SOME RECENT PREPARATIVE CHEMISTRY OF PROTACTINIUM

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I. Introduction

Protactinium, element 91, is a member of the actinide, or 5*f*, transition group [Th (90) to Lw (103) inclusive]. Previous reviews* (*51, 52, 69, 83, 92, 98, 109, 121, 124*) have dealt in detail with the discovery of the

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* New reviews have recently been published by Guillaumont *et al.* (*81a*) and Muxart *et al.* (*112a*).

element, separation and analytical procedures, solvent extraction and ion exchange behavior, and spectral properties. These topics and the preparation and radiochemical characteristics of the 14 known isotopes ($^{224}Pa \rightarrow {}^{237}Pa$ inclusive), recently reviewed in detail by Hyde (*88*), will not be discussed here.

Protactinium-231, an α-emitter, is the only isotope suitable for macrochemical studies [$t_{1/2} = 32,340$ years (*36*)] and in view of the radiochemical hazards associated with weighable amounts of this isotope, it is necessary to perform all manipulations in glove boxes or, in the case of solution chemistry, in well-ventilated fume hoods. An indication of the toxicity of protactinium-231 is given by the fact that the maximum permissible concentration in air is 10^{-8} mg/m^3 whereas that of hydrogen cyanide is 10 mg/m^3. Details of suitable handling procedures are adequately dealt with in other publications (*11*, *136*).

Prior to the recent isolation of approximately 100 gm of ^{231}Pa from uranium ore residues, the preparative chemistry of protactinium had been little investigated and few compounds were known. In fact, as recently as 1962, the only compounds which had been characterized were the pentahalides $PaCl_5$, $PaBr_5$, and PaI_5, the tetrahalides PaF_4 and $PaCl_4$, the oxides Pa_2O_5, PaO_2, PaO, and $PaO_{2.30}$ (this last later disproved), and a few miscellaneous compounds such as PaOS, PaH_3, $PaF_5 \cdot 2H_2O$, and K_2PaF_7. However, it should be noted that as long ago as 1934 von Grosse had determined the atomic weight of protactinium (*79*) using samples of the heptafluoroprotactinate(V), K_2PaF_7, obtaining the value 230.6 ± 0.5 which is in excellent agreement with the recently calculated figures, 231.05 (*77*) and 231.044 (*137*).

Progress in the preparative and structural fields of protactinium chemistry has been rapid during the past 6 years and there is now sufficient information available, particularly in the halide and oxide fields, to permit a more balanced comparison than has previously been possible with the properties of the actinide elements, on the one hand, and those of niobium and tantalum, on the other. In this connection one must, of course, bear in mind the fact that the ionic radii of protactinium in its various valence states [Pa(V), 0.90 Å and Pa(IV), 0.96 Å] are appreciably larger than those of niobium or tantalum and this itself will have a considerable influence on the chemical and crystallographic properties of the elements.

Protactinium exists naturally in the pentavalent state and although it is possible, by employing strongly reducing conditions, to obtain the tetravalent state in solution and in solid compounds this state is, in general, unstable in the presence of oxygen, exceptions being the tetrafluoride and dioxide, which are stable in the atmosphere. The potential of the couple Pa(V) → Pa(IV) + e^- has been estimated at 0.1 volt by Fried and Hindman (*74*) and, more recently (*86*), as 0.25 volt in 6 *M* hydrochloric acid. To date the only evidence for the existence of trivalent protactinium is the recent report that thermal decomposition of protactinium pentaiodide leads to the formation of a black solid, believed to be PaI_3, which is isostructural with cerium triiodide (*123*).

II. Metallic Protactinium

The preparation of the metal was first reported by von Grosse (*80*) who obtained it by bombarding protactinium pentoxide with 35 keV electrons in a high vacuum and by decomposing the pentachloride on a hot wire. No properties were reported for these products and more recently the pure metal has been obtained by reduction of protactinium tetrafluoride with lithium (*73*) or barium (*65*, *125*) vapor at 1300°–1400°C using the double crucible technique and on a larger scale by reduction with barium (*106*) or 10% magnesium in zinc alloy (*107*).

Protactinium metal possesses tetragonal symmetry (*65*, *106*), $a_0 = 3.929$, $c_0 = 3.241$ Å and each protactinium atom has ten nearest neighbors (8 at 3.212 Å and 2 at 3.238 Å) in a structural arrangement which is quite different from those found for other actinide metals; the calculated density is 15.37 gm/cm^3. There is some evidence for the existence of other crystalline forms (*65*, *106*), but none have been identified with certainty. The melting point, 1560° ± 20°C (*65*) or 1575° ± 20°C (*106*), lies between those of thorium (1750°) and uranium (1132°). The molar magnetic susceptibility (*65*) of protactinium metal, $\chi_m = 286 \pm 14 \times 10^6$ c.g.s. units, is virtually independent of temperature between 20° and 298°K. The metal is reported (*73*) to be superconducting below 1.4°K. Freshly prepared, clean samples are silvery in appearance, but a dark oxide film (PaO and PaO_2) forms rapidly on exposure to air, further oxidation occurring only slowly. Few chemical properties have been recorded but it is known to react with hydrogen at 250°–300°C to form the hydride PaH_3 (*125*) and with iodine vapor at 400°C *in vacuo* to yield the pentaiodide (*40*). Undoubtedly similar reactions with other halogens will yield the appropriate pentahalide.

III. Halides and Oxyhalides

During the past few years numerous new penta- and tetravalent protactinium halides and oxyhalides have been characterized, but of the possible trivalent compounds only PaI_3 has been reported. The presently known halides and oxyhalides are compared with those of the other actinide elements in Tables I and II, respectively. It is immediately

TABLE I

ACTINIDE HALIDES

Halide	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
Fluorides	AcF_3	—	—	UF_3	NpF_3	PuF_3	AmF_3	CmF_3	BkF_3	—	—	—	—	—	—
		ThF_4	PaF_4	UF_4	NpF_4	PuF_4	AmF_4	CmF_4							
			—	U_4F_{17}	—	Pu_4F_{17}									
			Pa_2F_9	U_2F_9	—	—									
			PaF_5	UF_5	—	—									
				UF_6	NpF_6	PuF_6									
Chlorides	$AcCl_3$	—	—	UCl_3	$NpCl_3$	$PuCl_3$	$AmCl_3$	$CmCl_3$	$BkCl_3$	$CfCl_3$	$EsCl_3$	—	—	—	—
		$ThCl_4$	$PaCl_4$	UCl_4	$NpCl_4$										
			$PaCl_5$	UCl_5											
				UCl_6											
Bromides	$AcBr_3$	—	—	UBr_3	$NpBr_3$	$PuBr_3$	$AmBr_3$	$CmBr_3$	$BkBr_3$	—	—	—	—	—	—
		$ThBr_4$	$PaBr_4$	UBr_4	$NpBr_4$										
			$PaBr_5$	UBr_5											
Iodides		ThI_2													
	AcI_3	ThI_3	PaI_3	UI_3	NpI_3	PuI_3	AmI_3	CmI_3	BkI_3	—	—	—	—	—	—
		ThI_4	PaI_4	UI_4											
			PaI_5												

TABLE II

ACTINIDE OXYHALIDES

Halide	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
Fluorides	AcOF	ThOF	—	—	—	PuOF	—	—	—	—	—
		$ThOF_2$	—	—	—	—					
			Pa_2OF_8	U_2OF_8	—	—					
			—	—	$NpOF_3$	—					
				UO_2F_2	NpO_2F_2	PuO_2F_2	AmO_2F_2				
Chlorides	AcOCl	—	—	UOCl	—	PuOCl	AmOCl	—	—	CfOCl	EsOCl
		$ThOCl_2$	$PaOCl_2$	$UOCl_2$	$NpOCl_2$						
			Pa_2OCl_8	—							
			$Pa_2O_3Cl_4$	$UOCl_3$							
			PaO_2Cl	UO_2Cl							
				UO_2Cl_2							
Bromides	AcOBr	—	—	—	—	PuOBr	—	—	BkOBr	—	—
		$ThOBr_2$	$PaOBr_2$	$UOBr_2$	$NpOBr_2$						
			$PaOBr_3$	$UOBr_3$							
			PaO_2Br	UO_2Br							
				UO_2Br_2							
Iodides	AcOI	—	—	—	—	PuOI	—	—	BkOI	—	—
		$ThOI_2$	$PaOI_2$	—	—						
			$PaOI_3$								
			PaO_2I								
				$[UO_2I_2]$[a]							

[a] Existence not proven.

apparent that there is scope for further research aimed at the preparation of both protactinium(V) and uranium(V) oxyfluorides and uranium(V) and neptunium(V) oxychlorides. In addition, it would be interesting to have information on the PaX_4–Pa (X = F, Cl, Br, and I) systems to permit a comparison with the results recently reported for analogous thorium systems (*62*, *122*) and, in particular, to see whether the trihalides, should they form, are isostructural with the ionic actinide trihalides or whether, like ThI_2 (*122*), they are "metallic." No magnetic properties, vapor pressure data,* or experimental heats of formation have yet been recorded for the protactinium halides, but crystallographic studies have established that protactinium exhibits coordination numbers of 6, 7, 8, and 9 in various halides and oxyhalides. The binary halides are all volatile at moderate temperatures in a vacuum, a property which can be employed for the preparation of radiochemically pure protactinium-231.

A. FLUORIDES

The only fluorides known at present are PaF_5, Pa_2OF_8, Pa_2F_9 (or Pa_4F_{17}), and PaF_4.

Protactinium pentafluoride, which is isostructural with β-UF_5 (Table III), is best prepared (*130*) by fluorination of the tetrafluoride at 700°C (Fig. 1). It has been obtained in an amorphous state (*38*) by hydrofluorination of the pentachloride at 200°C and, contaminated with

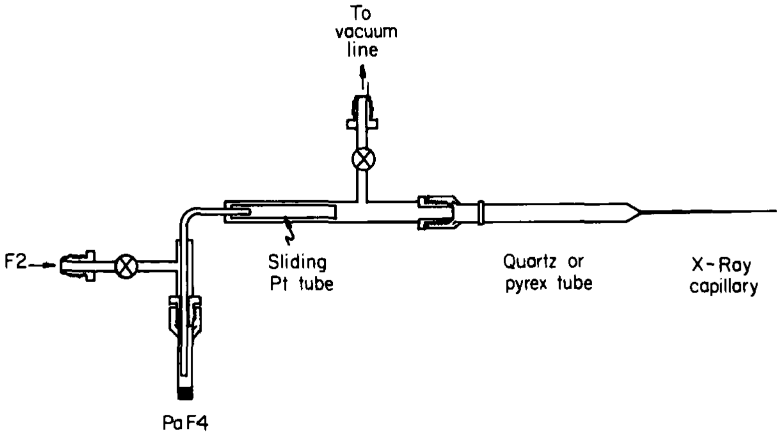

FIG. 1. Apparatus for the fluorination of PaF_4 (*130*).

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* For more recent information, see Appendix.

TABLE III

CRYSTALLOGRAPHIC DATA FOR THE PROTACTINIUM HALIDES

Compound	Symmetry[a]	Structure type or space group	Lattice parameters				Ref.
			a_0	b_0	c_0 (Å)	$\beta°$	
PaF_5	T	β-UF_5	11.53	—	5.19	—	(*131*)
$PaCl_5$	M	*C*2/*c* or *Cc*	8.00	11.42	8.43	106.38	(*47*)
α-$PaBr_5$	M	*P*2₁/*c*	12.69	12.82	9.92	108	(*54*)
β-$PaBr_5$	M	*P*2₁/*n*	8.385	11.205	8.950	91.1	(*53*, *54*)
PaI_5	O	—	7.22	21.20	6.85	—	(*104*)
Pa_2F_9	BCC	U_2F_9	8.494	—	—	—	(*38*)
PaF_4	M	UF_4	12.86	10.88	8.54	126.34	(*4*)
$PaCl_4$	T	UCl_4	8.377	—	7.479	—	(*44*)
$PaBr_4$	T	UCl_4	8.824	—	7.957	—	(*44*)
Pa_2OF_8	BCC	U_2F_9	8.406	—	—	—	(*131*)
$PaOBr_3$	M	*C*2	16.911	3.871	9.334	113.67	(*53*, *54*)
PaO_2I	H	—	12.64	—	4.07	—	(*40*)
$PaOCl_2$	O	*Pbam*	15.332	17.903	4.078	—	(*17*)
PaI_3	O	CeI_3	4.33	14.00	10.02	—	(*123*)

[a] T, tetragonal; M, monoclinic; O, orthorhombic; BCC, body centered cubic; H, hexagonal.

Pa_2OF_8 (*5*) or Pa_2F_9 (*38*), by the thermal decomposition of ammonium hexafluoroprotactinate(V), NH_4PaF_6. Attempts to obtain it by removing the water from the dihydrate, $PaF_5 \cdot 2H_2O$, have led to the formation of Pa_2OF_8 even in the presence of gaseous hydrogen fluoride at 160°C (*38*). Protactinium pentafluoride is a white, deliquescent solid which dissolves readily in aqueous media and which is appreciably less volatile than VF_5, NbF_5, and TaF_5, subliming only above 500°C *in vacuo*.

Diprotactinium(V) oxyoctafluoride, Pa_2OF_8, is easily prepared by a variety of methods which include, for example, fluorination of PaF_4 in the presence of oxygen at 600°C, treatment of the vacuum-dried pentavalent hydroxide with hydrogen fluoride at 160°C, and the reaction between the pentoxide and a mixture of hydrogen fluoride and oxygen at 500°C (*38*, *130*). In addition, vacuum evaporation of dilute hydrofluoric acid solutions containing protactinium(V) initially yields a mixture of $PaF_5 \cdot 2H_2O$, $PaF_5 \cdot H_2O$, and Pa_2OF_8, of which the first two are converted to Pa_2OF_8 on prolonged pumping at room temperature (*38*). It is a white, deliquescent solid which disproportionates at about 800°C in a vacuum to yield a sublimate of PaF_5 and to leave a residue of an, as yet, unidentified solid, (*130*) which is possibly a new oxyfluoride (cf. the disproportionation of the other oxyhalides discussed later in Sections III B, C, and D).

Like Pa_2F_9, diprotactinium(V) oxyoctafluoride is isostructural with U_2F_9 (Table III). Protactinium–oxygen stretching vibrations appear around 740 cm^{-1} in its infrared spectrum (*131*), suggesting the presence of Pa–O–Pa groups similar to those in $NbOCl_3$. In contrast, all protactinium–oxygen stretching vibrations for other known oxyhalides (Table IV) occur below 624 cm^{-1} and structural details for $PaOBr_3$ (*53*) and $PaOCl_2$ (*126*) have shown that in each case the coordination number of the oxygen atoms is greater than two. This appears to be a characteristic of protactinium oxycompounds and, in contrast to the many examples known for niobium(V), tantalum(V), and neptunium(V), no compounds* containing discrete PaO^{3+} or PaO_2^{+} groups have yet been reported.

