

The Protactinium(IV) Halides

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Protactinium tetrahalides, PaX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) have been prepared by reduction of the corresponding pentahalides by either aluminium or hydrogen at $400\text{--}450^\circ$. Protactinium tetrachloride and tetrabromide react with antimony trioxide at 200° in a vacuum to form the oxydihalides, PaOCl_2 and PaOBr_2 , respectively. A pink residue which forms on sublimation of protactinium tetraiodide has been identified, by X-ray powder diffraction analysis, as the oxydi-iodide, PaOI_2 . Some chemical properties, visible spectra, and X-ray powder diffraction results are reported for these compounds and for protactinium tetrafluoride, PaF_4 .

MOST of the recent preparative work on the chemistry of protactinium has consisted of studies with protactinium(V) (see, for example, refs. 1–3), and little work with the easily oxidised quadrivalent state has been reported. Thus, although all four pentahalides,^{4–10} and several quinequivalent oxyhalides, of the types^{4,6,8,10,11} Pa_2OX_8 ($\text{X} = \text{F}$ and Cl), PaOX_3 ($\text{X} = \text{Br}$ and I), and PaO_2X ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$), and the oxychloride $\text{Pa}_2\text{O}_3\text{Cl}_4$, have been characterised, the only quadrivalent halides known prior to our recent preliminary report¹² concerning the tetrabromide were^{13,14} the tetrafluoride and tetrachloride. Our own investigations have been extended, and we now report the preparation and some properties of protactinium tetraiodide, PaI_4 , and the oxydihalides PaOCl_2 , PaOBr_2 , and PaOI_2 , together with further details of the preparation and properties of the tetrachloride and tetrabromide.

Tetrahalides.—Protactinium tetrachloride was previously prepared^{13,14} either by reduction of the pentachloride with hydrogen at 800° or,¹³ less satisfactorily, by direct chlorination of the dioxide, PaO_2 , with carbon tetrachloride at 500° . We find that the former reaction is more easily carried out at 400° using stoichiometric quantities of the reagents for the reaction $2\text{PaCl}_5 + \text{H}_2 \longrightarrow 2\text{PaCl}_4 + 2\text{HCl}$ in a sealed Pyrex vessel. The tetrabromide is obtained similarly in virtually quantitative yield but the analogous reaction with the pentaiodide is less satisfactory, only 50% conversion being observed at about 520° . This can probably be attributed to the known instability of hydrogen iodide ($\Delta H = 31$ kcal.) and the fact that with the reaction carried out in a sealed tube the hydrogen iodide is not removed from the reaction zone as it is formed.

Although such reactions can be carried out safely using about 50 mg. of pentahalide in a 10-c.c. vessel, the combination of radiation hazards associated with protactinium-231 and the dangers inherent in sealing glass vessels containing hydrogen render the method unsafe with larger amounts. In addition, the use of a continuous flow of hydrogen over the pentahalide is not practicable owing to the fairly high volatility of the

pentahalides, particularly PaCl_5 , and the necessity for rigorous drying of the gas to prevent hydrolysis. However, we have successfully reduced 250-mg. amounts of the pentahalides with aluminium metal at $400\text{--}450^\circ$. With the appropriate reagents in a sealed evacuated Pyrex vessel the reactions proceed smoothly at this temperature; crystals of the yellow-green tetrachloride, bright red tetrabromide, or the black tetraiodide are deposited in a region of the vessel at 350° and the aluminium halide in a cooler region. When hot (350°), the tetrachloride is red and the tetrabromide is red-black; although crystals of the tetraiodide appear black the finely ground powder is dark green. The reactions apparently involve transport phenomena since the reaction temperature, $400\text{--}450^\circ$, is insufficient to volatilise the tetrahalides and yet they are obtained in a band well separated from the excess aluminium. During reduction of the pentaiodide, traces of the non-volatile, pink oxydi-iodide, PaOI_2 , are invariably formed in the region of the aluminium, but the tetrachloride and tetrabromide are obtained in virtually quantitative yields, although during one preparation of the tetrabromide a small amount (1–2 mg.) of a non-volatile, yellow solid which formed was identified crystallographically as the oxydibromide PaOBr_2 . Presumably this was due to incomplete degassing of the reaction vessel. Although an excess of aluminium is present in these reactions, we have not observed the formation of tervalent protactinium halides at the above temperatures.

