257. *Complex Fluorides. Part V.* Complexes formed by Molybdenum Hexafluoride, Tungsten Hexafluoride, and Rhodium Tetrafluoride.*

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The hexafluorides of molybdenum and tungsten combine with potassium, rubidium, and cæsium fluorides to form complexes of general formulæ M_2MoF_8 and M_2WF_8. The complex fluoride which is obtained by interaction of bromine trifluoride and sodium hexachlororhodate(III) is sodium hexafluororhodate(IV), Na_2RhF_6.

Ruff and Eisner[1,2] reported that the hexafluorides of molybdenum and tungsten combine with alkali-metal fluorides, but gave no details and described no compounds. The preparation of complexes of uranium hexafluoride[3,4] (*e.g.*, Na_3UF_9, K_2UF_8) suggested to us the possibility of finding evidence for unusual co-ordination numbers in complexes derived from molybdenum and tungsten hexafluorides, and we have therefore re-examined the interaction of these substances and the fluorides of sodium, potassium, rubidium, and cæsium.

Molybdenum hexafluoride has usually been made by the action of fluorine on the powdered metal; for the present purpose, however, the use of bromine trifluoride as the fluorinating agent has proved more convenient. The hexafluoride obtained by this method is contaminated with bromine, but for chemical work this is not a serious disadvantage, and the possibility of carrying out the preparation in a closed system greatly simplifies the essential task of rigidly excluding moisture. After any excess of bromine trifluoride had been frozen out, the mixture of molybdenum hexafluoride and bromine was condensed on the alkali-metal fluoride, absorption of the hexafluoride was allowed to take place, then the excess of molybdenum hexafluoride and the whole of the bromine were removed by distillation. The products obtained from potassium, rubidium, and cæsium fluorides had the general formula M_2MoF_8, and on a second treatment with the hexafluoride underwent no change in weight. Sodium fluoride absorbed only a negligible amount of the hexafluoride.

Essentially the same procedure was applied in the preparation of complexes of tungsten hexafluoride, and the compounds K_2WF_8, Rb_2WF_8, and Cs_2WF_8 were obtained; sodium fluoride again failed to react. All of the complex fluorides prepared are stable at room temperature in the absence of moisture; we have so far, however, been unable to obtain

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* Part IV, *J.*, 1956, 876.

[1] Ruff and Eisner, *Ber.*, 1905, **38**, 742.

[2] *Idem, Ber.*, 1907, **40**, 2926.

[3] Martin and Albers, *Naturwiss.*, 1946, **33**, 370.

[4] Martin, Albers, and Dust, *Z. anorg. Chem.*, 1951, **265**, 128.

satisfactory *X*-ray powder photographs of them or to learn anything concerning their structures. All are decomposed by bromine trifluoride, yielding the tetrafluorobromites.

It has been shown [5] that the action of bromine trifluoride on sodium hexachlororhodate(III), or on mixtures of sodium and rhodium halides, produces impure complex fluorides containing tetrapositive rhodium; the oxidation state of the rhodium has been confirmed by magnetic measurements.[6] It was originally thought that the pale blue product obtained from sodium hexachlororhodate had the formula Na_3RhF_7, and was analogous to the complex K_3CoF_7 described by Klemm and Huss.[7] Subsequent investigations by Klemm and his co-workers [8, 9] have shown that the compound to which the formula K_3CoF_7 was assigned is really K_3CoF_6, and that yellow complexes of formulæ K_2RhF_6, Rb_2RhF_6, and Cs_2RhF_6 are obtained by the action of fluorine on mixtures of alkali-metal and rhodium halides at about 320°. The interaction of bromine trifluoride and sodium hexachlororhodate(III) has therefore been re-investigated, making use of a technique first employed by Zachariasen [10]—the identification of a substance by its predicted *X*-ray powder pattern. From the lattice constants [11] of the isomorphous sodium salts of general formula Na_2XF_6, and the similarity in lattice constants [9, 12] of Cs_2RhF_6 and Cs_2PtF_6, it would be expected that Na_2RhF_6 and Na_2PtF_6 would be isomorphous and almost isodimensional. The fact that the principal phase present in the products obtained from bromine trifluoride and sodium chlororhodate or mixtures of sodium and rhodium chlorides is isomorphous and nearly isodimensional with Na_2PtF_6 and Na_2PdF_6 provides strong evidence for the formation of the complex Na_2RhF_6 in these reactions; the blue colour is perhaps due to the presence of a little rhodium tetrafluoride [6] arising by solvolysis of the complex. Lattice constants for Na_2RhF_6, which has a hexagonal unit cell, are $a = 9{\cdot}32$, $c = 5{\cdot}22$ Å; those for the isomorphous sodium hexafluoropalladate, which has been prepared for the first time during this investigation, are $a = 9{\cdot}23$, $c = 5{\cdot}25$ Å. The formation of the hexafluororhodate(IV) was further substantiated by showing that interaction of bromine trifluoride and mixtures of cæsium and rhodium chlorides gave only cæsium hexafluororhodate(IV), Cs_2RhF_6, identified by analysis and by comparison of its *X*-ray powder diagram with the data given by Weise and Klemm.[9]