Protactinium tetrafluoride, a dark brown solid, is most conveniently obtained by heating the pentoxide in a mixture of hydrogen and hydrogen fluoride at 500°–600°C (*38*, *130*). In order to prevent the formation of Pa_2F_9 (or Pa_4F_{17}), which can only be reduced at higher temperatures, it is essential to use a large excess of hydrogen (*38*). It is also advisable to use low-fired (~450°C) pentoxide to ensure complete hydrofluorination. The reaction between hydrogen fluoride and protactinium dioxide also produces PaF_4 (*125*), and undoubtedly some of the many reactions

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* For more recent information, see Appendix.

TABLE IV

INFRARED DATA FOR THE PROTACTINIUM OXYHALIDES

Compound	Color	ν(Pa–O)[a]	ν(Pa–X)[b]	Ref.
Pa_2OF_8	White	790sh, 740m, 690sh	450sbr	(*132*)
Pa_2OCl_8	White	500m, 460s	326m, 370s	(*47*)
$Pa_2O_3Cl_4$	White	540sbr, 426sh	342w, 378w	(*47*)
PaO_2Cl	White	624sh, 520sbr	396m	(*47*)
$PaOBr_3$	Green	515m, 476w, 364s, 303w	—	(*40*)
PaO_2Br	White	575m, 386s, 286w	—	(*40*)
$PaOI_3$	Brown	480m, 339s, 276w	—	(*40*)
PaO_2I	Brown	555m, 469vw, 386s, 281w	—	(*40*)
$PaOCl_2$	Green	555sh, 523s, 471s, 327s, 256sh, 243m	290w, 278w	(*17*)
$PaOBr_2$	Orange	546sh, 518s, 495s, 446s, 319s, 259m, 240vw	—	(*17*)
$PaOI_2$	Burgundy	459m, 434m, 303sbr	—	(*17*)

[a] s, strong; m, medium; w, weak; sh, shoulder; br, broad.

[b] X, halogen.

used for the preparation of thorium or uranium tetrafluoride (*30*) would be suitable provided a reducing atmosphere is maintained, but in view of the easy conversion of Pa_2O_5 these are likely to be of minor importance.

Protactinium tetrafluoride, like the other actinide tetrafluorides, possesses the 8-coordinate UF_4-type of structure (Table III) but no bond distances are available. It is easily the most stable tetravalent halide of protactinium and can be handled in the atmosphere, at least for a limited period, without hydrolysis or oxidation occurring. As mentioned earlier it is the usual starting material for the preparation of protactinium metal. Tetrafluoride hydrates have not been fully characterized, but a mixed fluorosulfate, $PaF_2SO_4 \cdot 2H_2O$ can be precipitated from aqueous solution (*131*). Protactinium tetrafluoride is soluble in aqueous ammonium fluoride solutions, for which some spectral properties have been recorded (*4*, *83*).

Protactinium(IV) oxydifluoride, $PaOF_2$, is the only tetravalent protactinium oxydihalide not yet characterized. This seems to be due solely to a lack of investigation since there are no negative reports concerning the most likely routes involving interaction of the tetrafluoride and either protactinium dioxide or antimony sesquioxide, both of which methods have been employed for the preparation of the other tetravalent oxydihalides.

A black solid observed to form during the hydrofluorination of protactinium pentoxide using 1:2 hydrogen:hydrogen fluoride mixtures, and as one of the thermal decomposition products of $(NH_4)_2PaF_7$, has variously been referred to as Pa_2F_9 (*38*) and Pa_4F_{17} (*131*). Although analysis indicates the latter composition, the compound is isostructural with U_2F_9 (Table III). Further work, possibly involving interaction of PaF_4 and PaF_5 together with a determination of the average valence state of the solid, is necessary to clarify the present situation.

B. CHLORIDES

Protactinium pentachloride was first prepared by von Grosse (*80*) who reacted the pentoxide with carbonyl chloride at 550°C. Conversion of the pentoxide has also been achieved by heating it in a nitrogen gas flow saturated with either carbon tetrachloride or a chlorine–carbon tetrachloride mixture (*47*, *57*, *63*, *71*, *72*, *123*) and by mixing it with carbon and heating in a chlorine flow (*63*). This type of reaction, however, involves rather complicated apparatus, requires rigorously dried nitrogen, and usually results in low yields. In addition, serious loss of protactinium pentachloride as a noncondensable smoke has been observed (*47*). Nevertheless, chlorination of the oxide in gas-flow systems has been employed to separate ^{233}Pa from irradiated thoria (*106*) and to purify macroquantities of ^{231}Pa by sublimation of the resulting pentahalide (*63*).

The most satisfactory method, which can also be used to prepare gram quantities, is to heat the vacuum-dried hydrous oxide in a sealed, evacuated Pyrex reaction vessel with thionyl chloride vapor at 350°–500°C, the volatile, yellow pentachloride (m.p. 306°C) being obtained in better than 95% yield (*47*). Thermal decomposition of $SO(PaCl_6)_2$ is less satisfactory (*15*) and only gives a partial yield of the pentachloride, leaving an unidentified black residue.

An alternative, reasonably satisfactory route to the pentachloride involves heating Pa_2O_5/C mixtures at 500°–600°C in a sealed tube containing carbon tetrachloride saturated with chlorine (*47*). It was this method of preparation which led to the characterization of the first pentavalent oxychloride, Pa_2OCl_8, the α-form of which is always produced together with the pentachloride under such conditions. The pentachloride is readily separated from Pa_2OCl_8 by vacuum sublimation at 180°–200°C.

Protactinium pentachloride possesses monoclinic symmetry (Table III), but is not isostructural with either niobium (*138*) or uranium pentachloride (*127*). The structure (*67*) comprises infinite chains of nonregular pentagonal bipyramidal $PaCl_7$ groups which share pentagon edges (Fig. 2a). Each protactinium is 7-coordinate with Pa–Cl bond lengths ranging from 2.43 to 2.46 Å for nonbridging chlorine atoms and from 2.70 to 2.76 Å for bridging chlorine atoms (Fig. 2b). Protactinium–chlorine stretching vibrations occur at 323 and 362 cm^{-1} in the infrared spectrum of the pentachloride (*47*).

Unlike uranium pentachloride, which is thermally unstable, protactinium pentachloride sublimes unchanged above 180°C *in vacuo*. It is a yellow, moisture-sensitive solid which is slightly soluble in benzene, tetrahydrofuran, and carbon tetrachloride. Visible absorption spectra have been recorded for solutions in the last two solvents and in alcohol (*110*). Reactions with hydrogen, aluminum, oxygen, and silicon tetraiodide are discussed below. It is unaffected by carbon monoxide at 350°C in a sealed tube.

The preparation of $\alpha\text{-}Pa_2OCl_8$ has been mentioned above; it is necessary to separate the pentachloride by slow sublimation below 220°C (10^{-4} mm Hg) because above 250°C $\alpha\text{-}Pa_2OCl_8$ disproportionates to yield the pentachloride and the nonvolatile diprotactinium(V) trioxytetrachloride, $Pa_2O_3Cl_4$, [Eq. (1)]. The tantalum(V) analog of

$$3Pa_2OCl_8 \xrightarrow[\textit{in vacuo}]{270^\circ C} Pa_2O_3Cl_4 + 4PaCl_5 \tag{1}$$

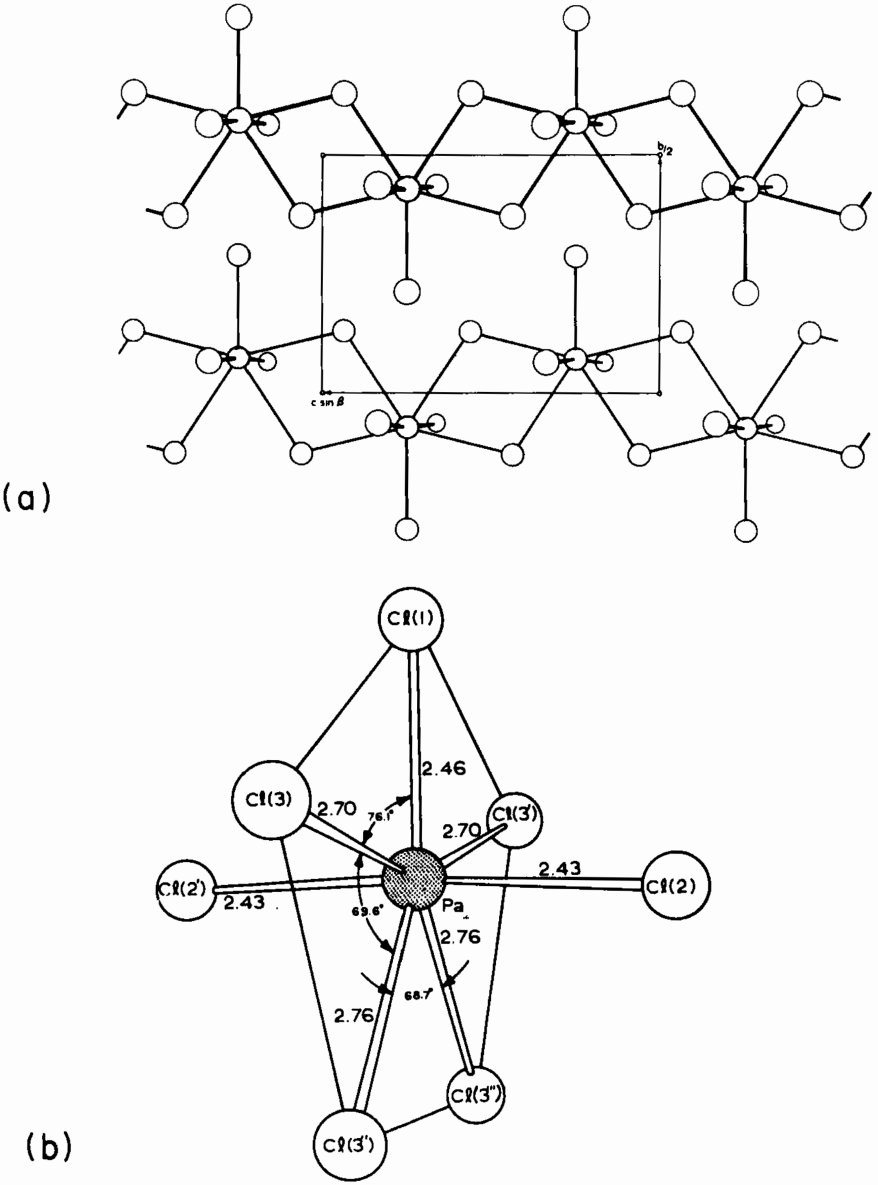
$$2Pa_2O_3Cl_4 \xrightarrow[\textit{in vacuo}]{520^\circ C} 3PaO_2Cl + PaCl_5 \tag{2}$$

$$4PaCl_5 + O_2 \xrightarrow[\text{sealed tube}]{400^\circ C} 2Pa_2OCl_8 + 2Cl_2 \tag{3}$$

$$4PaCl_5 + 3O_2 \xrightarrow[\text{sealed tube}]{500^\circ C} 2Pa_2O_3Cl_4 + 6Cl_2 \tag{4}$$

this compound is also known (*66*). At higher temperatures $Pa_2O_3Cl_4$ disproportionates, [Eq. (2)], and another pentavalent oxychloride, PaO_2Cl, is formed together with more pentachloride (*47*). These oxychlorides can be prepared directly by heating protactinium pentachloride with the appropriate amount of oxygen in a sealed vessel [Eqs. (3) and (4)], under which conditions the β-form of Pa_2OCl_8 is obtained. The interaction of the pentachloride and antimony sesquioxide will undoubtedly also yield oxychlorides (cf. oxybromide and oxyiodide formation). There is some evidence that an oxytrichloride, $PaOCl_3$, also exists, but satisfactory preparative methods have proved elusive and this compound may be stable only over a very limited temperature range (*47*). This behavior contrasts markedly with that of niobium(V) and uranium(V), both of which form stable oxytrichlorides. The range of protactinium(V) oxychlorides appears to be the largest known for any element in a single oxidation state.

No structural data are available for the pentavalent oxychlorides, but the positions of the protactinium–oxygen stretching vibrations



(Table IV) suggest they all possess polymeric oxygen-bridged structures. They are all white, moisture-sensitive compounds which are rapidly hydrolyzed by aqueous ammonia. Complexes with oxygen or nitrogen donor ligands [cf. $Pa_2O(NO_3)_8 \cdot 2CH_3CN$] are unknown.

Protactinium tetrachloride was first prepared (*125*) on the microgram scale by hydrogen reduction of the pentachloride at 800°C, a method since employed at 400°C for the preparation of 50-mg batches (*44*, *46*). It has also been prepared (*125*) by reacting the dioxide with carbon tetrachloride vapor, but since the pentachloride is much easier to prepare than the dioxide reduction of the former with aluminum at 400°C appears to be the most attractive route to the tetrachloride (*44*).

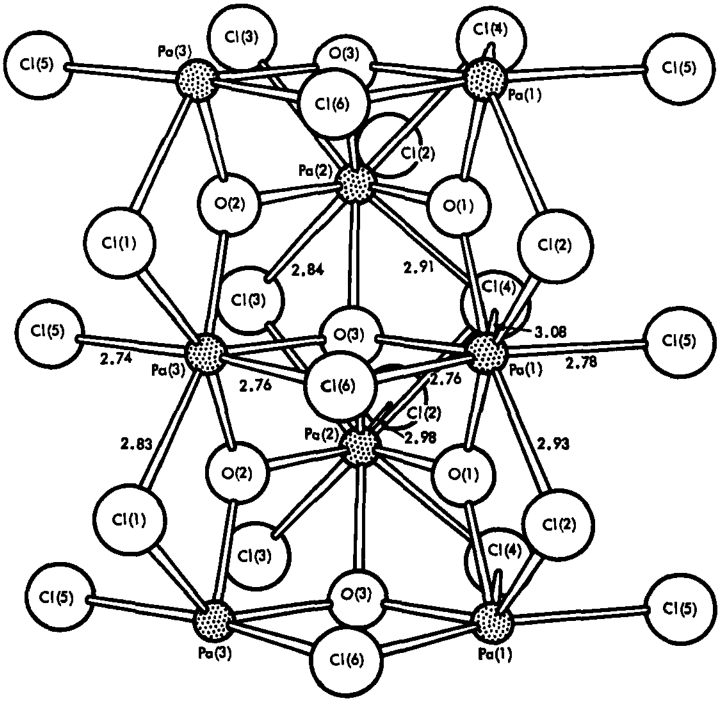
It is a greenish-yellow solid at room temperature, but above 300°C it is bright red. Like the other actinide tetrachlorides (Th–Np inclusive) it is known to possess the 8-coordinate UCl_4-type structure, but no bond lengths have been reported. Protactinium tetrachloride dissolves readily without hydrolysis in oxygen-free hydrochloric acid solution, and the spectral properties of such solutions have been reported (*16*, *74*). It reacts with antimony sesquioxide at about 200°C to yield protactinium(IV) oxydichloride, $PaOCl_2$, a dark green solid which can also be prepared by the interaction of the tetrachloride and dioxide (*44*). Unfortunately, the only direct preparation available for protactinium dioxide involves hydrogen reduction of the pentoxide at 1600°C which results in a relatively inert form of the dioxide. Both of the above methods have been used to prepare other tetravalent oxydihalides and the oxydichlorides of thorium, uranium, and neptunium are isostructural with $PaOCl_2$ (*17*).

