LA-AC-6899

83768

FEB 18 1965

Invited paper to be presented by L. B. Asprey at The International Conference on Protactinium Chemistry, July 2-8, 1965, Orsay (S-et-O), France.

MASTER

1

PREPARATION AND PROPERTIES OF SOME ALKALI FLUORIDE COMPLEXES OF PENTAVALENT PROTACTINIUM[1]

BY L. B. Asprey, R. A. Penneman, and F. H. Kruse

Los Alamos Scientific Laboratory, University of California,
Los Alamos, New Mexico, U. S. A.

CONF-650728-3

English Summary:

Complex fluorides containing pentavalent protactinium and alkali fluoride have been made, both from aqueous hydrofluoric acid solution and by fluorine oxidation of intimately ground mixtures containing PaF_4 and alkali fluoride. The major part of the work has been done on the rubidium - Pa(V) - fluoride system. X-ray data are reported. Correlation of the properties of the complex fluorides of pentavalent protactinium with those of pentavalent uranium are made.

French Summary:

On a préparé des complexes fluorures qui contiennent du protactinium pentavalent et de l'alcali fluorure à partir d'une solution d'acide aqueux fluorhydrique aussi bien que à partir de l'oxidation fluor de mélanges intimement moulus qui contiennent du PaF_4 et de l'alcali fluorure. On a fait la plupart du travail sur le système rubidium fluorure - Pa(V).On expose des données-rayons X. On fait la corrélation des propriétés des fluorures complexes du protactinium pentavalent avec celles de l'uranium pentavalent.

INTRODUCTION

Numerous compounds in the form of non-oxygenated fluoride complexes of the types M_aXF_{5+a} where X is a pentavalent heavy element and M is an alkali 2, 3, 4, 5, 6 or ammonium cation, have been prepared.[2, 3, 4, 5, 6] In the 5f series, the pentavalent uranium system has been studied extensively, particularly from the point of view of crystal structures of the compounds having various stoichiometric ratios of alkali to uranium.

Several synthetic routes to the preparation of these compounds have been developed. One method consists of heating in an inert atmosphere an intimate mixture of UF_5 and the desired alkali fluoride in some specific stoichiometric ratio.[4] Such preparations are micro-crystalline powders, yielding excellent X-ray powder diffraction patterns. A second method involves the dissolution of UF_5 in concentrated aqueous HF followed by addition of an alkali fluoride.[5] Crystals large enough for X-ray single crystal analysis are often obtained. Still another method which works even for the light alkalis utilizes anhydrous HF containing an alkali fluoride in solution.[6] Addition of UF_5 to this produces a blue solution characteristic of the UF_6^- complex. Slow evaporation of the solution yields large single crystals (up to several millimeters) suitable for optical studies. Complex compounds of pentavalent protactinium have been made by the first method, the only difference being that a mixture of PaF_4 and the alkali fluoride were treated with fluorine to give Pa(V). The second method used Pa_2O_5 instead of PaF_5 as the starting material. X-ray powder patterns were used as the primary means of identification.

