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.

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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 listed in Table 1 were considered to have been obtained from essentially uncontaminated collections and were assumed to be representative of the mean annual rate of accretion for metallic spherules at the collecting sites.

Particles of the same general size range (5 to about 200 μ, with a few particles up to 400 μ in diameter) were examined in all but three collections (*5–7*), in which the more limited size range from 3 to 35μ was considered. (Table 1). Accretion rates for the studies in the limited size range would be greater if larger particles were encountered, but the increase would probably not be appreciable as most mass is contributed by the large numbers of small particles.

The integrated, mean annual accretion rate for metallic spherules is about 7×10^4 metric tons. This suggests that metallic spherules represent about 10 percent of the total particle influx (*8*), a proportion consistent with the abundances of macroscopic metallic meteorites (*9*) and which may have significance with respect to particle origin.

The variation of estimated accretion rates with geographic latitude is shown in Fig. 1*A*. Generally, accretion rates are greater for sampling sites located at higher latitudes. The scatter evident in Fig. 1*A* may be reduced by plotting the rates as a function of geomagnetic latitude (Fig. 1*B*). Accordingly, we examined the interaction between a charged particle and the earth's geomagnetic field in an attempt to provide a theoretical basis for the latitude variation. The hypothesis that microscopic extraterrestrial particles carry an electric charge, and therefore would be affected by the earth's magnetic field, was discussed by Singer (*10*), who considered the net charge on a particle to be the result of photoionization and accretion of electrons from the interplanetary gas.

We assumed in our calculations that particles acquire their net charge through minimization of potential energy (*11*); this implies that electron accretion is the more important charging process. Störmer's theory (*12*) shows that a charged, microscopic particle could impinge upon the earth preferentially at high latitudes provided its magnetic rigidity, $H\rho$ (*13*) is $\leq 3.2 \times 10^7$ g cm sec^{-1} emu^{-1}. On the assumption that the particle velocity with respect to the earth is 3×10^6 cm sec^{-1}, H_ρ was computed for metallic spherules

Table 1. Estimates of annual deposit of metallic spherules upon the earth's surface.

Diameter range (μ)	Source	Geographic latitude	Geomagnetic latitude	Accretion rate, (metric ton yr^{-1})	Reference
10–230	Pacific sediments	7°S	10°S	1.25×10^2	(*17*)
10–230	*			1.7×10^2	(*18*)
30–250	Pacific sediments	15°N	20°N	2.4×10^3 to 5×10^3	(*19*)
30–250	Mediterranean sediments	34°N	34°N	3.3×10^3	(*20*)
†	Air	55°N	50°N	1.6×10^4	(*21*)
3–30	Air	34°N	44°N	3×10^4 to 3×10^5	(*5*)
10–384	Air	52°N	55°N	3×10^4	(*22*)
5–35	Sediments	44°N	45°N	3×10^4 to 1.5×10^5	(*6*)
5–60‡	Air	44°N	44°N	$>15\mu$; 5×10^4 total 1.6×10^5	(*23*)
1–120	Air	35°N	40°N	4×10^4 to 1.3×10^5	(*24*)
10–170	Antarctic snow	74°S	64°S	4×10^4 2.4×10^5 1.2×10^5 av.	(*25*)
20–180	Antarctic snow	82°S	75°S	1.84×10^5	(*26*)
>3	Air	38°–48°N	50°N	2×10^5	(*27*)
3–15	Air	34°N 65°N 75°N	45°N 65°N 83°N	5×10^5	(*7*)
5–160	Greenland snow	82°N	87°N	9.1×10^5	(*28*)
†	Air	40°N	35°N	3.1×10^6	(*3*)
†	Air	45°N	50°N	2.4×10^9	(*4*)

* Re-evaluation of data of Laevastu and Mellis with particle density of 7 g cm^{-3}. † Not reported. ‡ Total size range.