Distances and angles in $PaCl_5$

Pa–Cl(1)	2.461 ± 0.020 Å	Cl(3″) ... Cl(3‴)	3.11 ± 0.03 Å
Pa–Cl(2)	2.434 ± 0.016 Å	Cl(2) ... Cl(1)	3.52 ± 0.02 Å
Pa–Cl(3)	2.704 ± 0.014 Å	Cl(2) ... Cl(3″)	3.59 ± 0.02 Å
Pa–Cl(3″)	2.759 ± 0.014 Å	Cl(2) ... Cl(3′)	3.63 ± 0.02 Å
Cl(1) ... Cl(3)	3.19 ± 0.02 Å	Cl(2) ... Cl(3‴)	3.65 ± 0.02 Å
Cl(3) ... Cl(3″)	3.12 ± 0.03 Å	Cl(2) ... Cl(3)	3.68 ± 0.02 Å
Cl(1)–Pa–Cl(2)	92.1 ± 0.4°	Cl(2)–Pa–Cl(3‴)	89.2 ± 0.5°
Cl(1)–Pa–Cl(3)	76.1 ± 0.3°	Cl(3)–Pa–Cl(3″)	69.6 ± 0.5°
Cl(2)–Pa–Cl(3)	91.2 ± 0.5°	Cl(3″)–Pa–Cl(3‴)	68.7 ± 0.6°
Cl(2)–Pa–Cl(3′)	89.8 ± 0.5°	Cl(2)–Pa–Cl(2′)	175.8 ± 0.9°
Cl(2)–Pa–Cl(3″)	87.3 ± 0.5°	Pa–Cl(3)–Pa′	110.4 ± 0.5°

FIG. 2. The structure of protactinium pentachloride (*67*). (a) Portion of the infinite chains in $PaCl_5$. Coordination of Cl around each Pa is pentagonal bipyramidal. (b) Bond distances and angles within an isolated $PaCl_7$ group. The four Cl(3) atoms are bridging.

The structure of protactinium oxydichloride has recently been determined and found to consist of infinite polymeric chains which extend along the short *c* axis and which are cross-linked in the *ab* plane by bridging chlorine atoms (*68*). The protactinium atoms are 7-, 8-, and 9-coordinate and oxygen atoms are 3- or 4-coordinate. Protactinium–oxygen and protactinium–chlorine bond distances lie within the ranges 2.19–2.38 and 2.76–3.08 Å, respectively (Fig. 3).



Selected bond lengths (Å)

Pa(1)–O(1)	2.191	Pa(2)–Cl(2′)	2.982
Pa(1)–O(3)	2.376	Pa(2)–Cl(3)	2.843
Pa(1)–Cl(2)	2.925	Pa(2)–Cl(4)	2.913
Pa(1)–Cl(4)	3.082	Pa(3)–O(2)	2.226
Pa(1)–Cl(5)	2.778	Pa(3)–O(3)	2.341
Pa(1)–Cl(6)	2.762	Pa(3)–Cl(1)	2.826
Pa(2)–O(1)	2.261	Pa(3)–Cl(5)	2.743
Pa(2)–O(2)	2.268	Pa(3)–Cl(6)	2.760
Pa(2)–O(3)	2.337	Pa(3)–Cl(3)	3.462

FIG. 3. The structure of $PaOCl_2$ (*68*).

Like other tetravalent actinide oxydihalides $PaOCl_2$ is thermally unstable and disproportionates above 550°C *in vacuo* [Eq. (5)].

$$2PaOCl_2 \xrightarrow[in\ vacuo]{>550°C} PaCl_4 + PaO_2 \tag{5}$$

Protactinium–oxygen and protactinium–chlorine stretching vibrations are listed in Table IV.

C. BROMIDES

Protactinium pentabromide, a dark red solid, has been prepared by reacting the pentoxide with aluminum tribromide (*104*) at 400°C *in vacuo*, but this reaction is unsuitable for large scale preparations. Although it has been reported (*103*) that ^{233}Pa tracer as the pentoxide incorporated in Ta_2O_5 or HfO_2 mixed with excess carbon does not react with bromine vapor to yield a volatile bromide at temperatures up to 1000°C gram amounts of $PaBr_5$ are easily made (*45*) by heating ^{231}Pa pentoxide–carbon mixtures with excess bromine in a sealed silica vessel at 600°–700°C. The light green oxytribromide, $PaOBr_3$, always forms to some extent in this reaction, but the volatile pentabromide is easily purified by vacuum sublimation at about 300°C. Direct union of the elements has not yet been investigated but, in view of the oxidation of protactinium metal by iodine (Section III, D), can be expected to result in pentabromide formation.

Two crystal modifications, α and β, of protactinium pentabromide have been identified (Table III). Single crystal studies have shown that β-$PaBr_5$ (*53*, *54*) is isostructural with uranium pentachloride (*127*), each protactinium being 6-coordinate. The dimeric Pa_2Br_{10} unit is shown in Fig. 4 which also lists the bond lengths and angles. It is interesting to note that this structure is based on cubic closest packing of the halogen atoms, whereas those of niobium pentachloride and pentabromide are based on hexagonal closest packing. Structural information is not yet available for α-$PaBr_5$.

Protactinium pentabromide is appreciably more stable than uranium pentabromide, which decomposes to the tetrabromide at 160°C (*116*). It is moisture-sensitive and hydrolyzes rapidly on the addition of water. The few known complexes are discussed later.

As mentioned above, protactinium(V) oxytribromide is invariably obtained as a by-product during the preparation of the pentabromide. It is also formed (*32*, *45*) when stoichiometric amounts of the pentabromide and either oxygen [Eq. (6)] or antimony sesquioxide [Eq. (7)] are heated together in a sealed vessel at 350°C. Although it is found with

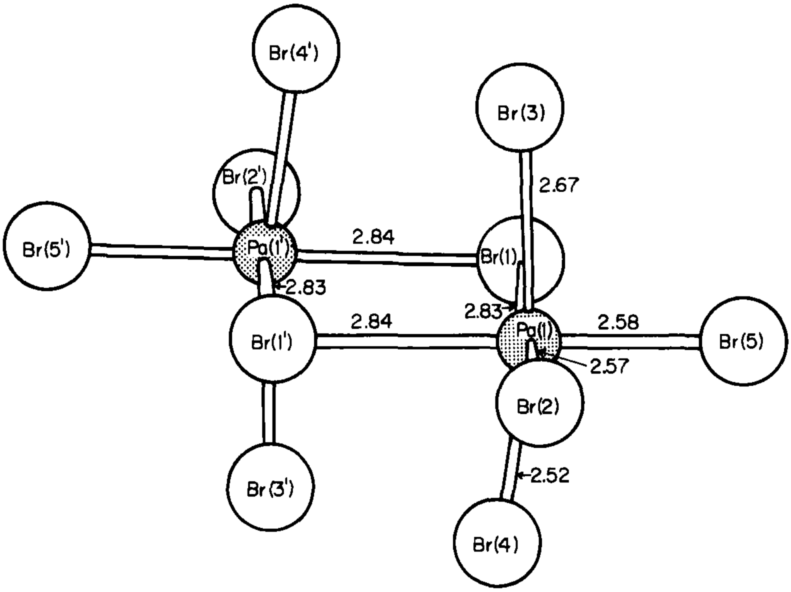


FIG. 4. The structure of β-protactinium pentabromide (*53*, *54*).

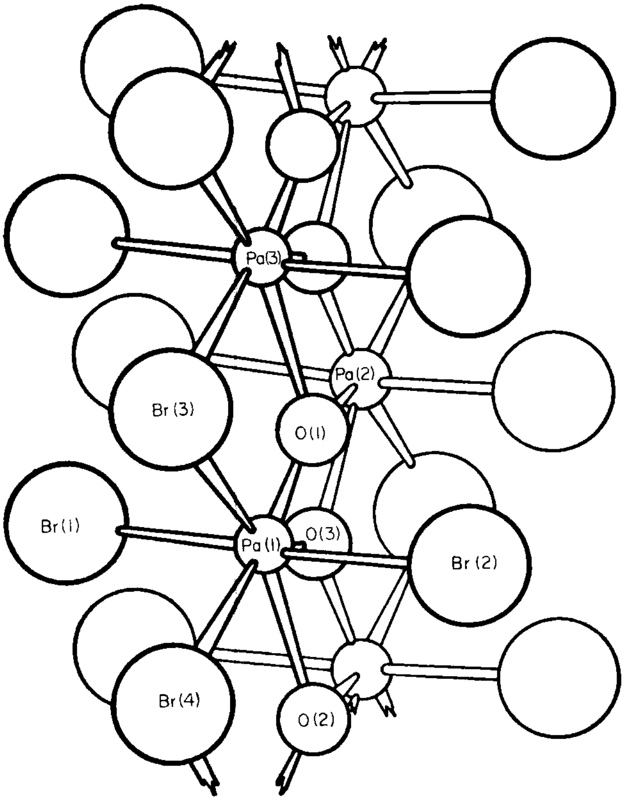
the initial sublimate during the pentabromide preparation, it is thermally unstable in the absence of the latter, disproportionating above 500°C *in vacuo*, [Eq. (8)] to the pentabromide and protactinium(V) dioxymonobromide, PaO_2Br. This is an off-white, nonvolatile solid which can alternatively be prepared by the pentabromide–antimony sesquioxide route. No evidence for the existence of Pa_2OBr_8 or $Pa_2O_3Br_4$ has yet been reported.

$$2PaBr_5 + O_2 \xrightarrow[\text{sealed tube}]{350°C\text{ in}} 2PaOBr_3 + 2Br_2 \qquad (6)$$

$$3PaBr_5 + Sb_2O_3 \xrightarrow[\textit{in vacuo}]{350°C} 3PaOBr_3 + 2SbBr_3 \qquad (7)$$

$$2PaOBr_3 \xrightarrow[\textit{in vacuo}]{500°C} PaO_2Br + PaBr_5 \qquad (8)$$

Protactinium(V) oxytribromide possesses monoclinic symmetry (Table III). The structure (*53*, *54*) comprises chains of protactinium atoms linked by bridging bromine atoms and cross-linked by 3-coordinate oxygen atoms. Each protactinium atom is 7-coordinate (Fig. 5) and protactinium–bromine bond lengths lie within the range 2.69–3.02 Å. It would be interesting to have structural information on the relatively unstable uranium(V) oxytribromide since the limited X-ray powder results available for the latter suggest that the compounds are not isostructural. Infrared data for the pentavalent oxybromides are listed in Table IV.



Bond lengths and angles in one pentagonal bipyramid

Pa–O(1)	2.14 Å	O(1)–Pa–Br(3)	80.7°
Pa–O(2)	2.25 Å	Br(3)–Pa–Br(4)	84.85°
Pa–O(3)	2.06 Å	Br(4)–Pa–O(2)	72.4°
Pa–Br(1)	2.69 Å	O(2)–Pa–O(3)	60.3°
Pa–Br(2)	2.56 Å	O(3)–Pa–O(1)	61.9°
Pa–Br(3)	2.76 Å	Br(1)–Pa–Br(2)	174.2°
Pa–Br(4)	3.02 Å		
		Pa(1)–O–Pa(2)	121.4°
		Pa(2)–O–Pa(3)	116.7°
		Pa(3)–O–Pa(1)	120.9°

FIG. 5. The structure of protactinium(V) oxytribromide (*53*).

Reduction of the pentabromide by hydrogen, or better, aluminum at 400°C results in the formation of protactinium tetrabromide (*44*, *46*). In the presence of excess aluminum no evidence for a lower oxidation state has been found. Protactinium tetrabromide, a red solid, is isostructural with α-thorium tetrabromide, possessing the 8-coordinate UCl_4-type of structure (Table III). There are four bromines at a distance of 2.83 Å from the metal atom and four at 3.01 Å (*53*). No second crystal form analogous to β-$ThBr_4$ has been recorded. Like $PaCl_4$, it can be sublimed above 500°C *in vacuo* with little decomposition. It reacts with antimony sesquioxide to form the orange oxydibromide, $PaOBr_2$, which is isostructural with other tetravalent actinide oxydibromides (*17*, *44*). This compound, like $PaOCl_2$, is thermally unstable above 550°C in a vacuum. Infrared data are listed in Table IV.

D. Iodides

Protactinium pentaiodide was first prepared by reacting the pentoxide with aluminum triiodide at 400°C in a vacuum (*104*). For large scale preparations, however, direct union of the elements or metathesis of the pentachloride or pentabromide with an excess of silicon tetraiodide are best (*40*). The latter reactions take place rapidly at about 180°C *in vacuo* and the black crystalline product is then purified by vacuum sublimation at 400°–450°C. Silicon tetraiodide also reacts with protactinium pentoxide, but temperatures in excess of 600°C are required with the reaction vessel completely enclosed in the furnace, and the yield is only about 70% (*40*).

Protactinium pentaiodide crystallizes with orthorhombic symmetry (*104*) (Table III). The pentaiodide is extremely moisture-sensitive and hydrolyzes immediately on contact with water. It is slightly soluble in methyl cyanide, but insoluble in isopentane and carbon tetrachloride.

The oxytriiodide, $PaOI_3$, and dioxymonoiodide, PaO_2I, have both been prepared (*40*) by reacting the pentaiodide with the stoichiometric amount of antimony sesquioxide [Eqs. (9) and (10)]. $PaOI_3$, a dark brown solid, is thermally unstable [Eq. (11)] *in vacuo* like certain of the oxychlorides and oxybromides. The positions of the protactinium–oxygen

$$3PaI_5 + Sb_2O_3 \xrightarrow[\textit{in vacuo}]{150°\text{–}200°C} 3PaOI_3 + 2SbI_3 \qquad (9)$$

$$3PaI_5 + 2Sb_2O_3 \xrightarrow[\textit{in vacuo}]{150°\text{–}200°C} 3PaO_2I + 4SbI_3 \qquad (10)$$

$$2PaOI_3 \xrightarrow[\textit{in vacuo}]{450°C} PaO_2I + PaI_5 \qquad (11)$$

stretching vibrations suggest extensively oxygen-bridged structures (Table IV). No structural information is available, but PaO_2I is reported to possess hexagonal symmetry (Table III).

Protactinium tetraiodide is a dark green solid which can be prepared by reducing the pentaiodide with aluminum at about 400°C (*44*). The structure is not known. On sublimation in silica above 500°C small amounts of the pink oxydiiodide, $PaOI_2$, are formed. Structural information is not available for the oxydiiodide, but it is known to be isomorphous with $ThOI_2$.