EXPERIMENTAL

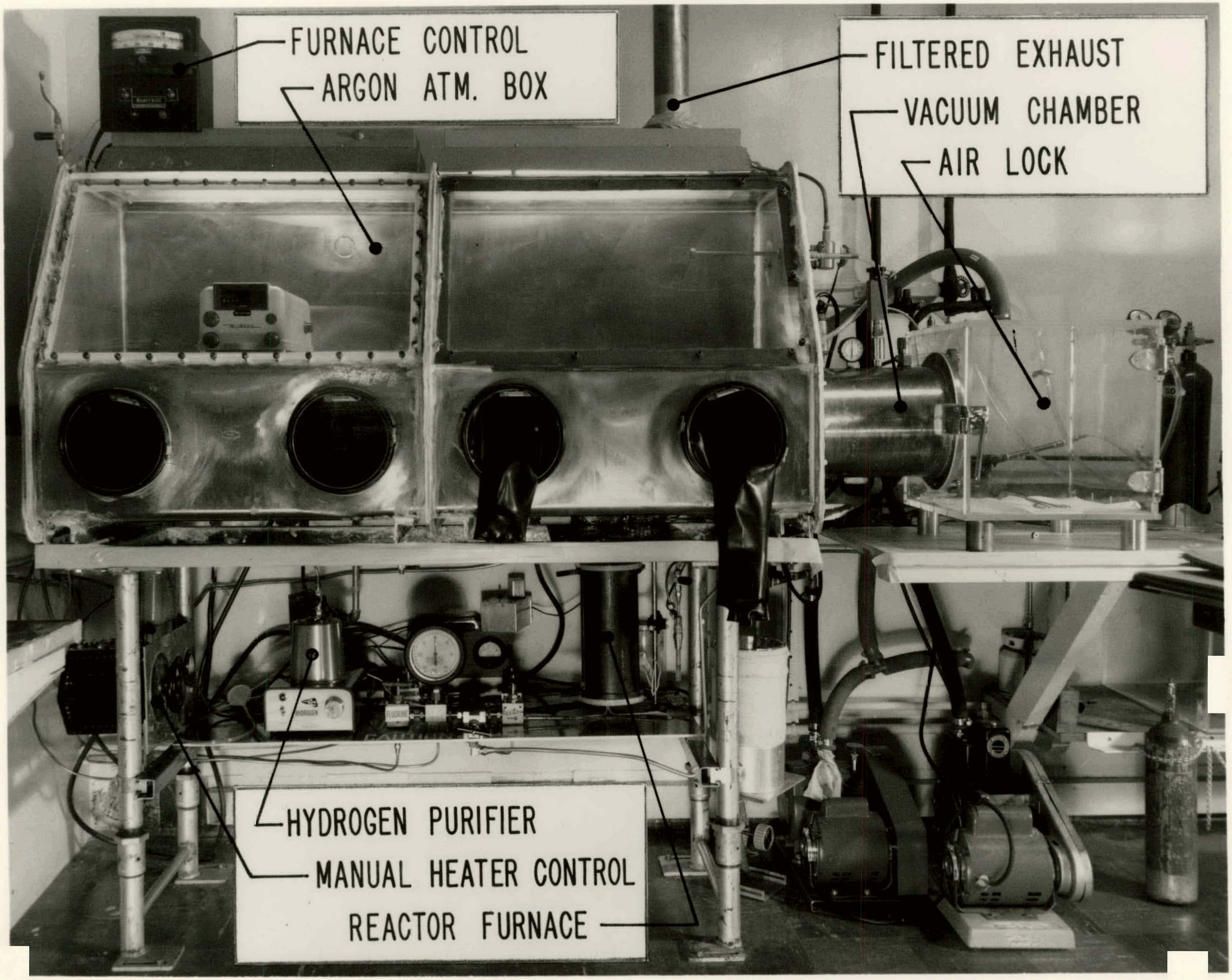
Materials. — Pa_2O_5 and PaF_4 were used as starting materials. The protactinium was that originally purified by the British workers and subsequently found to contain niobium impurity. Analysis of a 100 mg. portion showed our material to contain 2.2 percent Nb. This was reduced to < 0.1 percent by two precipitation steps utilizing K_2PaF_7. The PaF_4 was prepared by hydrofluorination of Pa_2O_5 in the presence of hydrogen. Anhydrous RbF was prepared by fluorination of commercial RbF at 300°C.

Technique. — Solution preparations were made using Reagent Grade materials. Platinum or polyethylene ware was used. Anhydrous reactions were carried out in an inert Argon atmosphere. The apparatus is shown in Fig. 1. Sapphire was usually used for fluorinations, platinum for hydrofluorination. The reactor was constructed of nickel.

X-ray powder diffraction patterns were obtained using a Debye-Scherrer 114.6 mm. camera with Ilford-G film and filtered Cu radiation. The samples were sealed in 0.2 mm. diameter Lindemann glass capillaries. Single crystal studies were made using Weissenberg and Buerger precession cameras. Optical studies were made using a Zeiss polarizing microscope.

Chemical analysis was performed on the uranium compounds only. Stoichiometry was established for the Pa compounds by weighing out the exact amounts of alkali fluoride and protactinium oxide or tetrafluoride to give the desired ratio. Analogy of the structure to U compounds (where possible) was used to confirm the formula of the protactinium compound.

Fig. 1. — Dry Box Assembly.


FURNACE CONTROL
ARGON ATM. BOX
FILTERED EXHAUST
VACUUM CHAMBER
AIR LOCK
HYDROGEN PURIFIER
MANUAL HEATER CONTROL
REACTOR FURNACE

RESULTS

Optical and X-ray Properties of $MPaF_6$ Compounds. — Optical examination shows that $RbPaF_6$ and $RbUF_6$ both give biaxial optic figures showing that they are of orthorhombic or lower symmetry. Single crystal X-ray examination shows that these compounds are pseudo-hexagonal but apparently monoclinic. There are a set of six compounds, $KPaF_6$, NH_4PaF_6, $RbPaF_6$, KUF_6, NH_4UF_6, and $RbUF_6$ which have very closely related structures. Further work is in progress and will be reported. Optical data on the uranium compounds has been completed and is given below as a guide to what the Pa compounds may be expected to be.