Protactinium tetrachloride, tetrabromide, and tetraiodide can be sublimed slowly above 500° in a vacuum (10^{-4}mm.) but at this temperature the tetraiodide invariably reacts to a certain extent with the silica vessel, leaving a pink residue of the non-volatile oxydi-iodide. We attribute the formation of protactinium(IV) oxydi-iodide under these conditions to direct reaction between PaI_4 and the silica rather than to the presence of traces of water in the silica, because on prolonged heating at $450\text{--}500^\circ$ prior to sublimation the tetraiodide appears quite stable.

¹ D. Brown and A. G. Maddock, *Quart. Rev.*, 1963, **17**, 289.

² C. Keller, *Angew. Chem., Internat. Edn.*, 1966, **5**, 23.

³ "Physico Chimie du Protactinium," Pub. No. 154, Centre National de la Recherche Scientifique, Paris, 1966.

⁴ L. Stein, *Inorg. Chem.*, 1964, **3**, 995.

⁵ A. V. Grosse, *J. Amer. Chem. Soc.*, 1934, **56**, 2200.

⁶ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 874.

⁷ A. G. Maddock and D. Toms, unpublished observations.

⁸ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 262.

⁹ D. Brown, J. F. Easey, and P. J. Jones, to be published.

¹⁰ D. Brown, ref. 3, p. 147.

¹¹ D. Brown and J. F. Easy, to be published.

¹² D. Brown and P. J. Jones, *Chem. Comm.*, 1966, 279.

¹³ P. A. Sellers, S. Fried, R. E. Elson, and W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

¹⁴ R. Elson, S. Fried, P. A. Sellers, and W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1950, **72**, 5791.

X-Ray powder diffraction results have confirmed that the tetrachloride is isostructural with other actinide tetrachlorides,¹⁵ and have shown that the tetrabromide is isostructural with the tetragonal modification of thorium

are in excellent agreement with those previously reported by others^{13,14} ($a_0 = 8.377$, $c_0 = 7.482 \pm 0.004$ Å). For the tetragonal cell of the tetrabromide we find $a_0 = 8.824$ and $c_0 = 7.957 \pm 0.002$ Å, giving a

TABLE 1
Partial X-ray powder diffraction patterns for protactinium tetrachloride and tetrabromide