Despite the fact that excess aluminum failed to reduce protactinium tetraiodide it was recently reported (*123*) that heating the pentaiodide in a continuously pumping vacuum at 350°C for 1 week resulted in the elimination of iodine and the black residue was identified crystallographically as PaI_3. The experiments were only performed using 1-mg amounts of pentaiodide and it would be interesting to have information concerning larger scale preparations together with analytical results.

E. Mixed Halides

The only mixed halide known is $PaBr_3I_2$, a black, crystalline solid which is isostructural with the pentaiodide. It is formed (*40*) when equimolar amounts of the pentabromide and pentaiodide are heated together at 300°C. Numerous uranium(IV) mixed halides are known (*34*) and undoubtedly many protactinium(IV) and (V) mixed halides could be prepared, but this field has so far been neglected.

IV. Halogeno Complexes

Numerous halogenoprotactinates(V) of the types $M^{I}_{3}PaX_8$ (M^{I} = univalent cation; X = F and Cl), $M^{I}_{2}PaF_7$, and $M^{I}PaX_6$ (X = F, Cl, Br, and I) and halogenoprotactinates(IV) of the types $M^{I}_{2}PaX_6$ (X = Cl, Br, and I) and $M^{I}_{7}Pa_6F_{31}$ are known. Additional tetravalent fluoro complexes which have been reported are $(NH_4)_4PaF_8$, Na_3PaF_7, and $LiPaF_5$. No oxyhalogeno complexes analogous to those known for niobium(V) and tantalum(V), e.g., Cs_2NbOCl_5, $CsTaOCl_4$, etc., have yet been characterized.

Protactinium(V) is stable in aqueous hydrofluoric acid at quite high concentrations, but irreversible hydrolytic condensation occurs in other halogen acid solutions even at protactinium(V) concentrations of the order of 10^{-3} to 10^{-4} *M*. Consequently, only fluoroprotactinates(V) have been prepared in aqueous solution. Raman studies (*97*) have established the existence of the complex ions PaF_6^- and PaF_7^{2-} in aqueous hydrofluoric acid and conductometric titration experiments have indicated that all members of the series PaF_4^+ to PaF_8^{3-} inclusive can exist in solution (*59*). Other halogenoprotactinates(V) can only be prepared using nonaqueous solvents such as thionyl chloride (chlorides only) and methyl cyanide (chlorides, bromides, and iodides).

Since protactinium(IV) is readily oxidized in the atmosphere halogenoprotactinates(IV) must be prepared in oxygen-free solvents or by heating the component halides together in an inert atmosphere. It is reported that solvent extraction studies have established the existence of the fluoro and chloro species PaX_2^{2+} and PaX^{3+} in aqueous acid solution (*81*)

A. FLUORO COMPLEXES

Fluoroprotactinates(V) of the types M^IPaF_6 (M^I = Li, Na, K, Rb, Cs, NH_4, and Ag), $M_2^IPaF_7$ (M^I = K, Rb, NH_4, and Cs) ,and $M_3^IPaF_8$ (M^I = Li, Na, K, Rb, and Cs) are known.

Hexafluoro complexes, apart from $LiPaF_6$ and $NaPaF_6$, can be prepared by crystallization from aqueous hydrofluoric acid containing equimolar amounts of the component fluorides (*5, 7, 37, 82, 97, 114*), but it is better to discard the first crop of crystals which often contains some heptafluoroprotactinate(V). Fluorine oxidation of 1:1 mixtures of PaF_4 and MF (M = Li and Na) constitutes an attractive alternative preparative procedure (*5, 14*) which will undoubtedly also be useful for the larger alkali metal cations. This technique has recently been used for the preparation of fluoroneptunates(V) (*2*) and fluoroplutonates(V) (*115*) since, although the NpO_2^+ ion is reasonably stable in dilute aqueous hydrofluoric acid, in contrast to the behavior observed with protactinium(V) and uranium(V) it is not possible to prepare fully fluorinated complexes of these elements from aqueous hydrofluoric acid. It is interesting to note that alkali metal hexafluorouranates(V) can be precipitated from hydrofluoric acid solution (*6, 76, 113, 133*), but that corresponding heptafluoro and octafluoro complexes cannot, whereas examples of all three classes of protactinium(V) complexes have been prepared in this way (*37*).

Potassium heptafluoroprotactinate(V), K_2PaF_7, was first prepared (*79*) by reacting $PaF_5 \cdot 2H_2O$ with potassium fluoride in water. However, this and other heptafluoro complexes (M^I = NH_4, Rb, and Cs), for which the solubility in water increases with the size of the unipositive cation, are conveniently precipitated from 17 *M* hydrofluoric acid solution by the addition of acetone (*37*). Li_2PaF_7 and Na_2PaF_7 are not obtained by this method and attempts to prepare them by direct evaporation of 2:1 mixtures in hydrofluoric acid, with (*5*) or without (*59*) subsequent fluorination at 400°C, and by direct fluorination of 2:1 mixtures of MF and PaF_4 (*5*) have also failed. Similarly, all attempts to prepare the pentavalent uranium analogs have met with no success.

Protactinium(V) octafluoro complexes, $M_3^IPaF_8$, have been prepared (*5*, *35*, *37*, *59*) by precipitation from aqueous hydrofluoric acid (M^I = Li, Na, and Rb), by heating the alkali metal fluoride with the corresponding heptafluoro complex in argon (M^I = K and Cs) or by fluorinating the product obtained by evaporation of a hydrofluoric acid solution containing 3:1 mixtures of MF and Pa(V).

The protactinium(V) fluoro complexes are all air-stable, white solids. Available crystallographic data are compared with those for analogous actinide complexes in Tables V and VI. Of the hexafluoro complexes only $AgPaF_6$, $LiPaF_6$, and $NaPaF_6$ have not been characterized structurally. The remaining complexes and certain of the hexafluorouranates(V),

TABLE V

CRYSTALLOGRAPHIC PROPERTIES OF SOME PENTAVALENT ACTINIDE HEXAFLUORO COMPLEXES[a]

Compound	Color	Symmetry[b]	Structure type or space group	Lattice parameters (Å) a_0	b_0	c_0
$LiUF_6$	Pale blue	R	$LiSbF_6$	5.262	—	14.295
$NaPaF_6$	White	T	—	5.35	—	3.98
$NaUF_6$	Pale blue	R	$LiSbF_6$	5.596	—	15.526
$NaUF_6$	Pale blue	FCC	$NaTaF_6$	8.608	—	—
$KPaF_6$	White	O	D_{2h}^{18}-$Cmca$	5.64	11.54	7.98
KUF_6	Yellow-green	O	D_{2h}^{18}-$Cmca$	5.61	11.46	7.96
NH_4PaF_6	White	O	D_{2h}^{18}-$Cmca$	5.84	11.90	8.03
NH_4UF_6	Yellow-green	O	D_{2h}^{18}-$Cmca$	5.83	11.89	8.03
$RbPaF_6$	White	O	D_{2h}^{18}-$Cmca$	5.86	11.97	8.04
$RbUF_6$	Yellow-green	O	D_{2h}^{18}-$Cmca$	5.82	11.89	8.03
$CsPaF_6$	White	O	D_{2h}^{18}-$Cmca$	6.14	12.56	8.06
$CsUF_6$	Pale blue	R	$KOsF_6$	8.04	—	8.39
$CsNpF_6$	Pink-violet	R	$KOsF_6$	8.017	—	8.386
$CsPuF_6$	Green	R	$KOsF_6$	8.006	—	8.370

[a] From Brown (*30*).

[b] R, rhombohedral; T, tetragonal; FCC, face centered cubic; O, orthorhombic.

TABLE VI

CRYSTALLOGRAPHIC PROPERTIES OF SOME PENTAVALENT ACTINIDE HEPTA-AND OCTAFLUORO COMPLEXES

				Lattice parameters (Å)			
Compound	Color	Symmetry	Space group	a_0	b_0	c_0	Ref.
Li_3PaF_8	White	Tetragonal	D_4^6-$P4_22_12$	10.386	—	10.89	(*37*)
Na_3PaF_8	White	Tetragonal	D_{4h}^{17}-$I4/mmm$	5.487	—	10.89	(*37*)
Na_3UF_8	Pale blue	Tetragonal	D_{4h}^{17}-$I4/mmm$	5.470	—	10.94	(*120*)
Na_3NpF_8	Lilac	Tetragonal	D_{4h}^{17}-$I4/mmm$	5.443	—	10.837	(*38*)
K_3PaF_8	White	FCC	O_h^5-$Fm3m$	9.235	—	—	(*37*)
K_3UF_8	Pale blue	FCC	O_h^5-$Fm3m$	9.200	—	—	(*135*)
Rb_3PaF_8	White	FCC	O_h^5-$Fm3m$	9.60	—	—	(*37*)
Rb_3NpF_8	Violet	FCC	O_h^5-$Fm3m$	9.51	—	—	(*38*)
Cs_3PaF_8	White	FCC	O_h^5-$Fm3m$	9.937	—	—	(*38*)
K_2PaF_7	White	Monoclinic	C_{2h}^6-$C2/c$	13.94	6.76 $\beta = 125.5°$	8.24	(*50*)
Rb_2NpF_7	Lilac	Monoclinic	K_2TaF_7	6.26	13.42 $\beta = 90°$	8.90	(*2*)
Rb_2PuF_7	Pink	Monoclinic	K_2TaF_7	6.27	13.41 $\beta = 90°$	8.88	(*115*)
Cs_2PaF_7	White	Monoclinic	K_2PaF_7	14.937	7.270 $\beta = 125.32°$	8.266	(*39*)

M^I = K, NH_4, and Rb for U(V), are isomorphous and possess the 8-coordinate structure recently determined for $RbPaF_6$ (*61*), in which each protactinium atom is bonded to four terminal fluorine atoms at a distance of 2.08 Å and to four bridging fluorine atoms at 2.35 Å (Fig. 6). $CsUF_6$, $CsNpF_6$, and $CsPuF_6$, on the other hand, possess the $KOsF_6$ type of structure (*114*, *119*) in which the anion is of octahedral symmetry.

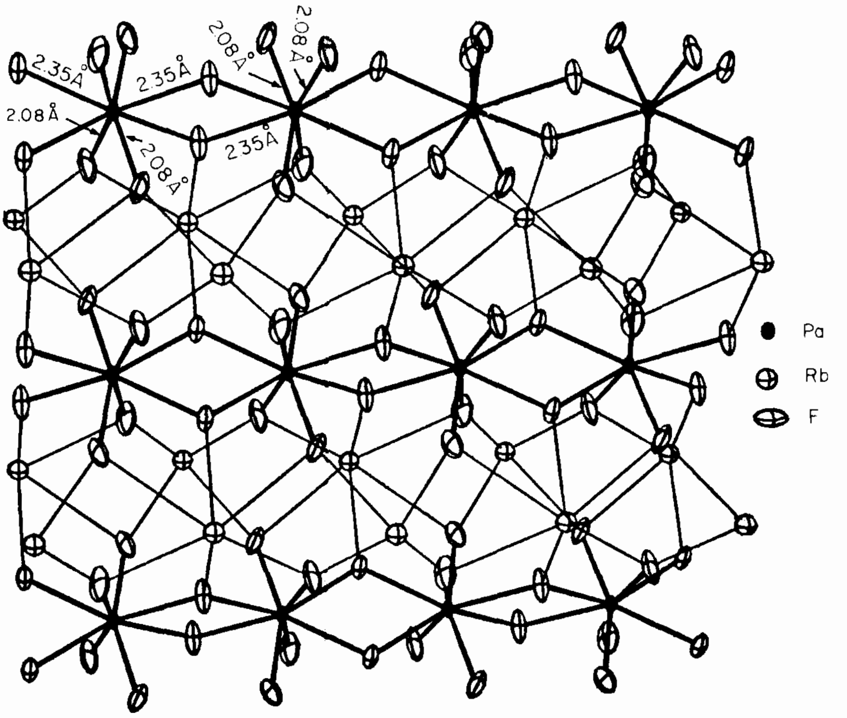
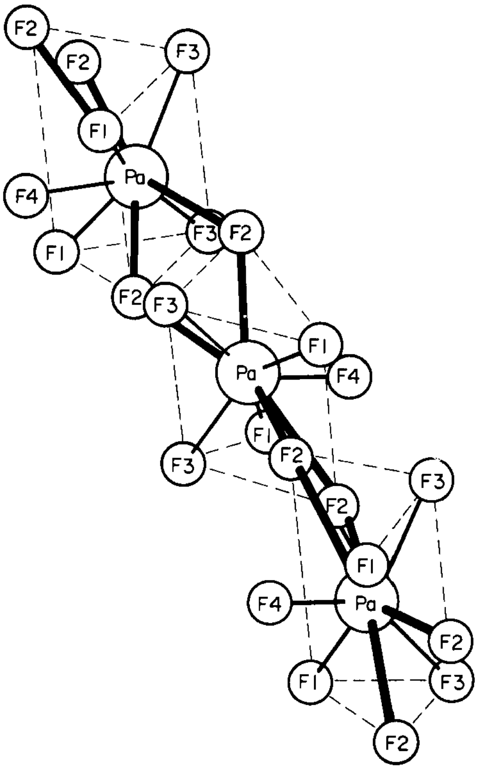


FIG. 6. A view of the structure of $RbPaF_6$ (*61*). The atoms are represented by their ellipsoids of thermal motion.

K_2PaF_7 possesses monoclinic symmetry; each protactinium atom is surrounded by nine fluorine atoms in an arrangement which may be idealized as a trigonal prism with three equatorial fluorines added (*50*, *56*). The PaF_9 units are linked in infinite chains parallel to [001] by two fluorine bridges. The structural arrangement is illustrated in Fig. 7 and bond distances are listed. The remaining heptafluoroprotactinates(V), M^I = NH_4, Rb, and Cs, are isostructural with K_2PaF_7 (*37*, *39*), but the analogous uranium(V) complexes possess different structures. The rubidium salts of pentavalent uranium, neptunium, and plutonium are, in fact, isostructural with K_2NbF_7, being therefore 7-coordinate.



Pa–F Bond Lengths

Pa–F(3)	2.14 Å
Pa–F(1)	2.16 Å
Pa–F(4)	2.19 Å
Pa–F(2)	2.31 Å
Pa–F(2′)	2.46 Å

F–F distances and angles at Pa

F(1)–F(2)	2.83 Å	78.4°
F(1)–F(2′)	2.54 Å	66.2°
F(1)–F(3)	2.67 Å	76.6°
F(1)–F(4)	2.58 Å	72.8°
F(2)–F(2′)	2.46 Å	62.1°
F(2)–F(3)	2.82 Å	78.7°
F(2)–F(4)	2.62 Å	71.1°
F(2′)–F(3)	2.73 Å	72.5°

FIG. 7. The structure of K_2PaF_7 showing the PaF_9 units (*50*).

Structural data are not available for any of the octafluoro complexes* although some X-ray powder results have been reported (Table VI). Available infrared data are shown in Table VII; Raman spectra have been

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* See Appendix.

recorded for $RbPaF_6$ and Rb_2PaF_7, sharp, strong bands being observed at 590 and 545 cm^{-1}, respectively (*97*).