Table I

Optical Properties of Crystalline MUF_6 Compounds

($M = K$, Rb, Cs, NH_4)

KUF_6

Light yellow-green chunky prisms or pseudo-hexagonal plates; parallel extinction.

Biaxial, positive

$n_x = 1.480$, $n_y \cong 1.483$, $n_z = 1.524$
2 V $\simeq$ 25° (Average of 30° calc and 20° visual estimate.)

Low dispersion

Small value of $n_y - n_x$ contributes to pseudo-hexagonal character of these biaxial fluoride complexes.

$RbUF_6$

Pale yellow-green laths or thick plates; parallel extinction. Internal striations and/or twinning parallel needle axis.

Biaxial, positive

$n_x = 1.481$, $n_y \cong 1.483$, $n_z = 1.518$
2 V $\cong$ 25°

Table I (Contd.)

$CsUF_6$

$\underline{a}_o = 5.417 \pm .004$ Å, $\alpha = 95°45'$; Rhombohedral $KOsF_6$ Structure Type.

Pale blue rhombs, rhombohedral cleavage, 45° extinction in thin rhombic plates. Polysynthetic twinning and striations parallel to rhomb edges evident.

Uniaxial, positive

$n_o = 1.468$, $n_\epsilon = 1.511$; birefringence = 0.043

NH_4UF_6

Yellow-green chunky prisms; parallel extinction but no striations or twinning was observed. Pseudo-hexagonal symmetry appeared, but not as evident as for KUF_6 and $RbUF_6$.

Biaxial, positive

$n_x = 1.488$, $n_y \cong 1.490$, $n_z = 1.520$

$2V \cong 60°$ (visual estimate)

$2V \cong 30°$ (calc. from approx. n_y)

Table II

X-ray Properties of $RbPaF_6$ and $RbUF_6$

$RbPaF_6$		$RbUF_6$	
d, Å	I/I_o	d, Å	I/I_o*
6.00	S	5.96	66
5.85	S	5.78	14
4.18	VS	4.15	97
4.02	M	4.01	40
3.66	W	3.64	12
3.46	W	3.40	9
3.33	VS	3.31	100
3.00	M	2.97	19
2.91	M	2.89	13
2.67	MW	2.64	9
2.63	W	2.61	3
2.39	VW	2.38	6
2.23	S	2.21	37
2.20	S	2.18	18
2.09	M	2.07	14
2.01	M	2.00	24
1.90	M	1.89	11
1.86	M	1.87	11
1.81	M	1.81	28
1.79	W	1.79	8

* Peak height from diffractometer scan normalized to 100.

Discussion

Single crystal studies of these 1:1 $MPaF_6$ compounds will be reported at the Conference. The $MPaF_6$ compounds are isostructural with the MUF_6 compounds when M = K, NH_4 and Rb. They have lower symmetry than the corresponding $MTaF_6$ compounds. The compounds of the class M_2PaF_7 where M = K, NH_4 and Rb are not isostructural with either M_2UF_7 or M_2TaF_7. The rubidium compound, Rb_3PaF_8, is again isostructural with the corresponding uranium compound, Rb_3UF_8. X-ray properties of the above will be available at the Conference.

References

1. This work was performed under the auspices of the U. S. Atomic Energy Commission.
2. R. D. W. Kemmitt, D. R. Russell, D. W. A. Sharp, J. Chem. Soc. 1963, 4408 (1963); B. Cox, ibid. 1956, 876 (1956).
3. L. B. Asprey and R. A. Penneman, Science 145, 924 (1964).
4. R. A. Penneman, G. D. Sturgeon, L. B. Asprey, Inorg. Chem. 3, 126 (1964).
5. L. B. Asprey and R. A. Penneman, Inorg. Chem. 3, 727 (1964).
6. George D. Sturgeon, R. A. Penneman, F. H. Kruse, and L. B. Asprey, "Synthesis of Alkali Uranium(V) Fluoride Complexes in Anhydrous Hydrofluoric Acid", Inorg. Chem. - In Press.