| PaCl ₄ | | | | PaBr ₄ | | | |
|-----------------------------|------------------------------|-------------|------------------|-----------------------------|------------------------------|----------|------------------|
| $\sin^2\theta_{\text{obs}}$ | $\sin^2\theta_{\text{calc}}$ | h,k,l | I_{est} | $\sin^2\theta_{\text{obs}}$ | $\sin^2\theta_{\text{calc}}$ | h,k,l | I_{est} |
| 0.0192 | 0.0193 | 1,0,1 | S | 0.0172 | 0.0173 | 1,0,1 | S— |
| 0.0340 | 0.0341 | 2,0,0 | S | 0.0310 | 0.0309 | 2,0,0 | S— |
| 0.0532 | 0.0532 | 2,1,1 | S— | 0.0479 | 0.0480 | 2,1,1 | W— |
| 0.0597 | 0.0597 | 1,1,2 | S— | 0.0532 | 0.0532 | 1,1,2 | M |
| 0.0680 | 0.0680 | 2,2,0 | W— | 0.0686 | 0.0686 | 2,0,2 | M+ |
| 0.0765 | 0.0766 | 2,0,2 | W+ | 0.0786 | 0.0786 | 3,0,1 | S— |
| 0.0872 | 0.0871 | 3,0,1 | S— | 0.0927 | 0.0926 | 1,0,3 | S |
| 0.1044 | 0.1043 | 1,0,3 | S— | 0.1092 | 0.1091 | 3,2,1 | M+ |
| 0.1213 | 0.1210 | 3,2,1 | S— | 0.1144 | 0.1144 | 3,1,2 | S— |
| 0.1274 | 0.1274 | 3,1,2 | S | 0.1227 | { | 0.1227 { | 4,0,0 |
| 0.1357 | 0.1357 | 4,0,0 | M | 0.1232 | { | 0.1232 { | 2,1,3 |
| 0.1383 | 0.1382 | 2,1,3 | M | 0.1396 | { | 0.1397 { | 4,1,1 |
| 0.1549 | 0.1548 | 4,1,1 | M— | 0.1536 | { | 0.1532 { | 4,2,0 |
| 0.1698 | 0.1701 | 0,0,4 | M— | 0.1537 | { | 0.1537 { | 3,0,3 |
| 0.1723 | 0.1721 | 3,0,3 | M— | 0.1600 | | 0.1602 | 4,0,2 |
| 0.1950 | 0.1951 | 3,3,2 | M+ | 0.1755 | | 0.1755 | 3,3,2 |
| 0.2139 | 0.2040 | 2,0,4 | W+ | 0.1813 | | 0.1812 | 2,0,4 |
| 0.2227 | 0.2225 | { | M+ | 0.2005 | 0.2007 | { | 4,3,1 |
| 0.2381 | 0.2378 | 4,3,1 | W+ | 0.2115 | | 0.2117 | 5,0,1 |
| 0.2396 | 0.2397 | 5,0,1 | M+ | 0.2149 | | 0.2147 | 2,2,4 |
| 0.2558 | 0.2561 | 2,2,4 | W+ | | | | 4,1,3 |
| 0.2627 | 0.2628 | 4,1,3 | M+ | 0.2269 | | 0.2270 | M+ |
| 0.2715 | 0.2713 | 5,2,1 | W— | 0.2366 | | 0.2366 | W— |
| 0.3051 | 0.3049 | 5,1,2 | W+ | 0.2732 | { | 0.2728 { | 4,0,4 |
| 0.3078 | 0.3054 | 4,0,4 | W+ | 0.2734 | { | 0.2734 { | 2,1,5 |
| 0.3078 | 0.3080 | 6,0,0 | M+ | 0.2756 | { | 0.2759 { | 5,0,1/4,3,1 |
| 0.3241 | 0.3240 | 4,0,4 | W+ | 0.2756 | { | 0.2755 { | 6,0,0 |
| 0.3304 | 0.3304 | 2,1,5 | M+ | 0.2922 | | 0.2922 | 6,1,1 |
| 0.3396 | 0.3393 | 6,1,1 | W— | 0.2976 | | 0.2974 | W |
| 0.3753 | 0.3756 | 5,3,2 | W+ | 0.3036 | | 0.3032 | 4,2,4 |
| 0.3901 | 0.3900 | 6,2,0 | M | 0.3059 | { | 0.3058 { | 6,2,0 |
| 0.3995 | 0.3993 | 5,2,3 | M | 0.3342 | { | 0.3342 { | 3,2,5 |
| 0.4087 | 0.4088 | 3,2,5 | W+ | 0.3532 | { | 0.3534 { | 1,1,6 |
| 0.4252 | 0.4254 | 4,1,5 | M— | 0.3646 | { | 0.3647 { | 4,1,5 |
| 0.4402 | 0.4402 | 7,0,1 | W— | 0.3676 | { | 0.3674 { | 6,1,3 |
| 0.4430 | 0.4427 | 6,4,0 | W | 0.3676 | { | 0.3676 { | 2,0,6 |
| 0.4594 | 0.4593 | 5,4,3 | W+ | 0.3836 | { | 0.3839 { | 7,0,1 |
| 0.4657 | 0.4656 | 7,2,1 | W— | 0.3972 | { | 0.3974 { | 6,4,0 |
| 0.4771 | 0.4765 | 5,0,5/4,3,5 | M | 0.4095 | { | 0.4098 { | 5,4,3 |
| 0.5085 | 0.5084 | 6,2,4 | M— | 0.4140 | { | 0.4141 { | 5,3,4 |
| 0.5110 | 0.5108 | 5,2,5 | M | 0.4191 | { | 0.4193 { | 7,2,1 |
| 0.5330 | 0.5332 | 7,3,2 | W+ | 0.4253 | { | 0.4249 { | 7,1,2 |
| | | | | | { | 0.4253 { | 5,5,2 |
| | | | | | { | 0.4555 { | 6,0,4 |
| | | | | | { | 0.4559 { | 5,0,5/4,3,5 |
| | | | | | { | 0.4801 { | 6,2,4 |
| | | | | | { | 0.4975 { | 5,2,5 |
| | | | | | { | 0.5055 { | 7,3,2 |
| | | | | | { | 0.5361 { | 2,1,7 |
| | | | | | { | 0.5362 { | 8,1,1 |
| | | | | | { | | 7,4,1 |
| | | | | | { | | 5,1,6 |

W, Weak; M, medium; S, strong.

tetrabromide^{16,17} and not with uranium tetrabromide which is reported to be monoclinic.¹⁸ The dimensions which we have obtained for the tetragonal unit cell of PaCl₄, namely $a_0 = 8.377$ and $c_0 = 7.479 \pm 0.001$ Å,

calculated density of 5.90 g. cm.⁻³ for 4 molecules per unit cell. The observed and calculated values of $\sin^2\theta$ for both the tetrachloride and tetrabromide are listed in Table 1 together with the visually estimated intensities

¹⁵ J. J. Katz and I. Sheft, *Adv. Inorg. Chem. Radiochem.*, 1960, **2**, 195.