EXPERIMENTAL

Reactions involving bromine trifluoride and *X*-ray powder photographic examinations were carried out as described in previous papers. For the study of complex formation by molybdenum and tungsten hexafluorides apparatus essentially similar to that described by Emeléus and Woolf [13] was employed. All operations on complex fluorides of molybdenum, tungsten, and rhodium were conducted in rigorously dried, closed systems or in a " dry-box."

Complexes of Molybdenum Hexafluoride.—Molybdenum powder was allowed to react with bromide trifluoride, and the resulting volatile products were passed through a trap at −23° (to remove excess of bromine trifluoride) and condensed at −196°. The mixture of molybdenum hexafluoride and bromine was then distilled on to a weighed quantity of the alkali-metal fluoride contained in a quartz flask, and, absorption of the hexafluoride having occurred, the excess of the latter compound and the whole of the bromine were removed by distillation. Alkali metal in the white residue was determined from the weight of halide taken or as chloroplatinate (after removal of molybdenum by treatment with bromine trifluoride, and decomposition of the resulting tetrafluorobromite by exposure to moist air); molybdenum was precipitated as its 8-hydroxyquinoline complex (with the formation of which fluoride ion was shown in model determinations not to interfere); fluorine was determined gravimetrically as calcium fluoride (Found, for the K *salt*: K, 24·1; Mo, 28·8. K_2MoF_8 requires K, 23·9; Mo, 30·1. Found, for

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[5] Sharpe, *J.*, 1950, 3444.
[6] Nyholm and Sharpe, *J.*, 1952, 3579.
[7] Klemm and Huss, *Z. anorg. Chem.*, 1949, **258**, 221.
[8] Klemm, *Angew. Chem.*, 1954, **66**, 468.
[9] Weise and Klemm, *Z. anorg. Chem.*, 1953, **272**, 211.
[10] Zachariasen, *Acta Cryst.*, 1948, **1**, 265; *J. Amer. Chem. Soc.*, 1948, **70**, 2147.
[11] Cox, *J.*, 1954, 3251.
[12] Cox and Sharpe, *J.*, 1953, 1783.
[13] Emeléus and Woolf, *J.*, 1950, 164.

the Rb *salt*: Rb, 44·0; Mo, 21·7; F, 34·5. Rb_2MoF_8 requires Rb, 40·7; Mo, 22·9; F, 36·2. Found, for the Cs *salt*: Cs, 48·7; Mo, 19·7; F, 31·6. Cs_2MoF_8 requires Cs, 51·7; Mo, 18·7; F, 29·6%).

Complexes of Tungsten Hexafluoride.—The experimental methods were analogous to those described in the preceding section. Tungsten was determined by the cinchonine hydrochloride–tannin method and ignition to the trioxide (Found, for the K *salt*: W, 44·9, 42·0. K_2WF_8 requires W, 44·4. Found, for the Rb *salt*: Rb, 33·9; W, 35·6. Rb_2WF_8 requires Rb, 33·7; W, 36·3. Found, for the Cs *salt*: Cs, 45·3; W, 28·9. Cs_2WF_8 requires Cs, 44·2; W, 30·5%).

Complexes of Rhodium Tetrafluoride.—Preparations and analyses for sodium compounds were as described previously.[5] Cæsium hexafluororhodate(IV) was made by interaction of bromine trifluoride and a mixture of cæsium chloride and hydrated rhodium chloride containing cæsium and rhodium in 2 : 1 proportions; the product was heated at 270° *in vacuo* (Found: F, 24·4. Calc. for Cs_2RhF_6: F, 23·6%). The powder pattern of the product was indexed on the basis of a hexagonal unit cell with $a = 6·28$, $c = 10·11$ Å, in agreement with values previously reported for the high-temperature form of this substance by Weise and Klemm.[9] *X*-Ray powder photography revealed no evidence for the formation of other complex fluorides of cæsium (or sodium) and rhodium when the proportions of the starting materials were varied.

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