Protactinium(IV) fluoro complexes of the types $M^{I}_{4}PaF_8$, $M^{I}_{3}PaF_7$, $M^{I}_{7}Pa_6F_{31}$, and $M^{I}PaF_5$ (M^{I} = variously Li, Na, K, Rb, and NH_4) are known, but relatively few compounds have been completely characterized (*3*, *4*, *114*). In all cases identification has been by X-ray powder diffraction analysis, the complexes being isostructural with their tetravalent actinide analogs. Unfortunately, this technique is of no value for complexes of the type $M^{I}_{3}PaF_7$ because, by analogy with uranium compounds, such complexes as K_3PaF_6, K_3PaF_7, and K_3PaF_8 are expected to give virtually identical X-ray powder patterns (*134*). However, using spectral methods Penneman *et al.* (*4*, *114*) showed that the compounds Na_3PaF_7, K_3PaF_7, and Rb_3PaF_7 do exist, although they were unable to assess the purity of their preparations. The spectrum of $Rb_7Pa_6F_{31}$ in the near-infrared region is shown in Fig. 8.

TABLE VII

METAL–HALOGEN STRETCHING FREQUENCIES FOR SOME HALOGENO COMPLEXES[a]

Complex	ν_{M-F}	Complex	ν_3	Complex	ν_3
PaF_6^-	523; 454	$PaCl_6^-$	305–310	$PaBr_6^-$	215–216
PaF_7^{2-}	430–438; 356	UCl_6^-	305–310	UBr_6^-	214–215
PaF_8^{3-}	395–422	$NbCl_6^-$	334–336	$NbBr_6^-$	240; 216–229
NpF_8^{3-}	~400	$TaCl_6^-$	319–323	$TaBr_6^-$	223–234; 205–214
		$PaCl_8^{3-}$	290		
		$ThCl_6^{2-}$	251–258	$ThBr_6^{2-}$	177–179
		$PaCl_6^{2-}$	255–266	$PaBr_6^{2-}$	180–182
		UCl_6^{2-}	253–259	UBr_6^{2-}	178–181
		$NpCl_6^{2-}$	265–267		

[a] Values given in cm^{-1}. From Bagnall, Brown *et al.* (*15*, *25*, *31*, *37*, *38*, *46*).

The protactinium(IV) fluoro complexes have been prepared either by hydrogen reduction of a pentavalent complex at 400°C or by heating together appropriate amounts of MF and PaF_4 in sealed vessels. The reaction between ammonium fluoride and protactinium tetrafluoride to yield $(NH_4)_4PaF_8$, the only octafluoro complex known, takes place when the component halides are ground together at room temperature (*4*, *114*).

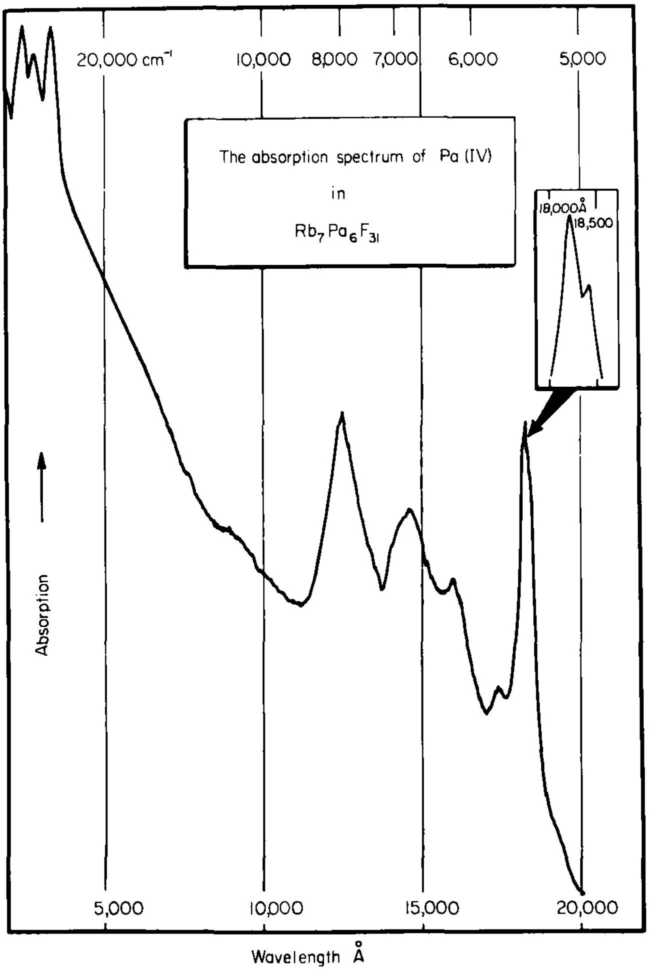

FIG. 8. The absorption spectrum of $Rb_7Pa_6F_{31}$ (*4*).

Unit cell dimensions for the tetravalent protactinium fluoro complexes are listed in Table VIII. $LiPaF_5$ is a member of an isostructural series of 1:1 complexes formed by the actinide elements thorium to curium inclusive (*91*). Structural details are available for $LiUF_5$ (*58*), but bond distances have not been reported for the protactinium complex. The 7:6 complexes, like their actinide(IV) analogs (Th–Cm with Na, Th–Cm with K, and Th–Pu with Rb) are all (*4*, *114*) isostructural with $Na_7Zr_6F_{31}$ (*60*) in which each zirconium atom is 8-coordinate and the

TABLE VIII

CRYSTALLOGRAPHIC PROPERTIES OF THE TETRAVALENT PROTACTINIUM FLUORO COMPLEXES[a]

			Lattice parameters (Å)		
Compound	Symmetry	Structure-type	a_0	b_0	c_0
$LiPaF_5$	T	$LiUF_5$	14.970	—	6.576
$Na_7Pa_6F_{31}$	R	$Na_7Zr_6F_{31}$	9.16	$\alpha = 107.8°$	—
$K_7Pa_6F_{31}$	R	$Na_7Zr_6F_{31}$	9.44	$\alpha = 107.15°$	—
$Rb_7Pa_6F_{31}$	R	$Na_7Zr_6F_{31}$	9.64	$\alpha = 107°$	—
$(NH_4)_4PaF_8$	M	—	13.18	6.71 $\beta = 117.16°$	13.22

[a] From Asprey *et al.* (*4*).

"extra" fluorine atom is enclosed in an octahedral array of zirconium atoms. Stability trends within the 1:1 and 7:6 series of tetravalent actinide fluoro complexes are discussed elsewhere (*33*).

It is noteworthy that complexes of the type $M^{I}_{2}PaF_6$ are unknown; this is all the more surprising since both thorium(IV) and uranium(IV) complexes of this type, where $M^{I} = Na$, K, Rb, and Cs, have been recorded. Attempts to prepare the protactinium(IV) complexes by the hydrogen reduction technique have been unsuccessful; for example, $K_7Pa_6F_{31}$ has been obtained from K_2PaF_7 (*4*, *114*). Nevertheless, it is probable that with the right experimental conditions the tetravalent 2:1 complexes will be prepared.

Although complexes of the type $M^{II}M^{IV}F_6$ (M^{II} = Ba, Ca, Sr, etc.; M^{IV} = actinide element) are known for several other actinide elements, the protactinium(IV) systems have not yet been studied.

B. CHLORO COMPLEXES

Both hexa- and octachloroprotactinates(V) have been reported, but heptachloro complexes are unknown (*15*, *35*). Vacuum evaporation of a solution of protactinium(V) in thionyl chloride results in the formation of the buff solid $SO(PaCl_6)_2$. In contrast to this, niobium(V) and tantalum(V) form the respective pentachlorides under these conditions and uranium(V) yields the dark red complex UCl_5SOCl_2. However, hexachloro complexes of all four elements are precipitated from thionyl chloride solution containing equimolar amounts of MCl_5 and $M^{I}Cl$ ($M^{I} = NMe_4$ NEt_4, NH_2Me_2, and Ph_4As) by the addition of carbon disulfide (*15*, *25*).

Cesium and ammonium hexachloro complexes precipitate when the component halides are reacted in thionyl chloride–iodine monochloride mixtures.

The octachloroprotactinate(V) $(NMe_4)_3PaCl_8$ has also been prepared in thionyl chloride solution (*15*). The uranium(V) analog is known (*25*), but niobium(V) and tantalum(V) octachloro complexes cannot be prepared in this way and, in fact, are presently unknown.

The pale yellow protactinium(V) complexes are moisture-sensitive solids which, apart from $CsPaCl_6$, decompose above 200°C in dry air. They react rapidly with liquid dinitrogen pentoxide to form hexanitratoprotactinates(V) as discussed later. $Ph_4AsPaCl_6$ and $CsPaCl_6$ are known to be isostructural with their uranium(V) analogs, but no structural details are available. Protactinium–chlorine stretching vibrations occur at about 308 cm^{-1} for the hexachloro complexes and at 290 cm^{-1} for $(NMe_4)_3PaCl_8$, the shift presumably occurring as a consequence of the increase in coordination number (Table VII).

Although protactinium(V) chloro complexes can also be prepared using methyl cyanide as the solvent (*32*) (cf. $PaBr_6^-$ and PaI_6^-), the use of thionyl chloride has several advantages. Thus, it means that one can start with protactinium(V) hydroxide and not the pentachloride, thionyl chloride itself affords protection against atmospheric moisture and dry-atmosphere boxes are not necessary for the preparations, and, in addition, protactinium(V) concentrations up to 0.5 *M* have been obtained by dissolving the hydroxide in thionyl chloride (*15*). Such solutions are quite stable in contrast to the hydrolytic condensation reactions which occur in concentrated hydrochloric acid at Pa(V) concentrations as low as 10^{-4} *M*.

Hexachloroprotactinates(IV), $M^I_2PaCl_6$, cannot be prepared by reactions in thionyl chloride [cf. UCl_6^{2-}, $ThCl_6^{2-}$ (*1, 31*)] owing to oxidation by the solvent. They have been prepared (*48*) by reacting the component chlorides in anhydrous, oxygen-free methyl cyanide ($M^I = NMe_4$ and NEt_4) or in oxygen-free 11 *M* hydrochloric acid ($M^I = Cs$). Both of these reactions have also been used to prepare other tetravalent actinide hexachloro complexes (*31*). With a given cation an isostructural series of complexes is formed (actinide elements = Th to Pu inclusive) and the available X-ray data are compared in Table IX. Full structural information is not available. The bright yellow hexachloroprotactinates(IV) are unstable in air, slowly being oxidized to uncharacterized pentavalent species, but can be stored indefinitely in an inert atmosphere. Optical spectroscopy and paramagnetic resonance absorption studies of Cs_2PaCl_6 in a Cs_2ZrCl_6 matrix have shown (*8–10, 101*) that protactinium(IV) has a $5f^1$ electronic configuration under these conditions. More recently, spin

TABLE IX

CRYSTALLOGRAPHIC DATA FOR SOME ISOSTRUCTURAL SERIES OF QUADRIVALENT HEXAHALOGENO COMPLEXES[a]

Compound	Symmetry	Space group	Unit cell dimensions (Å)		
			a_0	b_0	c_0
$(NMe_4)_2ThCl_6$	FCC	O_h^5-$Fm3m$	13.12	—	—
$(NMe_4)_2PaCl_6$	FCC	O_h^5-$Fm3m$	13.08	—	—
$(NMe_4)_2UCl_6$	FCC	O_h^5-$Fm3m$	13.06	—	—
$(NMe_4)_2NpCl_6$	FCC	O_h^5-$Fm3m$	13.02	—	—
Cs_2ThCl_6	Trigonal	D_{3d}^3-C3m	7.590	—	6.026
Cs_2PaCl_6	Trigonal	D_{3d}^3-C3m	7.546	—	6.056
Cs_2UCl_6	Trigonal	D_{3d}^3-C3m	7.478	—	6.026
Cs_2NpCl_6	Trigonal	D_{3d}^3-C3m	7.460	—	6.030
β-$(NEt_4)_2ThCl_6$	Orthorhombic	$D_{2h}^{23}-Fmmm$	14.26	14.84	13.37
$(NEt_4)_2PaCl_6$	Orthorhombic	$D_{2h}^{23}-Fmmm$	14.22	14.75	13.35
$(NEt_4)_2UCl_6$	Orthorhombic	$D_{2h}^{23}-Fmmm$	14.23	14.73	13.33
$(NEt_4)_2NpCl_6$	Orthorhombic	$D_{2h}^{23}-Fmmm$	14.20	14.69	13.30
$(NMe_4)_2ThBr_6$	FCC	O_h^5-$Fm3m$	13.49	—	—
$(NMe_4)_2PaBr_6$	FCC	O_h^5-$Fm3m$	13.40	—	—
$(NMe_4)_2UBr_6$	FCC	O_h^5-$Fm3m$	13.37	—	—

[a] From Brown (*31*).

relaxation effects (*117*) have been reported for the same system. Obviously, it would be interesting to have magnetic results and further spectral data for these presumably octahedral complexes, particularly in view of the close proximity of the 6*d* and 5*f* energy levels for protactinium. Infrared stretching vibrations have been located at 255–266 cm^{-1}, positions which are close to those reported for other tetravalent actinide chloro complexes (Table VII).

C. BROMO AND IODO COMPLEXES

It is convenient to discuss protactinium(IV) and (V) bromo and iodo complexes together since they have only been prepared by reacting together the component halides in anhydrous methyl cyanide (*40*, *46*, *48*). Thus NMe_4PaBr_6, NEt_4PaBr_6, and $Ph_3MeAsPaI_6$ are isolated (*40*, *46*) by removal of solvent *in vacuo* at room temperature. Hexabromoniobates(V) and tantalates(V) have been prepared in a similar manner (*46*). Attempts to obtain octabromo complexes for these three elements have been unsuccessful. The orange hexabromoprotactinates(V) are moisture-sensitive solids for which protactinium–bromine stretching vibrations occur at approximately 216 cm^{-1} (Table VII). NMe_4PaBr_6 possesses face-centered cubic symmetry with $a_0 = 12.9$ Å. No structural results are available for these pentavalent protactinium complexes.

The tetravalent, orange hexabromo complexes $(NMe_4)_2PaBr_6$ and $(NEt_4)_2PaBr_6$ and the deep blue iodo complex $(Ph_3MeAs)_2PaI_6$ crystallize from oxygen-free methyl cyanide at room temperature (*48*). X-Ray powder data, but no structural results, are available for $(NMe_4)_2PaBr_6$ and isostructural actinide analogs (Table IX). Infrared data are given in Table VII. Visible spectra and magnetic properties have not been reported for these complexes.

V. Halide Complexes with Donor Ligands

Actinide halides and oxyhalides are known to form numerous complexes with oxygen and nitrogen donor ligands and the preparation and properties of such compounds have recently been reviewed (*12*, *13*). Relatively few protactinium halide complexes are known, but this situation reflects the lack of research rather than a tendency not to form complexes. However, there is sufficient information available for certain ligands to permit a comparison with the behavior of other actinide halides and to illustrate the similarities and differences observed with the tetrahalides of thorium to plutonium inclusive and, to a lesser extent, with the protactinium and uranium pentahalides.