¹⁶ R. W. M. D'Eye, *J. Chem. Soc.*, 1950, 2764.

¹⁷ D. E. Scaife, *Inorg. Chem.*, 1966, **5**, 162.

¹⁸ R. M. Douglass and E. Staritsky, *Analyt. Chem.*, 1964, **29**, 459.

of the reflections. In a preliminary communication we stated that one of the reflections observed for PaBr_4 did not conform with the space group $I4_1/amd$ suggested by D'Eye¹⁶ for thorium tetrabromide. Further refinement has shown this to be in error and that in fact all the observed reflections (up to $\theta = 50^\circ$) can be satisfactorily indexed on the basis of this space group. However, in view of the recent work on ThBr_4 by Scaife,¹⁷ who has observed three reflections which do not fit $I4_1/amd$, this space group must be regarded as tentative until single-crystal results are available.

Although it is well established^{5,13} that protactinium tetrafluoride is formed by the action of an equimolar mixture of hydrogen and hydrogen fluoride on the pentoxide at 500° , and it is stated to be isostructural with other actinide tetrafluorides, only preliminary crystallographic data have yet been reported,¹⁹ and the unit cell ($a_0 = 12.70$, $b_0 = 10.70$, $c_0 = 8.42$ Å, $\beta = 126.3^\circ$) is not intermediate between those of thorium and uranium tetrafluoride as one might expect.

The observed powder reflections for our preparations of the tetrafluoride are in Table 2. It has been claimed²⁰

TABLE 2
Partial X-ray powder diffraction pattern for
protactinium tetrafluoride

| $\sin^2\theta_{\text{obs}}$ | I_{est} | $\sin^2\theta_{\text{obs}}$ | I_{est} |
|-----------------------------|------------------|-----------------------------|------------------|
| 0.0334 | M+ | 0.1634 | S |
| 0.0352 | W | 0.1680 | W— |
| 0.0376 | M | 0.1941 | W— |
| 0.0428 | S | 0.2011 | W— |
| 0.0458 | M | 0.2150 | W |
| 0.0533 | S— | 0.2335 | W— |
| 0.0795 | W— | 0.2405 | W— |
| 0.0945 | W— | 0.2582 | W— |
| 0.1314 | W+ | 0.2702 | W—, diffuse |
| 0.1391 | S, diffuse | 0.2861 | S— |
| 0.1483 | M— | 0.2944 | W— |
| 0.1544 | M | 0.3035 | W— |
| 0.1577 | M | 0.3109 | W— |

that similar results for uranium tetrafluoride can be unambiguously indexed, thus permitting refinement of the powder results to give accurate unit cell dimensions. We find, however, that for almost every reflection there are two or more sets of indices which would give good agreement between observed and calculated values of $\sin^2\theta$ and also satisfy the space group requirements (C_2/C_{2h}^6). In view of the sizes of the unit cells of the actinide tetrafluorides this is hardly surprising, and since Professor B Cunningham is currently²¹ carrying out single-crystal studies on protactinium tetrafluoride we report here only the observed powder pattern.

We have been unable to obtain good quality powder photographs of protactinium tetraiodide, and, although the few reflections observed were similar to those found on films of thorium tetraiodide, one cannot state unequivocally that the compounds are isostructural.

The changes in the unit cell dimensions of the isostructural actinide tetrachlorides and tetrabromides with decreasing ionic radius are illustrated in Table 3.

TABLE 3

Crystallographic data* for some actinide tetrachlorides† and tetrabromides

| Compound | Colour | Unit cell dimensions (Å) | | | Density (calc.) (g. cm. ⁻³) |
|-----------------------|--------------|--------------------------|-------|-------|---|
| | | a_0 | b_0 | c_0 | |
| ThCl_4 | White | 8.473 | — | 7.468 | 4.60 |
| PaCl_4 ‡ ... | Yellow-green | 8.377 | — | 7.479 | 4.68 |
| UCl_4 | Green | 8.296 | — | 7.487 | 4.87 |
| NpCl_4 | Red-brown | 8.290 | — | 7.460 | 4.92 |
| ThBr_4 † ... | White | 8.939 | — | 7.964 | 5.76 |
| PaBr_4 ‡ ... | Bright red | 8.824 | — | 7.957 | 5.90 |

* Unless otherwise stated, data quoted are those from Table IV, ref. 15. † All are tetragonal, space group $I4_1/amd$, $n = 4$. ‡ This work.

