Protactinium Fluorides, the New Class, $MPaF_6$

Abstract. *Complex fluorides of protactinium having a Pa/M ratio of one (where M = K, Rb, or NH_4) have been prepared from concentrated solutions of HF. These $MPaF_6$ compounds are isostructural with the corresponding compounds of pentavalent uranium but not with the tantalum analogs. The size of protactinium (V) is but slightly larger than that of uranium (V).*

We report here the synthesis and characterization of three representatives of a new class of double salts of protactinium. The compounds are of the type $MPaF_6$ (where M is rubidium, potassium, or ammonium). This is the first evidence for the existence of the PaF_6^- ion in the solid state. These salts are isostructural with the MUF_6 complex fluorides of pentavalent uranium reported by us (*1*) but do not have the same structure as the corresponding tantalum compounds (*2*). Heretofore, only one complex fluoride of Pa(V) had been prepared, the dipotassium protactinium (V) heptafluoride, K_2PaF_7, used by A. V. Grosse (*3*) in atomic weight determination some 30 years ago and recently reexamined (*4*).

Table 1. X-ray powder-diffraction data for $MPaF_6$ and MUF_6 compounds. Abbreviations: *d*, interplanar spacing (angstroms); *I*, intensity; VS, S, M, and W represent very strong, strong, medium, and weak; Br represents broad.

$MPaF_6$ compounds		MUF_6 compounds	
d	*I*	*d*	*I*
$KPaF_6$		*KUF_6*	
5.69	VS Br	5.63	100 Br
4.02	VS	4.01	100
3.27	S	3.27	70
2.84	W	2.83	35
2.17	M	2.15	35
2.14		2.13	35
2.02	W	2.00	35
NH_4PaF_6		*NH_4UF_6*	
5.92	VS Br	5.81	100 Br
4.19	S	4.13	80
4.00	W	3.99	30
3.33	S	3.30	80
2.90	M	2.88	50
2.22	M Br	2.20	70 Br
2.20			
2.10	W	2.07	30
2.00	W	2.00	35
$RbPaF_6$		*$RbUF_6$*	
5.92	M Br	5.82	50 Br
4.17	VS	4.12	100
3.32	S	3.31	90
2.22	MS	2.20	50
2.20	MS	2.18	50
2.09	M	2.07	40
2.01	W	2.00	30

The $MPaF_6$ compounds were crystallized from concentrated solutions of HF. The starting material was Pa_2O_5 which was ignited at 900°C to constant weight. A weighed amount (10 to 20 mg) of the oxide dissolved completely in an excess of concentrated, 48 percent HF in a platinum evaporating dish. To this solution was added a stoichiometric amount of either rubidium, potassium, or ammonium fluoride. Upon slow evaporation, relatively large, colorless crystals precipitated from the mother liquor. Further evaporation to dryness gave little or no additional residue. The dried crystals were scraped from the platinum; a small portion was reserved for single crystal analysis (*5*) and the remainder was finely ground to a powder for x-ray diffraction studies.

Some of the results of the x-ray diffraction studies are summarized in Table 1. A comparison of the characteristic lines shows clearly that the rubidium, potassium, and ammonium protactinium salts are isostructural with the corresponding MUF_6 salts and that Pa(V) is just slightly larger than U(V).

In our previous studies of uranium, the compounds were prepared both from HF solution and by the direct anhydrous reaction, $UF_5 + MF = MUF_6$. X-ray and chemical analyses of large samples showed that both methods gave anhydrous compounds of the type MUF_6. The fact that for the preparation of the new protactinium compounds a mole ratio M/Pa of one was used, plus the fact that the compounds are isostructural with the analogous U(V) compounds is taken as sufficient evidence that the formula of these double salts of protactinium is, indeed, $MPaF_6$.

L. B. Asprey
R. A. Penneman
*Los Alamos Scientific Laboratory,**
University of California,
Los Alamos, New Mexico

References and Notes

1. R. A. Penneman, G. D. Sturgeon, L. B. Asprey, *Inorg. Chem.* **3**, 126 (1964).
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. A. V. Grosse, *Proc. Roy. Soc. London Ser. A* **150**, 363 (1935); *J. Am. Chem. Soc.* **56**, 2501 (1934).
4. J. Flegenheimer, thesis, Cambridge University (1959), reported by D. Brown and A. G. Maddock, *Quart. Rev.* **17**, 289 (1963).
5. F. H. Kruse, in preparation.

* Sponsored by the AEC.

17 April 1964

Particle Accretion Rates: Variation with Latitude

Abstract. *Reported accretion rates for cosmic spherules ranging in diameter from 1 to 400 μ appear to increase with increasing latitude. The apparent variation is most closely related to geomagnetic latitude. Preliminary calculations suggest that electromagnetic interactions could cause only charged particles less than about 10^{-2} μ in diameter to impinge preferentially at high latitudes.*

Microscopic particles similar to those described by Murray (*1*) and presumed to be of cosmic origin have been collected at several places on or near the earth's surface. Estimates of the rate of accretion of particles by the earth (Table 1) were an important result of these investigations. The observed variation in estimated accretion rates has been attributed to differences in sampling methods, and might be thought to be entirely random. Consequently, most workers have assumed that particles are deposited on the earth at a uniform, but as yet imperfectly known rate. It was unexpected, therefore, that data compiled during a recent literature survey (*2*) suggested that accretion rates for metallic spherules increase with increasing latitude of the collecting site.

Criteria for selecting the accretion rates shown in Table 1 were as follows. (i) The estimate was derived from a surface-based collection. (ii) The estimate represents sampling sites located within a narrow latitude range. (iii) The particle sample was not contaminated by material of terrestrial origin. The last point requires further comment. It was the judgment of each investigator that because his particles appeared similar to meteoritic materials and because sources of terrestrial contamination were, in most cases, absent from the vicinity of sampling sites, an extraterrestrial origin for the particles was likely. In our opinion, most of the accretion rate estimates satisfy these criteria. However, the estimates greater than 10^6 metric tons per year are apparent exceptions which may reflect the influence of terrestrial contamination. These values (*3, 4*) were not included in our calculations because they were derived from collections made in urbanized areas where the possibilities for industrial contamination were greatly enhanced. The remaining estimates