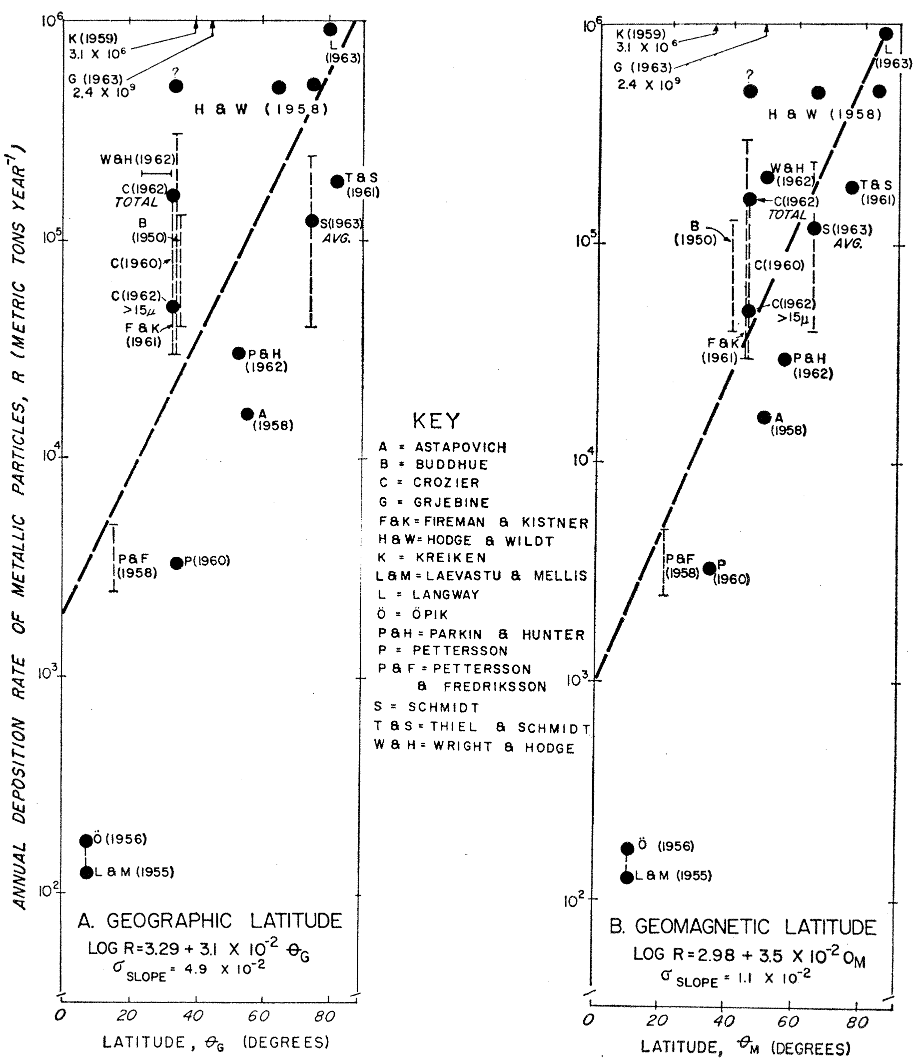

Fig. 1. Annual particle accretion rate for metallic spherules as a function of geographic latitude (*A*) and geomagnetic latitude (*B*). The standard deviation of the slope is substantially less when geomagnetic coordinates are employed.

of different sizes (Table 2). These calculations suggest that only particles on the order of the smallest found to date, 10^{-2} μ (*14*), could interact with the geomagnetic field to produce a latitude dependent accretion rate.

If particles greater than 10^{-2} μ in diameter are to impinge upon the earth preferentially at high latitudes through such an interaction, either the particle charge must be greater than we have considered, the velocity less, or both. For purposes of illustration, let us consider a metallic spherule 60 μ in diameter. If the ultimate tensile strength is assumed to be the only factor which limits particle charge, the maximum charge for such a spherule is three orders of magnitude greater than that acquired through minimization of potential energy. It is doubtful, however, that such a high charge could be retained. If particle velocity were $\leq 10^3$ cm sec^{-1}, such a highly charged spherule could be preferentially deposited at a high latitude. Recent indications are that small particles move approximately at escape velocity (*15*), and that slightly lower velocities may characterize particles in orbit about the earth (*16*). However, present knowledge of the processes by which particles are charged in space and of their velocities suggests that the conditions of this illustration are unlikely to be fulfilled. We conclude from these elementary calculations that a simple electromagnetic interaction does not contribute appreciably to the latitude variation in accretion rates as suggested by the data.

In an attempt to explain the apparent variation of particle accretion rates with latitude, it would be useful to conduct new particle collections at a series of surface-based stations along a line of longitude. As the proposed meridian should be determined by the availability of observation sites in contamination-free areas, we recommend consideration of that part of the Pacific Ocean between 150°W and 160°E. There, a sufficient number of islands could be occupied, which, together with drift stations in the Arctic and bases in the Antarctic, could form an adequate network for further observing the latitudinal dependence of particle accretion.

Table 2. Magnetic rigidity of metallic spherules.

Particle diameter (μ)	Magnetic rigidity, $H\rho$ (g cm sec^{-1} emu^{-1})
1	3.0×10^{11}
1	3.9×10^{10}
10^{-2}	3.0×10^{7}
10^{-2}	3.9×10^{6}

RICHARD A. SCHMIDT*
THEODORE J. COHEN
Geophysical and Polar Research Center, University of Wisconsin, Madison