Protactinium tetrachloride, tetrabromide, and tetraiodide, like their actinide analogues, are moisture sensitive, and hydrolysis, followed by oxidation, occurs fairly rapidly in the atmosphere. The tetrachloride and tetrabromide can be safely stored for several months in an argon atmosphere (oxygen content <30 p.p.m.; water content <60 p.p.m.). The stability of the tetraiodide under similar conditions has not been examined. There remains therefore the possibility of radiation decomposition on prolonged storage of the tetraiodide. The dark brown tetrafluoride, on the other hand, can be safely handled in the atmosphere for a limited period of time although hydrolysis and oxidation do take place slowly during several months.

Apart from the tetrafluoride, the tetrahalides all dissolve readily in aqueous mineral acids (excepting hydrofluoric acid), to form solutions which are quite stable in the absence of dissolved oxygen. However, as observed previously, aerial oxidation of such solutions is quite rapid²²⁻²⁶ and is followed, even in 11.8M-hydrochloric acid solution [$4 \times 10^{-3}\text{M Pa(IV)}$], by hydrolytic condensation and precipitation of the resulting protactinium(v). Dilute solutions of the tetrachloride [$\sim 10^{-4}\text{M Pa(IV)}$] are colourless in molar hydrochloric acid and pale green in 11.8M-hydrochloric acid; at higher concentrations [$\sim \text{M-Pa(IV)}$] 11.8M-hydrochloric acid solutions are an intense yellow-green colour and those in 8M-hydrobromic acid are pale green. Previous reports¹ that solutions of protactinium(IV) in aqueous mineral acids are colourless are quite consistent with these observations, since only dilute acid solutions, approximately 10^{-4}M in Pa(IV) , were examined. The tetrahalides, when dissolved in molar hydrochloric acid solution, all showed the characteristic²²⁻²⁶ protactinium(IV) spectrum although bromide and iodide "cut-off" in the ultraviolet prevented

¹⁹ L. Stein, ref. 3, p. 101.

²⁰ J. Shankar, P. G. Khubchandani, and V. M. Padmanabhan, *Analyt. Chem.*, 1957, **29**, 1374.

²¹ B. B. Cunningham, personal communication.

²² D. Brown, Thesis, Sheffield University, 1960.

²³ D. Brown and R. G. Wilkins, *J. Chem. Soc.*, 1961, 3804.

²⁴ S. Fried and H. Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 4863.

²⁵ K. W. Bagnall and D. Brown, *J. Chem. Soc. (A)*, 1967, 275.

²⁶ P. Guillaumont, Thesis, Paris University, 1966.

measurement of all three peaks in the case of the tetrabromide and of the tetraiodide. We find that the spectrum of protactinium(IV) changes with increasing hydrochloric acid concentration; the results of these investigations have recently been published²⁵ elsewhere.

Protactinium tetrachloride, tetrabromide, and tetraiodide, like their thorium and uranium analogues,^{27,28} react with anhydrous, oxygen-free methyl cyanide to form¹² the sparingly soluble complexes $\text{MX}_4 \cdot 4\text{MeCN}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). Their solutions in methyl cyanide are respectively green-yellow, orange, and burgundy in colour. They are also soluble in acetone and alcohol but insoluble in isopentane. The tetrachloride reacts with caesium chloride in 11.8M-hydrochloric acid to form the sparingly soluble hexachloro-salt Cs_2PaCl_6 , and similar hexahalogeno-complexes R_2PaX_6 ($\text{R} = \text{NMe}_4, \text{NEt}_4, \text{Ph}_3\text{MeAs}$; $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) can be prepared by reaction of the appropriate halides in anhydrous methyl cyanide as for the thorium(IV) and uranium(IV) complexes.^{27,29} These hexahalogeno-complexes have recently been the subject of a separate communication.³⁰

The addition of an excess of oxygen-free aqueous ammonia to solutions of protactinium(IV) or to the solid tetrahalides themselves results in the formation of the characteristic³⁰ gelatinous black quadrivalent hydroxide which on exposure to air is oxidised to the white protactinium(V) hydroxide. As discussed in a previous publication³⁰ the report³¹ that protactinium(IV) hydroxide is white appears to be incorrect and the other precipitation reactions described for protactinium(IV), which are also³¹ strikingly similar to those given by protactinium(V) (for a comparison see ref. 1, p. 298), should be treated with reserve pending future work.

