver: K_3UF_9, Na_3UF_9, Ag_3UF_9, Rb_2UF_8. Cox and Sharp ([8]), on the basis of the above works, obtained complex compounds formed by the hexafluorides of Mo and W with alkali fluorides, of the general formula M_2MoF_8 and M_2WF_8, where M—Na, K, Rb, Cs. The principal method for synthesizing such compounds was to carry out the reaction between gaseous hexafluorides and fluorides of the alkali elements by an adsorption type of process. Hargreaves and Peacock ([9],[10]) report that, by the interaction of molybdenum and tungsten hexafluorides with iodides and fluorides of alkali metals in solutions of iodine pentafluoride, alongside salts of the general formula M_2MeF_8, rubidium and cesium heptafluorotungstates and heptafluoromolybdates were obtained. However, the authors apparently did not succeed in isolating the salts in pure form, as is indicated by the data of the analyses presented.

The present communication is devoted to the synthesis of complex compounds of molybdenum, tungsten, and uranium hexafluorides with cesium and ammonium fluorides, of the general formula $MMeF_7$. For the synthesis of these compounds a fundamentally new method was used, based on the interaction of the hexafluorides of Mo, W, and U with alkali-metal fluorides in solutions of chlorine trifluoride according to the proposed scheme:

$$ClF_3 \rightleftharpoons ClF_2^+ + F^-;$$

$$n[ClF_2^+ - F^-] + MeF_6 \rightleftharpoons [ClF_2]_{nMeF_{6+n}};$$

$$MF + [ClF_2]_{nMeF_{6+n}} \rightleftharpoons M_{nMeF_{6+n}} + nClF_3,$$

where Me—Mo, W, U; M—an alkali element.

The equilibrium relating to the dissociation of chlorine trifluoride was established earlier (^{11}). The solubilities of the individual components in chlorine trifluoride, determined by us at 0°, proved to be: MoF_6 95.1 ± 0.5%; WF_6 99 ± 1%; UF_6 49.13 ± 0.3%; CsF_3 16.05 ± 0.4%. The value found for the solubility of uranium hexafluoride in chlorine trifluoride coincides with that theoretically calculated according to Raoult' s law (^{12}). It was not possible to determine the solubility of ammonium fluoride in ClF_3 because of

···rapid combustion of the salt. The combustion may assume the character of an explosion. The solubilities of other alkali-metal fluorides proved to be insignificant.

The reactions under investigation were carried out in Teflon vessels of 100 ml capacity by mixing the reacting solutions in quantities ensuring the preparation of 30–40 g of salt. The homogeneous character of the reactions and the absence of side processes in solutions of chlorine trifluoride (reduction, hydrolysis) were expected to ensure the purity of the product.

The hexafluorides used in the work were prepared by fluorinating the metals with gaseous chlorine trifluoride. As a result of reactions between solutions of MoF_6, WF_6, UF_6 and a solution of cesium fluoride, precipitates were formed that were poorly soluble in an excess of chlorine trifluoride. This made it possible to wash these precipitates with chlorine trifluoride. By such washing followed by evacuation of traces of chlorine trifluoride, pure salts free of the initial reagents were obtained.

Because ammonium fluoride is decomposed in ClF_3, a different procedure was used for the synthesis of the ammonium salts. Dry NH_4F was added in small portions to solutions of the hexafluorides of Mo, W, and U in ClF_3, saturated while cooled with dry ice. It should be noted that the addition of NH_4F requires special caution because of possible decomposition of the ammonium salt. The crystals that precipitated were ground and subjected to additional treatment with a solution of the hexafluoride, after which they were washed three times with ClF_3 and evacuated under cooling. Cooling is necessary to prevent reduction.

The isolated salts were subjected to complete chemical analysis. The fluorine content was determined by titration with a solution of aluminum chloride. Cesium was determined gravimetrically as $Cs[Co(NO_2)_6] \cdot H_2O$, and ammonia by distillation from concentrated alkali followed by titration with acid. For the analysis of molybdenum, tungsten, and uranium, both volumetric and gravimetric methods were used; the metals were determined as oxides and by precipitation with *o*-oxyquinoline. The results of the analyses are presented in Table 1.

Table 1

Compound	F, wt. %, calculated	F, wt. %, found	Cs, wt. %, calculated	Cs, wt. %, found	NH_4, wt. %, calculated	NH_4, wt. %, found	Mo, wt. %, calculated	Mo, wt. %, found	W, wt. %, calculated	W, wt. %, found	U, wt. %, calculated	U, wt. %, found	Note
$Cs(MoF_7)$	37.0 ± 0.5	36.754	36.0 ± 0.3	36.729			26.67 ± 0.3	26.515					white
$Cs(WF_7)$	30 ± 0.5	29.566	28.7 ± 0.3	29.546					41 ± 0.4	40.886			white
$Cs(UF_7)$	26.32 ± 0.5	26.389	26.4 ± 0.4	26.372							47.35 ± 0.2	47.237	yellow
$NH_4(MoF_7)$*	53.45 ± 0.5	53.848			7.15 ± 0.5	7.303	39.2 ± 0.1	38.847					white
$NH_4(WF_7)$*	40.1 ± 0.6	39.706			5.5 ± 0.1	5.385			55.1 ± 0.2	54.908			white
$NH_4(UF_7)$*	34.57 ± 0.2	34.180			4.83 ± 0.2	4.636					61.11 ± 0.2	61.183	yellow

* Obtained for the first time.

Attention is drawn to the fact that in the compounds obtained a rather rare coordination number, 7, is realized. This agrees with O' Brie—

···ta(13), who believes that "halogens in general (especially fluorine), apparently, promote the formation of compounds with this coordination number."

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CITED LITERATURE

1. O. Ruff, [[unclear: initial/name]], Eisner, *Ber.*, **38**, 742 (1905).
2. O. Ruff, F. Eisner, *Ber.*, **40**, 2926 (1907).
3. O. Ruff, A. Heinzelmann, *Zs. anorg. Chem.*, **72**, 63 (1911).
4. H. Martin, A. Albers, *Naturwiss.*, **33**, 370 (1946).

5. H. Martin, A. Albers, H. Dust, *Zs. anorg. Chem.*, **265**, 128 (1951).
6. S. H. Smiley, D. C. Brater et al., *Ind. and Eng. Chem.*, **51**, 191 (1959).
7. G. I. Cathers, M. R. Bennet, R. L. Jolley, *Ind. and Eng. Chem.*, **50**, 1709 (1958).
8. B. Cox, D. W. A. Sharp, A. G. Sharpe, *J. Chem. Soc.*, 1956, 1242.
9. G. B. Hargreaves, R. D. Peacock, *J. Chem. Soc.*, 1957, 4390.
10. G. B. Hargreaves, R. D. Peacock, *J. Chem. Soc.*, 1958, 2170.
11. N. S. Nikolaev, I. M. Malyukov, *ZhKh*, **2**, 1587 (1957).
12. Kh. Bernhardt, E. Barber et al., Second International Conference on the Peaceful Uses of Atomic Energy, report No. 932, Geneva, 1958.
13. *Chemistry of Coordination Compounds*, ed. J. Bailar, IL, 1960.

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