

## Some Protactinium(IV) Halides, their Complexes and Hexahalogeno-salts

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Most of the recent preparative work on the chemistry of protactinium has consisted of studies with protactinium(v) (see, for example, references 1—3) and little work with the less stable quadrivalent state has been reported. Only<sup>4</sup> the tetrafluoride, tetrachloride, oxysulphide, dioxide, and, more recently,<sup>5</sup> some fluoroprotactinates(IV) such as  $\text{LiPaF}_5$  and  $\text{Rb}_7\text{Pa}_6\text{F}_{31}$  have previously been recorded. This Communication describes the preparation and some properties of the tetrabromide, tetraethylammonium hexachloro- and hexabromo-protactinates(IV) and some complexes formed by  $\text{PaCl}_4$  and  $\text{PaBr}_4$  with oxygen and nitrogen donor ligands. (Table.)

Protactinium tetrachloride has previously been prepared<sup>4</sup> by hydrogen reduction of the pentachloride at 800°. We find that it, and the tetrabromide, are readily obtained in high yield by hydrogen reduction of the appropriate pentahalide at 400° in a sealed Pyrex vessel containing stoichiometric quantities of the reagents for the reaction  $2\text{PaX}_5 + \text{H}_2 \rightarrow 2\text{PaX}_4 + 2\text{HX}$  (X = Cl or Br). 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.

However, we have been able to effect the reduction with aluminium metal and this method should be more easily applied to large-scale reductions. The reaction proceeds smoothly at 400° with the reagents in a sealed evacuated Pyrex vessel, when the yellowish-green tetrachloride (red when hot) or the bright red tetrabromide (reddish-black when hot) are obtained as large crystals in a region of the vessel at 350°. Preliminary X-ray powder diffraction studies indicate that the tetrabromide is

powder results for these complexes have not yet been interpreted.

The above tetrahalides react with methyl cyanide and hexamethylphosphoramide (HMPA) to form complexes analogous to those formed<sup>9,10</sup> by the thorium and uranium tetrahalides. It is interesting to note that although PaBr<sub>4</sub> is isostructural with ThBr<sub>4</sub> and not UBr<sub>4</sub> it forms a 2:1 complex with HMPA, as does UBr<sub>4</sub>, whereas ThBr<sub>4</sub> forms<sup>9</sup> the 3:1 complex, ThBr<sub>4</sub>·3HMPA.

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Compound	Colour	Properties
PaCl <sub>4</sub>	Yellowish-green	Isostructural with UCl <sub>4</sub>
PaBr <sub>4</sub>	Bright red	Isostructural with ThBr <sub>4</sub>
(NEt <sub>4</sub> ) <sub>2</sub> PaCl <sub>6</sub>	Apple-green	Isostructural with (NEt <sub>4</sub> ) <sub>2</sub> UCl <sub>6</sub> ; sol. MeCN
(NEt <sub>4</sub> ) <sub>2</sub> PaBr <sub>6</sub>	Orange	Isostructural with (NEt <sub>4</sub> ) <sub>2</sub> UBr <sub>6</sub> ; sol. MeCN
PaCl <sub>4</sub> ·4MeCN	Yellowish-green	Insol. MeCN; $\nu_{C=N}$ at 2275 cm. <sup>-1</sup>
PaBr <sub>4</sub> ·4MeCN	Orange	Insol. MeCN; $\nu_{C=N}$ at 2274 cm. <sup>-1</sup>
PaCl <sub>4</sub> ·2HMPA	Mustard	Insol. HMPA; sol. MeCN; $\nu_{P=O}$ at 1042 cm. <sup>-1</sup>
PaBr <sub>4</sub> ·2HMPA	Green	Sol. HMPA; sol. MeCN; insol. isopentane.

isostructural with thorium tetrabromide<sup>6,7</sup> possessing tetragonal symmetry with  $a_0 = 8.824$ ,  $c_0 = 7.957 \pm 0.002$  Å. Of the observed reflections (up to  $\theta = 50^\circ$ ) only one, of *W*-intensity, does not conform with the space group  $I4_1/amd$  suggested by D'Eye<sup>6</sup> for ThBr<sub>4</sub> and recently questioned by Scaife.<sup>7</sup>

Protactinium tetrachloride and tetrabromide react with the appropriate tetraethylammonium halide in anhydrous methyl cyanide to form the slightly soluble hexahalogeno-complexes (NEt<sub>4</sub>)<sub>2</sub>-PaCl<sub>6</sub> (apple-green) and (NEt<sub>4</sub>)<sub>2</sub>PaBr<sub>6</sub> (orange) respectively. Under such conditions (NEt<sub>4</sub>)<sub>2</sub>PaCl<sub>6</sub> crystallises with orthorhombic symmetry, space group *Fmmm*, with  $a_0 = 14.22$ ,  $b_0 = 14.75$ , and  $c_0 = 13.35 \pm 0.01$  Å, being isostructural<sup>8</sup> with (NEt<sub>4</sub>)<sub>2</sub>UCl<sub>6</sub> and  $\beta$ -(NEt<sub>4</sub>)<sub>2</sub>ThCl<sub>6</sub>. However, the dimorphism recently reported<sup>8</sup> for (NEt<sub>4</sub>)<sub>2</sub>ThCl<sub>6</sub> is not observed, behaviour which is similar to that of the uranium(IV) analogue. The hexabromoprotactinate(IV) is isostructural with the corresponding thorium(IV) and uranium(IV) salts but the X-ray

The complexes were prepared by treating approximately 5 mg. of tetrahalide with 25  $\mu$ l. of ligand, the excess of the latter being removed by vacuum evaporation at room temperature.

Owing to the rapid oxidation of protactinium(IV) in the atmosphere, all compounds were prepared and subsequently handled in an argon-filled box (oxygen content < 25 p.p.m., water content < 40 p.p.m.). All have been identified by X-ray powder diffraction analysis for they are isostructural either with the thorium(IV) or the uranium(IV) analogue.<sup>10</sup> Further studies of these and of other protactinium(IV) compounds are now in progress and it is intended to obtain them in amounts sufficient for magnetic-susceptibility studies which, in conjunction with their near-infrared spectra, may throw further light on the question of whether Pa<sup>4+</sup> possesses a  $6d'$  or  $5f'$  electron configuration; the latter appears to be the more probable.<sup>11</sup>

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<sup>3</sup> Proceedings of International Conference on Protactinium Chemistry, Orsay (Paris), July 1965, to be published.

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<sup>10</sup> K. W. Bagnall, D. Brown, and P. J. Jones, unpublished observations.

<sup>11</sup> Ru-Tao Kyi, U.S. Report UCRL-9109, 1960.