Oxydihalides.—Protactinium tetrachloride and dioxide react at 600° to form the oxydichloride, PaOCl_2 ; the reaction does not, however, go to completion even in the presence of excess of tetrahalide. This is probably due to the inert nature of the dioxide which was prepared by hydrogen reduction of the pentoxide at 1600°, and although the above technique is applicable to the preparation of thorium(IV) and uranium(IV) oxydihalides³² it is not as satisfactory for the preparation of pure protactinium(IV) compounds.

However, the tetrachloride and tetrabromide react at 150–200° with antimony trioxide, Sb_2O_3 , to yield pure samples of the dark green PaOCl_2 and orange-yellow PaOBr_2 , respectively. Similar reactions have recently been used to prepare the first³³ oxychlorotantalates(V), e.g., CsTaOCl_4 , and certain thorium(IV) and uranium(IV) oxydihalides.³⁴ The protactinium(IV) compounds are isostructural with the latter; values of $\sin^2\theta$ for the reflections observed on X-ray powder diffraction patterns

of these two protactinium(IV) oxydihalides are in Table 4. The results have not yet been interpreted. The analogous reaction involving protactinium tetraiodide has not been attempted, but traces of a pink, non-volatile solid obtained on vacuum-sublimation of the tetraiodide have been identified as PaOI_2 by X-ray powder diffraction analysis. The observed X-ray powder diffraction pattern of PaOI_2 is compared with that³⁵ of ThOI_2 in

TABLE 4
Partial X-ray powder diffraction patterns for
 PaOCl_2 and PaOBr_2

| PaOCl_2 | | | | PaOBr_2 | | | |
|-----------------------------|------------------|-----------------------------|------------------|-----------------------------|------------------|-----------------------------|------------------|
| $\sin^2\theta_{\text{obs}}$ | I_{est} | $\sin^2\theta_{\text{obs}}$ | I_{est} | $\sin^2\theta_{\text{obs}}$ | I_{est} | $\sin^2\theta_{\text{obs}}$ | I_{est} |
| 0.0100 | S | 0.0926 | W | 0.0091 | S | 0.1139 | W |
| 0.0189 | W | 0.0978 | W | 0.0172 | W– | 0.1186 | W– |
| 0.0266 | W– | 0.1010 | W | 0.0358 | M+ | 0.1249 | W– |
| 0.0296 | W | 0.1052 | W– | 0.0436 | W | 0.1327 | W+ |
| 0.0367 | W | 0.1069 | W | 0.0451 | W | 0.1429 | M+ |
| 0.0395 | M+ | 0.1166 | W | 0.0465 | M | 0.1482 | W– |
| 0.0466 | W– | 0.1211 | W | 0.0525 | M | 0.1513 | W– |
| 0.0485 | S– | 0.1279 | W | 0.0627 | M | 0.1635 | W+ |
| 0.0559 | M | 0.1434 | M– | 0.0643 | W | 0.1793 | M |
| 0.0580 | M | 0.1470 | M | 0.0723 | M | 0.1898 | W– |
| 0.0613 | M+ | 0.1548 | M+ | 0.0743 | M | 0.2198 | W+ |
| 0.0661 | M– | 0.1574 | M | 0.0784 | M+ | 0.2268 | W+ |
| 0.0689 | M | 0.1773 | M– | 0.0845 | W+ | 0.2335 | W+ |
| 0.0762 | M | 0.1861 | W | 0.0902 | M+ | 0.2415 | W |
| 0.0791 | M | 0.1901 | W– | 0.0953 | M– | 0.2458 | W |
| 0.0844 | W+ | 0.1945 | M– | 0.1002 | M– | 0.2536 | W– |
| 0.0865 | W+ | 0.2133 | M– d | 0.1045 | W+ | 0.2686 | W– |
| 0.0895 | W– | 0.2249 | W | 0.1089 | W+ | 0.2829 | W+ |

TABLE 5
Partial X-ray powder diffraction patterns for
 PaOI_2 (this work) and ThOI_2 (ref. 35)