A. Oxygen Donors

The only protactinium halide known to form hydrates is PaF_5 (*38*, *79*, *131*); although other pentahalides certainly will not form hydrates it is probable that tetrafluoride hydrates analogous to those known for ThF_4 and UF_4 will exist (*30*). $PaF_5 \cdot 2H_2O$ was first prepared by von Grosse (*78*) by crystallization from aqueous hydrofluoric acid. It can also be prepared by heating the pentavalent hydroxide with gaseous hydrogen fluoride at 40°C, a reaction which yields the monohydrate at 60°C (*38*). Both hydrates are deliquiscent, water-soluble, white solids which on vacuum decomposition at room temperature yield the oxyfluoride Pa_2OF_8.

Protactinium pentachloride (*42*) and pentabromide (*43*) form both 1 : 1 and 1 : 2 complexes with phosphine oxides, the former being analogous to those formed by niobium, tantalum, and uranium pentahalides (*26*, *42*, *43*). Unlike niobium and tantalum pentachloride (*42*, *64*) however, they do not react with excess triphenylphosphine oxide (TPPO) to form oxychloro complexes of the type $MOCl_3 \cdot 2TPPO$. An extremely large shift in the position of the P=O stretching vibration occurs on coordination of phosphine oxides to the pentahalides (Table X). More recently

TABLE X

PROTACTINIUM(IV) AND (V) HALIDE COMPLEXES WITH DONOR LIGANDS

Complex	Color	$\nu_{P=O}$, $\nu_{C=O}$, $\nu_{S=O}$, $\nu_{P=S}$, $\nu_{P=Se}$, or $\nu_{C=N}$	$\Delta\nu$	Ref.
$PaCl_5 \cdot Ph_3PO$	Buff	990	202	(*42*)
$PaCl_5 \cdot 2Ph_3PO$	Yellow	1020	172	(*43*)
$PaCl_5 \cdot BzPh_2PO$	Pale yellow	987	194	(*42*)
$PaBr_5 \cdot Ph_3PO$	Orange-yellow	960	232	(*43*)
$PaBr_5 \cdot 2Ph_3PO$	Orange-red	985	207	(*43*)
$PaBr_5 \cdot Ph_2POCH_2POPh_2$	Orange-yellow	1060	130	(*43*)
$PaCl_5 \cdot Ph_3PS$	Yellow	578	53	(*43*)
$PaCl_5 \cdot Ph_2PSCH_2PSPh_2$	Orange	—	—	(*43*)
$PaBr_5 \cdot Ph_3PS$	Red	578	53	(*43*)
$PaBr_5 \cdot Ph_2PSCH_2PSPh_2$	Red	—	—	(*43*)
$PaCl_5 \cdot Ph_3PSe$	Yellow-orange	533	22	(*43*)
$PaCl_5 \cdot Ph_2PSeCH_2PSePh_2$	Brown	—	—	(*43*)
$PaBr_5 \cdot Ph_3PSe$	Orange-red	540	15	(*43*)
$PaBr_5 \cdot Ph_2PSeCH_2PSePh_2$	Dark red	—	—	(*43*)
$PaBr_5 \cdot 3(CH_3)_2NCOCH_3$	Orange	1608	39	(*23*)
$PaBr_5 \cdot 3CH_3CN$	Orange	2278	29	(*45*)
$PaCl_4 \cdot 4CH_3CN$	Yellow-green	2275	26	(*48*)
$PaBr_4 \cdot 4CH_3CN$	Orange	2275	26	(*48*)
$PaCl_4 \cdot 3(CH_3)_2NCOCH_3$	Yellow	1608	39	(*24*)
$PaCl_4 \cdot 2.5(CH_3)_2NCOCH_3$	Yellow	1608	39	(*24*)
$PaBr_4 \cdot 5(CH_3)_2NCOCH_3$	Yellow	1608	39	(*24*)
$PaBr_4 \cdot 2.5(CH_3)_2NCOCH_3$	Yellow	1608	39	(*24*)
$PaCl_4 \cdot 5(CH_3)_2SO$	Yellow	940	105	(*18*)
$PaCl_4 \cdot 3(CH_3)_2SO$	Yellow	950	95	(*18*)
$PaCl_4 \cdot 2(NMe_2)_3PO$	Mustard	1042	159	(*55*)
$PaCl_4 \cdot 2Ph_3PO$	Yellow	1070	121	(*55*)
$PaBr_4 \cdot 2(NMe_2)_3PO$	Greenish-yellow	1023	178	(*55*)
$PaBr_4 \cdot 2Ph_3PO$	Greenish-yellow	1038	154	(*55*)

stable 1:1 complexes of protactinium pentabromide with bisphosphine oxides have been prepared (*43*), and probably protactinium pentachloride and the analogous uranium pentahalides will form similar complexes.

N,*N*-Dimethylacetamide (DMA) forms a 1:3 complex with protactinium pentabromide (*23*), but its reaction with other pentahalides has not been studied.

Like other actinide tetrahalides, protactinium tetrachloride and tetrabromide form stable complexes with phosphine oxides (*48*, *55*) and *N*,*N*-dimethylacetamide (*24*), but the tetrachloride–dimethyl sulfoxide

TABLE XI

A COMPARISON OF CERTAIN ACTINIDE HALIDE COMPLEXES

Ligand	Halide	Stoichiometry for M =				
		Th	Pa	U	Np	Pu
R_3PO (R=Ph and NMe_2)	MCl_5		1:1	1:1		
			1:2	*a*		
	MBr_5		1:1	1:1		
			1:2	*b*		
	MCl_4	1:2	1:2	1:2	1:2	*a*
	MBr_4	1:3	*b*	*b*	*b*	*b*
		1:2	1:2	1:2	1:2	1:2
$Ph_2POCH_2POPh_2$	MCl_5		*a*	*a*		
	MBr_5		1:1	*a*		
Ph_3PS and Ph_3PSe	MCl_5		1:1	*a*		
	MBr_5		1:1	*a*		
$Ph_2PSCH_2PSPh_2$ and $Ph_2PSeCH_2PSePh_2$	MCl_5		1:1	*a*		
	MBr_5		1:1	*a*		
DMA	MCl_5		*a*	*a*		
	MBr_5		1:3	*a*		
	$MOBr_3$		*a*	1:2.5		
	MCl_4	1:4	*b*	*b*	*b*	*b*
		1:3	1:3	*b*	*b*	*b*
		b	1:2.5	1:2.5	1:2.5	1:2.5
	MBr_4	1:5	1:5	1:5	*a*	*a*
		b	1:2.5	1:2.5	*a*	*a*
	MI_4	1:6	*a*	*b*		
		b	*a*	1:4		
DMSO	MCl_4	*b*	*b*	1:7	1:7	1:7
		1:5	1:5	1:5	(1:5)[c]	*b*
		1:3	1:3	1:3	1:3	1:3
	MBr_4	1:6	*a*	1:6	*a*	*a*
CH_3CN	MCl_5		*a*	*a*		
	MBr_5		1:3	*a*		
	MCl_4	1:4	1:4	1:4	1:4	*a*
	MBr_4	1:4	1:4	1:4	1:4	1:4
	MI_4	1:4	1:4	*b*		

[a] System not yet investigated.

[b] Compound formation not observed.

[c] Values in parentheses indicate unstable compounds.

(DMSO) complexes (*18*) are relatively unstable toward oxidative decomposition. The known complexes are listed in Table X, together with infrared data, and are compared with the complexes formed by other actinide halides in Table XI. The protactinium(IV) complexes have been prepared by reacting the anhydrous halide with the appropriate ligand in nonaqueous, oxygen-free solvents such as methylene dichloride, chloroform, or methyl cyanide.

It is interesting to note that only thorium tetrabromide forms 1:3 complexes with triphenylphosphine oxide and hexamethylphosphoramide (*21*, *55*) [uranium tetrachloride is known to form the 1:3 complex $UCl_4 \cdot 3Me_3PO$ (*75*), but the behavior of other actinide halides with this ligand has not yet been investigated] possibly as a result of the slight difference in the ionic radii of Th^{4+} and Pa^{4+} (0.99 and 0.96 Å, respectively). The 1:2 series of phosphine oxide complexes formed by the actinide tetrachlorides (Th to Np inclusive) are isostructural and the 1:2 tetrabromide complexes (Th to Pu inclusive) form another isostructural series.

The actinide tetrachloride–DMA complexes cover quite a range of stoichiometry (*22*, *24*, *27*) and the behavior of protactinium tetrachloride is intermediate between that observed for thorium and uranium tetrachloride (Table XI). $PaCl_4 \cdot 2.5$ DMA is isostructural with the γ-modification of the other 1:2.5 complexes and with $PaBr_4 \cdot 2.5$ DMA (*24*). However, the uranium tetrabromide complex, $UBr_4 \cdot 2.5$ DMA, possesses a different structure. The 1:5 tetrabromide–DMA complexes (Th to U inclusive) are isostructural (*24*).

The actinide tetrachloride–DMSO complexes are particularly interesting (*18*). There is a pronounced change in stability proceeding along the actinide series with 1:5 complexes being the most stable for thorium and protactinium and the 1:3 complexes for the remaining actinides. The 1:7 complex could not be obtained pure with thorium tetrachloride and under the preparative conditions required, namely, recrystallization from hot dimethyl sulfoxide, protactinium(IV) was oxidized. The solid 1:5 and 1:3 protactinium tetrachloride compounds are, in fact, unstable in dry nitrogen, behavior which contrasts markedly with the stability of the tetrahalide–phosphine oxide and DMA complexes.

No other complexes with oxygen donor ligands have been reported and there is obviously scope for some interesting research in this field.

B. SULFUR AND SELENIUM DONORS

Both protactinium pentachloride and pentabromide react with triphenylphosphine sulfide and selenide to form stable 1:1 complexes

(*43*). Similar compounds with bis(diphenylphosphino)methane disulfide and the corresponding diselenide have also been prepared (Table X). These are the first examples of coordination of sulfur and selenium donors to actinide pentahalides and it will be interesting to see whether uranium pentahalides behave in a similar fashion since the analogous niobium(V) and tantalum(V) compounds are also known (*43*).

C. NITROGEN DONORS

Even fewer complexes with nitrogen donor ligands have been reported and all are methyl cyanide adducts (Tables X and XI). Protactinium pentabromide forms a soluble 1:3 complex in contrast to the 1:1 complexes formed by niobium and tantalum pentahalides (*46*). Other actinide pentahalide–methyl cyanide complexes are still unknown. Protactinium tetrachloride, tetrabromide, and tetraiodide react with anhydrous, oxygen-free methyl cyanide to form slightly soluble 1:4 complexes (*44*, *48*) which are isostructural with their actinide tetrahalide analogs.

VI. Oxides

In addition to the pentoxide and dioxide several intermediate oxide phases have been characterized. Mixed oxide phases have been reported with the oxides of mono-, di-, tri-, tetra-, and pentavalent elements.

A. PROTACTINIUM PENTOXIDE

The pentavalent oxide, Pa_2O_5, is obtained when the hydroxide is heated in air or oxygen above 650°C. It is a stoichiometric phase and is useful in analytical procedures. Recent investigations (*118*, *128*, *129*) have shown that several crystal modifications can be prepared, depending on the temperature to which the pentoxide is heated, but the existence of the orthorhombic phase reported by Sellers *et al.* (*125*) and also by Kirby (*99*) has not been confirmed. The properties of the various crystal modifications are listed in Table XII. It has been suggested that the low temperature cubic modification may, in fact, be the tetragonal phase T3 in a poorly crystalline state (*118*). Above 1000°C the T3 phase transforms to the hexagonal phase and a rhombohedral phase (R2) has been identified above 1240°C.

B. PROTACTINIUM DIOXIDE AND INTERMEDIATE PHASES

Hydrogen reduction of Pa_2O_5 at 1550°C yields the black dioxide PaO_2 which possesses the fluorite type of structure like the other actinide dioxides (*118*, *125*). Black phases of composition $PaO_{2.30}$ were reported several years ago (*125*), but it was only recently that the very thorough investigation by Roberts and Walter (*118*) satisfactorily characterized the phases which exist between PaO_2 and Pa_2O_5. By analysis of the products obtained by reduction of the pentoxide and of those obtained by oxidation of the dioxide, coupled with X-ray powder diffraction studies using a Guinier focusing camera, four intermediate phases were identified. These are listed in Table XII. Some evidence indicating that the T3 phase may be stable over a limited range of composition, $PaO_{2.476} \rightarrow PaO_{2.500}$, was also found.

The entire oxide system between PaO_2 and Pa_2O_5 depends on the incorporation of oxygen into interstitial sites in the fluorite lattice of PaO_2 with subsequent ordering to give superstructures of the fluorite lattice. The structures of the T3, H, and R2 forms of the pentoxide are also probably closely related to the fluorite structure. These results, and the available information of the oxidation of solid solutions of PaO_2 in ThO_2, show clearly that protactinium behaves like a member of the actinide series in the formation of its oxides, which bear little resemblance to those of niobium and tantalum (*118*).

C. PROTACTINIUM MONOXIDE

Oxide films form readily on protactinium metal and the monoxide PaO has been identified (*125*) by X-ray powder diffraction. It is cubic, like other actinide monoxides, with $a_0 = 4.961$ Å and slowly oxidizes to PaO_2.

D. MIXED OXIDE PHASES

The results of solid state reactions of protactinium dioxide and pentoxide with other metal oxides (*89*, *93–96*) support the view that the oxide systems of protactinium resemble those of other actinide elements rather than those of niobium and tantalum. However, when assessing results of this type one must always bear in mind the relative ionic radii of the respective M^{4+} and M^{5+} ions since they obviously play a large part in determining the structures of the complex phases. This comment applies equally well, of course, to the structural properties of other types of compound and in particular to the high coordination numbers exhibited by protactinium(V) in its chloro and nitrato complexes.

TABLE XII

BINARY PROTACTINIUM OXIDE PHASES

Composition	Color	Symmetry[a]	Lattice parameters (Å) a_0	b_0	c_0	Range of existence (°C)	Ref.
Pa_2O_5	White	Cubic	5.446	—	—	650–700	(*125*)
Pa_2O_5	White	Tetragonal (T3)[b]	5.429	—	5.503	700–1000	(*118*)
Pa_2O_5	White	Hexagonal	3.817	—	13.220	1000–1500	(*118*)
Pa_2O_5	White	Rhombohedral (R2)[c]	5.424	$\alpha = 89.76°$	—	1240–1400	(*118*)
Pa_2O_5	White	Orthorhombic	6.92	4.02	4.18	?	(*125*)
$PaO_{2.42}$-$PaO_{2.44}$	White	Rhombohedral (R1)	5.449	$\alpha = 89.65°$	—	—	(*118*)
$PaO_{2.40}$-$PaO_{2.42}$	White	Tetragonal (T2)	5.480	—	5.416	—	(*118*)
$PaO_{2.33}$	Black	Tetragonal (T1)	5.425	—	5.568	—	(*118*)
$PaO_{2.18}$-$PaO_{2.21}$	Black	Cubic (C2)	5.473	—	—	—	(*118*)
PaO_2	Black	Cubic (C1)	5.505	—	—	—	(*118*, *125*)
PaO	—	Cubic	4.961	—	—	—	(*125*)

[a] C1, T1, etc. refer to the phases reported by Roberts and Walter (*118*).