References and Notes

1. J. Murray, *Proc. Roy. Soc. Edinburgh* **12**, 474 (1883).
2. R. A. Schmidt, *Univ. Wisconsin Geophysical and Polar Research Center Research Report 63-2* (1963).
3. E. A. Kreiken, *Planetary Space Sci.* **2**, No. 1, 39 (1959).
4. T. Grjebine, *Compt. Rend.* **256**, 3735 (1963).
5. E. L. Fireman and G. A. Kistner, *Geochim. Cosmochim. Acta* **24**, 10 (1961).
6. W. D. Crozier, *J. Geophys. Res.* **65**, 2971 (1960).
7. P. W. Hodge and R. Wildt, *Geochim. Cosmochim. Acta* **14**, 126 (1958).
8. M. Dubin, *National Aeoronautics and Space Administration Tech. Note D-1839* (Oct. 1963); C. W. McCracken and W. M. Alexander, in *Smithsonian Contrib. Astrophys.* **7**, 71 (1962); C. de Jager, *Mem. Soc. Roy. Sci. Liège 4 Ser.* **15**, 174 (1955).
9. E. L. Krinov, *Principles of Meteoritics* (Pergamon, New York, 1960).
10. S. F. Singer, in *Scientific Uses of Earth Satellites*, J. A. Van Allen, Ed. (Univ. of Michigan Press, Ann Arbor, ed. 2, 1958), p. 301; *Trans. Am. Geophys. Union* **44**, 29 (1963), abstract.
11. M. L. Coffman, *J. Geophys. Res.* **68**, 1955 (1963).
12. C. Störmer, *The Polar Aurora* (Oxford Univ. Press, London, 1955).
13. The magnetic rigidity $H\rho$ of a particle is given by: $H\rho = mv/Ze$, where m, Ze, and v are the mass, charge, and velocity of the particle, respectively.
14. G. L. Hemenway, E. F. Fullam, L. Phillips, *Nature* **190**, 868 (1961).
15. M. Dubin, *Space Research* **1**, 1042 (1960); S. H. Dole, *Planetary Space Sci.* **9**, 541, (1962).
16. G. S. Hawkins, *Harvard College Observatory Radio Meteor Project Research Report No. 3* (Aug. 1963).
17. T. Laevastu and O. Mellis, *Trans. Am. Geophys. Union* **36**, 385 (1955).
18. E. J. Öpik, *Irish Astron. J.* **32**, 143 (1962).
19. H. Pettersson and K. Fredriksson, *Pacific Sci.* **12**, 71 (1958).
20. H. Pettersson, *Sci. Am.* **202**, 123 (1960).
21. I. S. Astapovich, in *Meteoric Phenomena in the Earth's Atmosphere* (State Publishing House of Physics and Mathematical Literature, Moscow, 1958).
22. D. W. Parkin and W. Hunter, *Advan. Astron. Astrophys.* **1**, 105 (1962).
23. W. D. Crozier, *J. Geophys. Res.* **67**, 2543 (1960).
24. J. D. Buddhue, *University of New Mexico Publications in Meteorites Report No. 2* (1950).
25. R. A. Schmidt, *University of Wisconsin Geophysical and Polar Research Center Report No. 63-3* (1963).
26. E. Thiel and R. A. Schmidt, *J. Geophys. Res.* **66**, 307 (1961).
27. F. W. Wright and P. W. Hodge, *Nature* **195**, 269 (1962).
28. C. C. Langway, Jr., *Intern. Assoc. Sci. Hydrology Publ. 61* (1963), pp. 189–198.
29. We thank Dr. C. R. Bentley, Dr. R. P. Meyer, and Dr. J. C. Rose at the Geophysical and Polar Research Center of the University of Wisconsin for valuable discussions. Supported by a grant from NSF. Contribution No. 123 of the Geophysical and Polar Research Center.
* Present address: NAS Research Associates, Ames Research Center, Moffett Field, Calif.

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Vitamin K Induced Prothrombin Formation: Antagonism by Actinomycin D

Abstract. *Actinomycin D inhibits vitamin K induced formation of prothrombin in chicks deficient in vitamin K. The administration of actinomycin in doses which inhibit prothrombin formation also inhibits synthesis in the liver of RNA from adenosine triphosphate as detected with adenine-8-C^{14}. The results are consistent with a genetic action of vitamin K in inducing RNA formation for the synthesis of clotting proteins.*

The molecular action of vitamin K has remained an enigma since discovery of the vitamin by Dam in 1935 (*1*), despite a large volume of research directed towards the elucidation of its function. In microorganisms, evidence has been advanced to implicate vitamin K homologs and their chromanols in electron transport and oxidative phosphorylation (*2*). Attempts to explain the antihemorrhagic activity of the K vitamins in mammals on the same basis have not been as successful, although Martius and colleagues suggested in 1954 (*3*) that the defect in prothrombin formation in vitamin K-deficient chicks could be explained on the basis of a primary disorder of energy conservation. Unfortunately for this hypothesis, the uncoupling of oxidative phosphorylation in liver mitochondria from vitamin K-deficient or dicumarol-treated rats and chicks has not been generally confirmed (*4*). Attempts to demonstrate the presence of vitamin K in the prothrombin molecule or effects of vitamin K upon clotting in vitro have likewise failed.

Since administering vitamin K to deficient animals or birds results in the prompt (2 to 6 hours) synthesis and secretion of prothrombin by the liver, vitamin K might directly influence the formation of the messenger RNA required as a template for prothrombin