| PaOI_2 | | | | ThOI_2 | | | |
|-----------------------------|------------------|-----------------------------|---------|-----------------------------|---------|-----------------------------|---------|
| $\sin^2\theta_{\text{obs}}$ | I_{est} | $\sin^2\theta_{\text{obs}}$ | I/I_0 | $\sin^2\theta_{\text{obs}}$ | I/I_0 | $\sin^2\theta_{\text{obs}}$ | I/I_0 |
| — | — | 0.0706 | M | 0.0053 | 100 | 0.0693 | 15 |
| 0.0079 | S– | 0.0732 | S– d | 0.0077 | 80 | 0.0710 | 70 |
| — | — | — | — | 0.0099 | 10 | 0.0727 | 50 |
| 0.0149 | M | 0.0780 | M– | — | — | — | — |
| 0.0312 | M | 0.0797 | M– | 0.0306 | 30 | 0.0776 | 50 |
| 0.0345 | M+ | 0.0873 | M– | 0.0333 | 30 | 0.0850 | 50 |
| — | — | 0.0893 | M– | 0.0367 | 5 | — | — |
| 0.0424 | W | 0.0911 | M– | 0.0421 | 25 | 0.0888 | 60 |
| 0.0442 | M | 0.0957 | M– | 0.0429 | 40 | 0.0930 | 25 |
| 0.0498 | M+ | 0.0977 | W– | 0.0481 | 40 | 0.0969 | 5 |
| 0.0525 | W– | 0.1034 | W+ | — | — | 0.1012 | 25 |
| 0.0545 | W+ | 0.1089 | W | 0.0535 | 10 | 0.1065 | 20 |
| 0.0560 | W+ | 0.1128 | W– | — | — | 0.1105 | 10 |
| 0.0583 | W | 0.1216 | W d | — | — | 0.1174 | 10 |
| 0.0602 | M+ | 0.1306 | W d | 0.0583 | 50 | 0.1277 | 25 |
| 0.0633 | W | 0.1342 | W– | 0.0625 | 15 | — | — |
| 0.0662 | M | 0.1391 | M+ | 0.0643 | 40 | 0.1341 | 60 |
| 0.0685 | S | — | — | 0.0671 | 100 | — | — |

Table 5. The position of the first strong line reported for ThOI_2 , $\sin^2\theta = 0.0053$, is below the cut-off on our films of PaOI_2 , but from the marked similarities on the remainder of the two patterns it is obvious that the

²⁷ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, 1965, 350.

²⁸ K. W. Bagnall, D. Brown, and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 1763.

²⁹ D. Brown, *J. Chem. Soc. (A)*, 1966, 766.

³⁰ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 243.

³¹ G. Boussières and M. Haissinsky, *Bull. Soc. chim. France*, 1951, 18, 146.

³² K. W. Bagnall, "International Review of Halogen Chemistry," Academic Press, London, 1967, in press.

³³ I. S. Morozov and A. I. Morozov, *Zhur. neorg. Khim.*, 1966, 11, 335.

³⁴ K. W. Bagnall, D. Brown, and J. F. Easey, unpublished observations.

³⁵ D. E. Scaife, A. G. Turnbull, and A. W. Wylie, *J. Chem. Soc.*, 1965, 1432.

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two compounds are isostructural. They appear to possess low symmetry, and the results have not been interpreted.

Protactinium dioxychloride and dioxybromide disproportionate slowly above 575° in a vacuum to yield a sublimate of the respective tetrahalide, leaving a residue of the dioxide PaO_2 . The dioxide obtained in this manner is isostructural with that prepared by hydrogen reduction¹³ of the pentoxide at 1500°.

EXPERIMENTAL

All work with protactinium was carried out in glove-boxes on account of the radioactive hazards associated with weighable quantities of protactinium-231, the isotope used in this work. The quadrivalent halides and oxyhalides were prepared and subsequently handled in an argon-filled box (oxygen content <30 p.p.m., water content <60 p.p.m.) owing to the rapid oxidation of protactinium(IV) in the atmosphere. Samples were prepared for X-ray powder diffraction and analysis under similar conditions, whereas samples for ultraviolet and visible spectra studies were prepared in an argon-atmosphere box in which no precautions against the presence of moisture were taken.

Materials.—Protactinium-231, available as part of the batch recently isolated from "ethereal" sludge residues, was purified from niobium as described³⁶ previously. Subsequent recovery and purification for re-use were carried out as described³⁷ recently. Protactinium pentachloride,⁶ pentabromide,⁸ and tetrafluoride^{4,13} were prepared by methods already described, whilst the pentaiodide was prepared by reaction of a mixture of protactinium (60–70%) and thorium metals with iodine at 450° and was purified by vacuum-sublimation above 400° (Found: Pa, 26.72; I, 73.77. PaI_5 requires Pa, 26.67; I, 73.33%). This metal mixture, of which only a limited quantity (~280 mg.) was available, was kindly provided by A. Marples (Metallurgy Division, A.E.R.E., Harwell). "Specpure" aluminium metal and B.D.H. 1-litre flasks of "Specpure" hydrogen were used for the reductions, and all glass apparatus was evacuated and heated at 500° before use to ensure the absence of adsorbed moisture. "Specpure" antimony trioxide and AnalaR iodine and hydrochloric acid were used. Individual preparations involved 20–50 mg. of protactinium-231.