[b] Stchouzkoy *et al.* (*128*, *129*) quote a_0 and b_0 values twice those listed.

[c] Mixed with the hexagonal phase (*118*, *128*, *129*).

The various phases which have been identified in the Pa_2O_5–M^I_2O, Pa_2O_5–$M^{II}O$, Pa_2O_5–$M^{III}_2O_3$, Pa_2O_5–$M^V_2O_5$, PaO_2–$M^{IV}O_2$, PaO_2–$M^V_2O_5$, and BaO–Pa_2O_5–$M^{III}_2O_3$ phase systems are listed in Table XIII together with preparative details and crystallographic results (*89*, *93–96*).

Ternary oxides of the type $Pa^{IV}M^{IV}O_4$ (M^{IV} = Ge and Si), analogous to those formed by other tetravalent actinides, are known for protactinium(IV), but not for niobium(IV) and tantalum(IV). In addition, the protactinium(V) phase $PaNb_3O_{10.67}$ corresponds to $UNb_3O_{10.67}$, and with the sesquioxides of the lanthanides and actinides double oxides of the type $(M^{III}_{0.5}Pa^V_{0.5})O_2$ are formed which take up more $MO_{1.5}$ (*44*) or $PaO_{2.5}$ (*89*) in solid solution without destroying the fluorite type of structure. The variation in the lattice parameter of the phases of the types $M^{III}_{0.5}Pa_{0.5}O_2$ and $M^{III}_{0.25}Pa_{0.75}O_{2.25}$ (M^{III} = lanthanide element) with the ionic radius of the lanthanide element is illustrated in Fig. 9. In contrast to the behavior of protactinium(V) Nb_2O_5 and Ta_2O_5 react with lanthanide sesquioxides to form four distinct types of compound (*89*). The fluorite phases $(M^{III}_{0.5}, Pa^V_{0.5})O_2$ react with BaO above 1350°C to

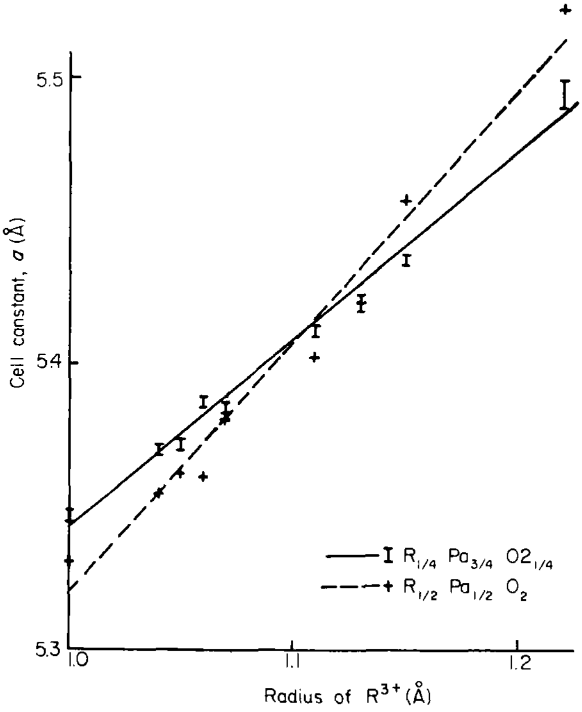

FIG. 9. Unit cell constants of $R_xPa_{1-x}O_{2.5-x}$ (*89*).

TABLE XIII

MIXED OXIDE PHASES OF PROTACTINIUM[a]

Compound	Preparative method	Symmetry/ structure type	Lattice parameters				Isostructural compounds with Pa replaced by:
			a	b	c	$\beta°$	
$LiPaO_3$	$LiO + Pa_2O_5/600°C/2 \times 8\ h/O_2$[e]	Unknown	—	—	—	—	—
Li_3PaO_4	$LiO + Pa_2O_5/600°C/2 \times 8\ h/O_2$	Tetragonal, Li_3UO_4	4.52	—	8.48	—	U, Np, Pu, Am
Li_7PaO_6	$LiO + Pa_2O_5/600°C/2 \times 8\ h/O_2$	Hexagonal, Li_7BiO_6	5.55	—	15.84	—	U, Np, Pu, Am
$(2–4)Li_2O \cdot Pa_2O_5$[d]	$Li_2CO_3 + Pa_2O_5$	Cubic, fluorite phase	—	—	—	—	—
$(2–4)Na_2O \cdot Pa_2O_5$[d]	$Na_2CO_3 + Pa_2O_5$	—	—	—	—	—	—
$NaPaO_3$	$Na_2O_2 + Pa_2O_5/500°C/2 \times 8\ h/Ar$	Orthorhombic, $GdFeO_3$	5.82	5.97	8.36	—	U
Na_3PaO_4	$Na_2O_2 + Pa_2O_5/500°C/2 \times 8\ h/Ar$	Tetragonal, Li_3SbO_4	6.68	—	9.60	—	—
$KPaO_3$	$K_2CO_3 + Pa_2O_5/600°C/2 \times 8\ h/O_2$	Cubic, $CaTiO_3$	4.341	—	—	—	U
$RbPaO_3$	$Rb_2CO_3 + Pa_2O_5/500°C/2 \times 8\ h/O_2$	Cubic, $CaTiO_3$	4.368	—	—	—	U
$CsPaO_3$	$Cs_2CO_3 + Pa_2O_5/500°C/2 \times 8\ h/O_2$	Unknown	—	—	—	—	—
$BaPaO_3$[c]	$BaO + PaO_2/1200°C/8\ h/vacuum$	Cubic, $CaTiO_3$	4.45	—	—	—	U, Np, Pu, Am
$SrPaO_3$[c]	$SrO + PaO_2/1200°C/8\ h/vacuum$	Unknown	—	—	—	—	—
$Ba(Ba_{0.5}, Pa_{0.5})O_{2.75}$[c]	$BaO + Pa_2O_5/1350°C/2 \times 6\ h/O_2$	Cubic, Ba_3WO_6	8.932	—	—	—	Nb, Ta, U
$Ba(Sr_{0.5}, Pa_{0.5})O_{2.75}$[c]	$BaO + SrO + Pa_2O_5/2 \times 6\ h/O_2$	Cubic, Ba_3WO_6	8.860	—	—	—	—
$Sr(Ba_{0.5}, Pa_{0.5})O_{2.75}$	$BaO + SrO + Pa_2O_5/2 \times 6\ h/O_2$	Cubic, Ba_3WO_6	8.784	—	—	—	—
$GaPaO_4$	$Ga_2O_3 + Pa_2O_5/1200°C/8\ h/O_2$	Unknown	—	—	—	—	—

$(La_{0.5}, Pa_{0.5})O_2$	$La_2O_3 + Pa_2O_5$/1100°C/2 × 8 h/O_2	Cubic, CaF_2	5.525	—	—	—	b
$Ba(La_{0.5}, Pa_{0.5})O_3$	$BaO + (La_{0.5}, Pa_{0.5})O_2$/1350°C/ 12 h/O_2	Cubic, Ba_3WO_6	8.885	—			b
$Sr(La_{0.5}, Pa_{0.5})O_3$	—	Cubic	8.462	—	—	—	b
α-$PaGeO_4$	$PaO_2 + GeO_2$/1100°C/2 × 12 h/ vacuum	Tetragonal, $CaWO_4$	5.106	—	11.38	—	Th, U, Np, Pu, Am
β-$PaGeO_4$[c]	α-$PaGeO_4 \xrightarrow{1200°C}$ hydrothermal/ 230°C/5d	Tetragonal, $ZrSiO_4$	7.068	—	6.509	—	Th, U, Np
α-$PaSiO_4$[c]	Hydrothermal/230°C/5d[e]	Tetragonal, $ZrSiO_4$	7.068	—	6.288	—	Th, U, Np, Pu, Am
β-$PaSiO_4$[c]	α-$SiO_4 \xrightarrow{1200°C} PaO_2 + SiO_2$/ 1250°/8 h/vacuum	Monoclinic, $CePO_4$	6.76	6.92	6.45	104° 50′	Th
Pa_2O_5/ThO_2	$Pa_2O_5 + ThO_2$/1100°C/8 h/O_2	Cubic, fluorite phase	—	—	—	—	—
	$(Pa, Th)O_2 + O_2$/400°C	—	—	—	—	—	—
$PaO_2 \cdot 2Nb_2O_5$[c]	$PaO_2 + Nb_2O_5$/1200°C/20 min/ vacuum	Tetragonal, $Th_{0.25}NbO_3$	7.76	—	7.81	—	U, Np, Pu
$PaO_2 \cdot 2Ta_2O_5$[c]	$PaO_2 + Ta_2O_5$/1250°C/8 h/vacuum	Tetragonal	7.77	—	7.79	—	U, Np, Pu
$Pa_2O_5 \cdot 3Nb_2O_5$	$Pa_2O_5 + Nb_2O_5$/1150°C/8 h/O_2	Hexagonal, $UTa_3O_{10.67}$	7.48	—	15.81	—	—
$Pa_2O_5 \cdot 3Ta_2O_5$	$Pa_2O_5 + Ta_2O_5$/1200°C/8 h/O_2	Hexagonal	7.425	—	15.76	—	—

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[a] From Keller *et al.* (*93–96*).

[b] Isostructural compounds when La was replaced by lanthanide, Sc, Y, In, Pu, Am, and Cm.

[c] Could not be prepared in the pure state, always contained varying amounts of Pa(V).

[d] Range of composition.

[e] *h*, hours; *d*, days.

form compounds of the type $Ba(M^{III}_{0.5}, Pa^{V}_{0.5})O_3$ which possess an ordered perovskite structure (*93*). Analogous uranium(V), niobium(V), and tantalum(V) compounds are known.

VII. Nitrates

Protactinium pentanitrate is unknown, but a few hexanitrato complexes of the type $M^IPa(NO_3)_6$ and the oxynitrates $Pa_2O(NO_3)_8 \cdot 2CH_3CN$ and $PaO(NO_3)_3 \cdot xH_2O$ $(1 < x < 4)$ have been prepared.

A. OXYNITRATES

Protactinium pentoxide is insoluble in fuming nitric acid, but the freshly prepared hydroxide, the pentachloride, pentabromide, and the complex $SO(PaCl_6)_2$ all dissolve rapidly to form stable concentrated solutions (*49*, *90*). The rapid, almost quantitative dissolution of the hydroxide, yielding solutions 0.5 *M* in Pa(V), contrasts markedly with weak complexing in aqueous nitric acid (up to 12 *M*) and the instability of solutions $>10^{-5}$ *M* Pa(V) in this solvent. Hydrolytic condensation is not observed during several days in fuming nitric acid solution and vacuum evaporation of such solutions obtained by dissolution of the pentahalides yields an oxytrinitrate hydrate of variable water content, $PaO(NO_3)_3 \cdot xH_2O$ $(1 < x < 4)$. This compound decomposes in a vacuum above 50°C, but no other stable nitrates are formed, the ultimate product being the pentoxide. It has been suggested (*49*), on the basis of infrared results, that the hydrate is polymeric with Pa–O–Pa groups present rather than discrete PaO^{3+} groups. The stability of protactinium(V) solutions in concentrated (16 *M*) nitric acid has been utilized during the recent determination of the half-life of protactinium-231 (*36*).

Protactinium pentahalides react with gaseous dinitrogen tetroxide in anhydrous methyl cyanide to form $Pa_2O(NO_3)_8 \cdot 2CH_3CN$, a white, soluble solid (*49*). Infrared results show that the nitrates are covalently bonded and that Pa–O–Pa bridges are present in this complex. It is not possible to remove the coordinated methyl cyanide by vacuum heating without effecting complex decomposition to the pentoxide. This behavior differs from that observed with niobium(V) which forms the polymeric complex, $Nb_3O_6(NO_3)_3CH_3CN$ $(NbO_2NO_3 \cdot 0.67CH_3CN)$ under similar reaction conditions (*20*).

B. HEXANITRATO COMPLEXES

Pentavalent hexanitrato complexes of the type $M^IPa(NO_3)_6$ (M^I = Cs, NMe_4, and NEt_4) have been prepared by the reaction between hexachloroprotactinates(V) and liquid dinitrogen pentoxide at room temperature (*49*, *90*). The white, moisture-sensitive solids, are obtained by removal of excess dinitrogen pentoxide *in vacuo*. Infrared studies have shown that the nitrate is covalently bonded. In contrast to these reactions hexachloroniobates(V) and tantalates(V) react to form oxytetranitrato complexes of the type $M^{I}M^{V}O(NO_3)_4$ (M^{I} = NMe_4, NEt_4; M^{V} = Nb, Ta). Uranium(V) nitrato complexes are unknown.

Attempts to prepare protactinium pentanitrate by reacting pentahalides with liquid dinotrogen pentoxide have resulted in the formation of $HPa(NO_3)_6$, possibly as a result of traces of anhydrous nitric acid present in the N_2O_5 (*49*). The presence of the proton has not been confirmed by electron spin resonance studies, but infrared results have shown that all the nitrate is covalently bound and vibrations associated with the nitronium and nitrosonium cations were not observed. Niobium and tantalum pentahalides react under similar conditions to form the anhydrous oxytrinitrates, $M^{V}O(NO_3)_3$ (*20*, *87*).

No structural data are available for any of the pentavalent nitrates. Tetravalent protactinium nitrates are unknown. Fuming nitric acid oxidizes protactinium(IV) and obviously N_2O_4 and N_2O_5 will do the same. However, it may be possible to prepare hexanitratoprotactinates(IV), $M^{I}_2Pa(NO_3)_6$, or even complexes of the type $Pa(NO_3)_4 \cdot xL$ (L = oxygen donor ligand), analogous to those known for uranium(IV), by metatheses in nonaqueous solvents.

VIII. Sulfates and Selenates

It was originally reported that $Pa_2(SO_4)_5$ crystallized from sulfuric acid (*100*), but more recent investigations (*14*, *19*) have shown that the product is trihydrogen-oxytrisulfatoprotactinate(V), $H_3PaO(SO_4)_3$. The analogous selenato complex, $H_3PaO(SeO_4)_3$, can be prepared by crystallization from selenic acid (*14*, *19*). It is important to remove excess acid by washing with nitrobenzene (H_2SO_4) or ethyl acetate (H_2SeO_4) at room temperature because decomposition occurs when the compounds are heated *in vacuo*. Controlled vacuum decomposition of $H_3PaO(SO_4)_3$ leads to the successive formation of $HPaO(SO_4)_2$, 375°–400°C, $HPaO_2SO_4$, 525°C, and finally Pa_2O_5, >600°C. $H_3PaO(SeO_4)_3$, however, decomposes directly to the pentoxide. Uranium(V) and neptunium(V) sulfates are unknown, the pentavalent state of both elements being unstable in sulfuric acid solution and there is little similarity between the protactinium(V) sulfates and those reported for niobium(V) and tantalum(V). Thus the compounds $M^{V}_2O(SO_4)_4$ (M^{V} = Nb and Ta), $Nb_2O_3(SO_4)_2$, $Nb_2O_2(SO_4)_3$, $Nb_2O_4SO_4$, and $Ta_2(SO_4)_5$ [or $(TaO_2)_2S_5O_{16}$]

have been characterized (*70*) and it would be interesting to investigate the protactinium(V)–sulfate system further using alternative preparative methods.

