

cerning the mechanistic pathway connecting R⁺ and the *endo* isomer. Presumably the classical ion is an intermediate in this step.²⁻⁵ It seems likely that the barrier for capture of the nonclassical ion is larger than that for capture of the less stable classical ion, in which case ΔE_a represents a lower limit for the energy difference of the classical and nonclassical ions.

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Alkali Fluoride Complexes of Tetravalent Protactinium

Sir:

We wish to report the first preparation of alkali fluoride complexes of *tetravalent protactinium*. The compounds were prepared by two methods: (1) vacuum heating of PaF₄ with alkali fluoride, and (2) hydrogen reduction of pentavalent protactinium compounds, which was the method yielding purer preparations. Compounds of tetravalent protactinium were obtained which are isostructural with known compounds of tetravalent uranium. In fluorine, the tetravalent protactinium compounds are oxidized to the starting compounds of pentavalent protactinium, identified by their own characteristic X-ray powder patterns. This hydrogen reduction-fluorine oxidation cycle can be repeated. Although a number of fluoride complexes of *pentavalent* protactinium are known, e.g., K₂PaF₇,² MPaF₆ (M = NH₄, K, and Rb),³ and Na₃PaF₈,⁴ no fluoride complexes of *tetravalent* protactinium have been reported previously.

In our recent studies of MXF₆ compounds (X = U or Pa; M = alkali)^{3,5} it was shown that RbUF₆ and RbPaF₆ are isostructural; more recent single crystal measurements have established their structure as orthorhombic.⁶ In the review of the alkali fluoride-uranium tetrafluoride systems by Thoma,⁷ it was shown that rhombohedral compounds of the type 7MF·6UF₄ occur frequently, and a prediction of this structure for the then unknown compound 7RbF·6PaF₄ was made. Thus, X-ray powder techniques offered an excellent method of establishing both the reduction of protactinium(V) fluoride complexes to protactinium(IV) compounds and also the reverse reaction.

The chemistry of the conversion was investigated as follows. Into a depression ground in a sapphire dish was placed a few milligrams of RbF and PaF₄ in the mole ratio Rb:Pa = 7:6. Into another sapphire dish was placed crystalline RbF·PaF₅ prepared as previously described.³ Both materials were heated in a fluorine atmosphere (1-1.2 atm.) for ~2 hr. at 390°. X-Ray powder patterns established that RbF·PaF₅ was the only phase detectable in each sample. Without

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(6) L. B. Asprey, F. H. Kruse, and R. A. Penneman, manuscript in preparation.

(7) R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

removal from the sapphire dishes, they were then exposed to very pure hydrogen (made from UH₃) for 4 hr. at 450°. The X-ray powder patterns of the reduction products showed that rhombohedral 7RbF·6PaF₄ was the major phase in each case; it was isostructural with 7RbF·6UF₄. Treatment with fluorine oxidized both samples to the original orthorhombic RbPaF₆ phase. Hydrogen reduction again formed the rhombohedral protactinium(IV) compound.

Identification of the tetravalent protactinium compound was accomplished by comparison with our X-ray data⁸ for rhombohedral 7NH₄F·6UF₄ and with the 7RbF·6UF₄ data listed by Brunton, *et al.*⁹ A partial list of the indexed X-ray powder pattern data for 7RbF·6PaF₄ is given in Table I.

Table I.^a X-Ray Powder Pattern Data for 7RbF·6PaF₄

<i>hkl</i>	<i>I</i> / <i>I</i> ₀	<i>d</i> _{obsd.} , Å.	<i>d</i> _{calcd.} , Å.
101	7	8.36	8.32
110	2	7.73	7.71
021	3	5.65	5.66
012	4	4.98	4.94
211	4	4.58	4.56
300	3	4.45	4.45
202	2	4.18	4.16
220	2	3.85	3.86
122	2	3.70	3.66
221	2	3.58	3.58 ^b
003	10	3.51	3.54
131			3.50

^a Cu K α radiation, Debye-Scherrer camera, 114.6 mm., Ilford "G" film; hexagonal indices, space group R3-C_{3i}²; *a*₀ = 15.43, *c*₀ = 10.63 Å. (rhombohedral, *a*₀ = 9.587 Å., α = 107° 9').

^b This line appears in typical patterns; not indexable in R $\bar{3}$.

Further work with the remaining alkali and ammonium fluorides is in progress.

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(9) G. D. Brunton, H. Insley, T. M. McVay, and R. E. Thoma, ORNL-3761, Feb. 1965.

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σ -Overlap of p-Orbitals in Cyclic π -Electron Systems. *cis,cis,cis*-1,5,9-Cyclododecatriene

Sir:

Recently investigated^{1a-g} *cis,cis,cis*-1,4,7-cyclononatriene (I) is a cyclic six- π -electron system wherein σ -overlap of the p-orbitals could have been significant. Whether this overlap lowers the ground-state energy below that expected for the same cyclic system composed of "isolated" double bonds remains undecided in the case of I.^{1a,f,g} The important feature of this kind of system is not that the double bonds be homo-

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