Protactinium Tetrahalides.—Two methods have been used. For the first, and most satisfactory, the appropriate protactinium pentahalide was heated at 400–450° in a sealed evacuated Pyrex tube with a 100% excess of aluminium metal for the reaction $3\text{PaX}_5 + \text{Al} \rightarrow 3\text{PaX}_4 + \text{AlCl}_3$. By use of a graded furnace, the crystalline tetrahalide was obtained in a region of temperature 350° while the aluminium trihalide condensed in a cooler portion of the tube. Alternatively, an evacuated glass tube of known volume containing the pentahalide was filled with hydrogen at the correct pressure to give just sufficient hydrogen for the reaction $2\text{PaX}_5 + \text{H}_2 \rightarrow$

$2\text{PaX}_4 + 2\text{HX}$. The gas pressure was measured on a mercury manometer incorporated in the vacuum line. The Pyrex reaction tube was then sealed at a predetermined point using an oxygen-gas flame in the usual manner, and the reactants were heated together in a furnace at 400–450°. The preparation of the tetraiodide by either method invariably resulted in the simultaneous formation of traces of the oxydi-iodide PaOI_2 (Found: Pa, 61.82; Cl, 38.01. PaCl_4 requires Pa, 61.96; Cl, 38.04%. Found: Pa, 41.78; Br, 58.32. PaBr_4 requires Pa, 41.95; Br, 58.05%. Found: Pa, 30.94; I, 68.65. PaI_4 requires Pa, 31.27; I, 68.72%).

Protactinium Oxydihalides.—Protactinium tetrachloride or tetrabromide was intimately mixed with the stoichiometric amount of antimony trioxide for the reaction, $3\text{PaX}_4 + \text{Sb}_2\text{O}_3 \rightarrow 3\text{PaOX}_2 + 2\text{SbX}_3$ (X = Cl or Br), and the mixture heated in a sealed evacuated vessel at 150–200°. The volatile antimony trihalide condensed in a cold part of the reaction tube following which the residual oxydihalide was heated at 400° for approximately 6 hr. to improve the crystallinity of the product (Found: Pa, 72.10; Cl, 23.8. PaOCl_2 requires Pa, 72.60; Cl, 23.32%. Found: Pa, 54.86; Br, 40.30. PaOBr_2 requires Pa, 56.78; Br, 39.28%). Protactinium oxydi-iodide was obtained as a by-product during the preparation and sublimation of the tetraiodide and pentaiodide. Only 5–10 mg. of the compound were available, and it was identified by X-ray powder diffraction analysis. The results in Table 5 are provided in support of these deductions.

Analysis.—Protactinium-231 was weighed as the pentoxide after ignition of the hydrous oxide obtained by hydrolysis of the compounds with aqueous ammonia. The black protactinium(IV) hydroxide initially obtained upon hydrolysis rapidly oxidised and turned white when washed in the atmosphere. Alternatively, where only small amounts of the tetraiodide were available for analysis (20–30 mg.), the precipitated hydroxide was dissolved in 5 ml. of 0.5M-hydrofluoric acid and determined by a combination of α -assay and α -pulse analysis (specific activity³⁸ of $^{231}\text{Pa} = 1.08 \times 10^8 \alpha$ d./min./mg.). Halide in the supernatant aqueous ammonia solutions was determined potentiometrically against 0.1N- or 0.01N-silver nitrate depending on the amount available. In the latter instance, the solution before titration was adjusted to 50% (v/v) acetone-4M-nitric acid; "boiled-out" nitric acid was used to prevent oxidation of the iodide to iodine. The compounds were hydrolysed by the "freezing" technique described earlier,³⁹ in order to prevent loss of halide.

Physical Measurements.—X-Ray powder diffraction photographs were obtained using a Debye-Scherrer 19-cm. camera or, in the case of PaF_4 , a Guinier focusing camera with filtered Cu K_α radiation ($\lambda_1 = 1.54051 \text{ \AA}$). Scales were contact printed on the Guinier films prior to development, in order to combat film shrinkage during processing. The results from the 19-cm. camera were refined using the Cohen-Hess least-squares fitting programme which incorporates the Nelson Riley extrapolation. Visible spectra were measured as described²⁵ earlier.

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³⁶ D. Brown and P. J. Jones, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2296.

³⁷ D. Brown and P. J. Jones, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2529.

³⁸ D. Brown, S. N. Dixon, K. M. Glover, and G. Rogers, unpublished observations.

³⁹ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 733.