$H_3PaO(SO_4)_3$ and $H_3PaO(SeO_4)_3$ are isostructural, possessing hexagonal symmetry (Table XIV). Full structural details are not available, but infrared studies have indicated the presence of bidentate sulfate and selenate groups.

TABLE XIV

CRYSTALLOGRAPHIC DATA FOR SOME MISCELLANEOUS PROTACTINIUM COMPOUNDS

Compound	Color	Symmetry	Lattice parameters (Å)		Ref.
			a_0	c_0	
$H_3PaO(SO_4)_3$	White	Hexagonal	9.443	5.506	(*19*)
$H_3PaO(SeO_4)_3$	White	Hexagonal	9.743	5.679	(*19*)
PaOS	Yellow	Tetragonal	3.832	6.704	(*125*)
PaH_3	Black	Cubic	6.648	—	(*125*)

Although it is known that protactinium(V) precipitates from dilute sulfuric acid on the addition of potassium sulfate, the product, believed to be $K_3PaO(SO_4)_3$, has not been satisfactorily characterized (*19*, *28*, *105*). There is obviously scope for further research on the preparation of sulfato (and selenato) complexes of pentavalent protactinium. In addition, tetravalent protactinium sulfates, selenates, and their complexes have not been studied.

IX. Miscellaneous Compounds

The remaining compounds of protactinium are more conveniently dealt with together since they belong to several different classes.

Protactinium metal reacts with hydrogen to form the black hydride, PaH_3, which is isostructural with other actinide trihydrides; it has only been prepared in submilligram amounts and identified by X-ray powder diffraction analysis (*125*).

No binary sulfide has been reported, but the bright yellow oxysulfide, PaOS, isostructural with other actinide oxysulfides, has been obtained (*125*) by heating protactinium pentachloride or pentoxide in a mixture of carbon disulfide and hydrogen sulfide at 900° and 1200°C, respectively

(Table XIV). Gaseous ammonia reacts with both the penta- and the tetrachloride to yield a yellow solid believed to be a nitride and some evidence for the existence of a monocarbide has been observed during the reduction of protactinium tetrafluoride in a carbon crucible (*125*). Vapor pressure data for ^{233}Pa carbide produced by neutron irradiation of ThO_2 have recently been reported (*101*), but there is obviously scope for further studies involving the hydride, nitride, carbide, and sulfide systems of protactinium.

The fluorosulfate dihydrate, $PaF_2SO_4 \cdot 2H_2O$, analogous to the known uranium(IV) compound (*132*), is precipitated on the addition of aqueous hydrofluoric acid to solutions of protactinium(IV) in dilute sulfuric acid (*131*). Others (*71*, *84*) have reported the formation of a white, insoluble precipitate in hydrofluoric acid, believed to be a tetrafluoride hydrate, but the product has not been completely characterized.

A pentavalent protactinium peroxide is known to precipitate on the addition of hydrogen peroxide to mineral acid solutions of protactinium(V) (*28*, *29*, *78*, *127*, *129*, *135*) and this has been utilized during purification procedures, particularly to effect a separation from niobium(V) (*135*). The product from dilute sulfuric acid has been assigned the formula $Pa_2O_9 \cdot 3H_2O$ (*129*); at 200°C in air this decomposes to yield the pentoxide hydrate $Pa_2O_5 \cdot H_2O$. The peroxyprotactinate (V), $NaPaO_6 \cdot nH_2O$, has also been isolated from aqueous solution. It is a white solid which is insoluble in both 2 M NaOH and 1 M H_2O_2, but which dissolves in a mixture of these solutions.

It is well known that protactinium(V) can be precipitated from oxalic acid solution by the addition of hydrochloric acid. The resulting white solid has recently been reported (*111*, *112*) to have the composition $PaO(OH)C_2O_4 \cdot xH_2O$ $(1.5 < x < 4.0)$. Protactinium oxygen stretching vibrations observed at 778 cm^{-1} indicate the presence of Pa–O–Pa groups (*112*), but there is no evidence for the presence of discrete Pa=O groups. It is insoluble in dilute hydrochloric and oxalic acid solutions; it dissolves in 8 M HCl and is unstable in air, decomposing to the pentoxide at 340°C.

X. Appendix

THE THIRD INTERNATIONAL PROTACTINIUM CONFERENCE, SCHLOSS ELMAU, 1969

While this article was in press the Third International Conference on Protactinium Chemistry was held at Schloss Elmau, Mittenwald, West Germany in April, 1969. Many of the papers presented at this meeting contained new information on various aspects of the preparative chemistry of protactinium. In particular, the first examples of organometallic compounds and of protactinium(IV) and (V) chelates were reported, and new methods for the preparation of metallic protactinium were described, together with information on the carbides. The proceedings of the meeting will be published in full by the *Gesellschaft Deutscher Chemiker* and, therefore, in the following brief summary only the authors' names are quoted.

Twenty-mg batches of protactinium metal were prepared by lithium reduction of the tetrafluoride contained in a tapered tungsten spiral (Cunningham). The melting point of the metal, which does not react with tungsten under these conditions, was found to be 1565°C, which is close to the previously reported values of 1560° and 1575°C. An attractive alternative, so far only applied to thorium/protactinium mixtures, involves reduction of the iodide at 1200°–1400°C using the Van Arkel technique. The iodide was prepared *in situ* by iodination of the carbide (Lorenz and Scherff). Examination of the resulting Th/Pa alloys indicated protactinium solubilities in the α-thorium phase of 6.7% at 1300°C and 4.5% at room temperature. The possible formation of a Pt/Pa alloy (possibly Pt_3Pa) when PaO_2 is heated in a platinum boat in a hydrogen atmosphere at 700°–1400°C was also reported (Knoch and Schieferdecher).

The first reliable information on the protactinium–carbon system was reported by Lorenz and Scherff who prepared the monocarbide, PaC, by carbothermic reduction of Pa_2O_5. The dioxide, PaO_2, is first obtained at approximately 1100°C and is then converted to PaC above 1900°C. In the presence of excess carbon there is some evidence for the formation of the tetragonal dicarbide. Protactinium monocarbide is isostructural with other actinide monocarbides possessing the fcc NaCl-type of structure with $a_0 = 5.0608$ Å. In contrast to ThC and UC, however, it is stable in the atmosphere and is relatively inert toward acid solutions. By measuring the CO equilibrium pressures for the reaction,

$$PaO_2 + 3C \rightarrow PaC + 2CO$$

in the temperature range 1290°–1400°C, Lorenz and Scherff calculated the free energy of formation of PaO_2 as (0.039T–259.8) kcal mole^{-1}.

Protactinium(V) dioxymonofluoride, PaO_2F, is obtained by thermal decomposition of Pa_2OF_8 in air at 270°C (Bagnall *et al.*). It is a white, air-stable solid which decomposes to another, as yet unidentified, oxyfluoride at 450°–470°C which, in turn, decomposes to Pa_2O_5 above 650°C. Other papers on the protactinium halides describe a new, improved preparation of the pentabromide (Brown *et al.*) by metathesis of $PaCl_5$ using liquid boron tribromide and the first information on the heats of solution of tetravalent protactinium halides and oxydihalides (Fuger and Brown). In addition, Weigel *et al.* report that the vapor pressure of protactinium pentachloride is given by the equations:

$$\log P_{mm} = 17.27 - \frac{7377}{T} \text{ (liquid)}$$

and

$$\log P_{mm} = 23.87 - \frac{11162}{T} \text{ (solid)}$$

and that the melting and boiling points are, respectively, 306° and 420°C with $\Delta H_{fus.} = 22.2$ kcal $mole^{-1}$ and $\Delta H_{vap.} = 14.65$ kcal $mole^{-1}$.

Single crystal X-ray diffraction studies have shown that in Na_3PaF_8 each protactinium atom is surrounded by 8 fluorine atoms at the vertices of an almost perfect cube (Brown *et al.*). The Pa—F bond distance is 2.21 Å with F—F approaches of 2.47 and 2.60, respectively (Fig. 10); the sodium atoms are located between the PaF_8^{3-} cubes. This complex provides the first example of cubic 8-coordination for which it is believed the participation of *f*-orbitals in the bonding is necessary. Metal—fluorine bond distances for the isostructural Na_3UF_8 and Na_3NpF_8 are 2.21 and 2.19 Å, respectively.

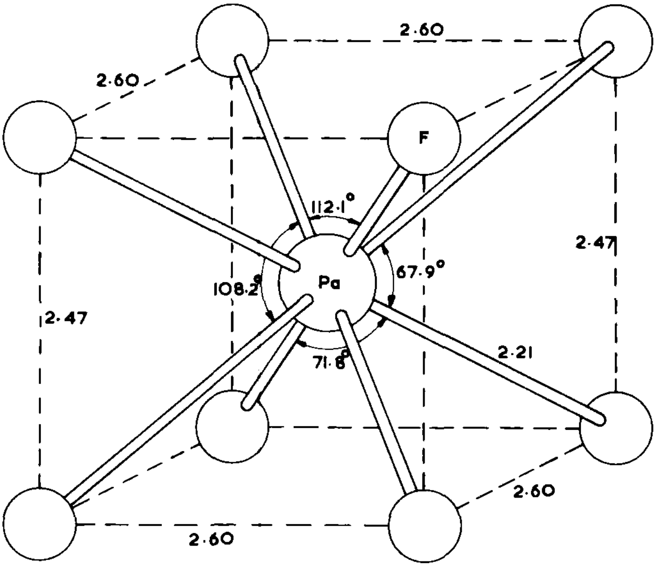

FIG. 10. Coordination around the protactinium atom in Na_3PaF_8.

The triphenylphosphine oxide–oxytrihalide complexes $PaOCl_3 \cdot 2TPPO$ and $PaOBr_3 \cdot 2TPPO$ are easily prepared by the addition of ethanol to the appropriate 1:2 pentahalide complex. Infrared studies suggest that these complexes are the first examples of protactinium(V) compounds containing the elusive Pa=O group, a strong, sharp band being observed at 920 cm^{-1} (Brown *et al.*).

Kanellakopulos has reported the preparation of the tetravalent dicyclopentadienyl, $Pa(C_5H_5)_4$, which is the first organometallic compound known for protactinium. It is obtained by heating the pentachloride with $Be(C_5H_5)_2$ in a vacuum, followed by removal of excess $Be(C_5H_5)_2$ at 80°C (10^{-3} mm Hg) and extraction of the residue with benzene. $Pa(C_5H_5)_4$ is an orange-yellow, air-sensitive solid which is slightly soluble in benzene, and is isostructural with analogous tetravalent actinide compounds. Protactinium pentaiodide is similarly reduced by phthalodinitrile in 1-chloronaphthalene at approximately 120°C to form the bisphthalocyanine complex $PaPc_2$, analogous to the recently reported thorium and uranium complexes (Lux *et al.*). Alternatively, it can be prepared directly from PaI_4. $PaPc_2$ is a dark-blue, air-stable solid, volatile *in vacuo* above 500°C (10^{-5} mm Hg) and is isostructural with $ThPc_2$ and UPc_2. Preliminary infrared and electron-spin resonance results are reported.

The protactinium pentahalides react with an excess of tropolone to form air-stable chelates of the type PaT_4X (T = tropolone; X = Cl, Br, and I) and with sodium diethyl dithiocarbamate(Nadtc) to form the moisture-sensitive compounds $Padtc_4Cl$ and $Padtc_4Br$ (Brown and Rickard). Attempts to replace the final halogen atom in these chelate compounds have been unsuccessful, but PaT_4Cl reacts with lithium tropolonate in alcohol to form PaT_4OEt, a red, air-stable solid which is converted to PaT_4Cl by 6 *M* HCl in acetone (50% v/v). PaT_4Cl is virtually insoluble in organic solvents but it reacts with dimethyl sulfoxide in methylene dichloride to yield dark red crystals of the complex $PaT_4Cl \cdot DMSO$. Single crystal studies (Brown and Rickard) have shown this complex to possess triclinic symmetry, space group $P\bar{1}$ with $a_0 = 9.87$, $b_0 = 12.60$, $c_0 = 15.96$ Å, $\alpha = 119.8°$, $\beta = 103.6°$, and $\gamma = 103.0°$. Infrared studies indicate that the chlorine atom in PaT_4Cl is ionic whereas it is covalently bonded in $Padtc_4Cl$ (ν_{Pa-Cl} at 317 cm^{-1}).

Although $PaCl_4$ is oxidized by tropolone in oxygen-free methylene dichloride, the reaction between lithium tropolonate and the tetrachloride yields either PaT_4 or $LiPaT_5$, depending on the amount of LiT used. These blue-green, air-sensitive solids are isostructural with their thorium(IV) analogs (Brown and Rickard). Np(IV), in contrast to Th(IV), Pa(IV), and U(IV), does not form the pentakis lithium salt. This is probably a consequence of the actinide contraction, Np(IV) (ionic radius, 0.92 Å) apparently being just too small to accommodate five-bonded tropolone molecules.

The acetylacetonate $Pa(acac)_2Cl_3$ has been prepared by direct reaction between protactinium pentachloride and acetylacetone in methylene dichloride. The addition of isopentane to this reaction mixture results in the formation of long, bright yellow needles of the complex, and single crystal studies have shown these to possess monoclinic symmetry, space group $P2_1/c$ with $a_0 = 8.01$, $b_0 = 23.42$, $c_0 = 18.63$ Å, and $\beta = 98.9°$ (Brown and Rickard). The structure of this compound is currently being determined.

Attempts to characterize the pentavalent iodate obtained by the addition of iodic acid to a solution of protactinium(V) in sulfuric acid (Muxart *et al.*) have indicated that the product contains a variable amount of iodate ($Pa{:}IO_3$ between 1:0.75 and 1:2.0) and more than twelve molecules of water. The infrared vibration associated with the iodate was observed as a broad band between 600 and 870 cm^{-1}. The white solid slowly decomposes with the liberation of iodine. The pentavalent phosphate, which precipitates from sulfuric acid solution on the addition of orthophosphoric acid is reported to have the composition $PaO(OH)PO_4 \cdot H_2O$ (Lecloarec and Muxart). Although infrared studies confirmed the presence of the PO_4^- ion it was not possible to unambiguously identify a band due to the $Pa{=}O$ group [cf. $H_3PaO(SO_4)_3$ (*19*)].

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