581. *Some Chloro-complexes of Quinquevalent Protactinium, Niobium, and Tantalum.*

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Hexachloroprotactinates(v) of the type M^IPaCl_6 ($M^I = Cs^+$, Me_4N^+, and Ph_4As^+) and the octachloroprotactinate(v) $(Me_4N)_3PaCl_8$ have been prepared from thionyl chloride solutions of protactinium pentachloride. Some analogous hexachloro-complexes of niobium(v) and tantalum(v) ($M^I = Cs^+$, NH_4^+, and Me_4N^+) have been prepared in the same way. The crystallographic and spectral properties of the compounds are discussed. A simple method of preparing the pentachlorides is reported.

Ammonium and alkali-metal hexachloroniobates(v) and hexachlorotantalates(v) have been prepared[1] by heating the appropriate chlorides together in a sealed system. More recently,[2] the analogous tetraethylammonium salts were prepared by reaction of the chlorides in thionyl chloride solution, a solvent which has also been used in the preparation of chloro-complexes of rhenium(iv),[3] zirconium(iv),[4] tungsten(v), and uranium(v).[5] Although protactinium pentachloride has been prepared,[6] usually by the action of carbon tetrachloride on the pentoxide at temperatures above 300°, chloroprotactinates(v) appear to be unknown, and it seemed worthwhile to attempt the preparation of such compounds in non-aqueous media and to seek a simpler route to the pentachlorides. Niobium and tantalum pentachlorides have been obtained by numerous methods,[7] amongst them the reaction of the pentoxides with thionyl chloride in a sealed system.[8]

We now find that niobium hydroxide reacts vigorously with thionyl chloride at room temperature, dissolving almost completely within 24 hours; the yield of pentachloride, after vacuum-evaporation of the solution and sublimation of the resulting solid, is generally greater than 95%. In addition to the obvious preparative advantages, the pentachloride is obtained completely free from niobium oxytrichloride, $NbOCl_3$, which is almost always formed to some extent in other preparative procedures and which is difficult to separate completely from the pentachloride. Reaction of niobium hydroxide which has been precipitated with aqueous ammonia and washed only with water and acetone prior to vacuum-drying results in dissolution of between 50 and 70% of the niobium as pentachloride, the remainder being precipitated as yellow ammonium hexachloroniobate(v) through reaction with adsorbed ammonium ion. Two washings of the hydroxide with 0·5M-nitric acid solution are sufficient to remove the adsorbed ammonium ion and permit almost quantitative conversion of the hydroxide into pentachloride. With tantalum(v) and protactinium(v) hydroxides, however, the reaction is less efficient, only 60% of the former and 85% of the latter dissolving in thionyl chloride, probably a result of rapid ageing of the hydroxide precipitates with condensation to polynuclear oxygen-bridged species which are more resistant to complete chlorination under the conditions employed. The white residue obtained in these instances could not be identified and is probably a mixture of pentoxide and oxychlorides. Vacuum-evaporation of the thionyl chloride solutions of tantalum(v) yields the pentachloride which, like the niobium pentachloride, can be sublimed almost completely. With protactinium(v), however, the initial product is a

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[1] *E.g.*, Morozov and Korshunov, *Zhur. neorg. Khim.*, 1956, **1**, 145; Morozov, Korshunov, and Simonich, *ibid.*, p. 1646; Palkin and Chikanov, *ibid.*, 1959, **4**, 407; Morozov and Simonich, *ibid.*, 1957, **2**, 1907; Morozov and Toptygin, *ibid.*, 1958, **3**, 1637.

[2] Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.

[3] Bagnall, Brown, and Colton, *J.*, preceding Paper.

[4] Sandhu and Chakkal, *Current Sci.*, 1959, **28**, 442.

[5] Bagnall, Brown, and du Preez, *J.*, 1964, 2603.

[6] Sellers, Fried, Elson, and Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935; Flegenheimer, Thesis, Cambridge, 1959; Brown and Wilkins, *J.*, 1961, 3804.

[7] " Nouveau Traité de Chimie Minérale," ed. P. Pascal, Masson, Paris, 1958, Vol. XII, p. 415.

[8] Hecht, Jander, and Schlappmann, *Z. anorg. Chem.*, 1947, **254**, 255.

thionyl chloride adduct which decomposes at 150° under a vacuum to the volatile pentachloride and an unidentified black residue. Protactinium and chlorine analyses suggest that the initial product is $(PaCl_5)_2,SOCl_2$ but the sulphur analyses were low and variable, probably owing to loss of sulphur as sulphur dioxide on hydrolysis. The infrared spectrum has a peak at 1406 cm.$^{-1}$, probably due to a sulphur–oxygen vibration. No other peaks occur between 3 and 35 μ, and, since thionyl chloride [9] shows several vibrations in this region, the spectrum is consistent with the structure $SO^{2+}(PaCl_6)_2^-$. Protactinium(v) at concentrations greater than 10^{-3}M is extremely unstable with respect to hydrolysis in aqueous acid solutions [10] but in thionyl chloride solution we find that concentrations as high as 0·5M-protactinium(v) are easily attainable and such solutions are quite stable.

With tetramethylammonium chloride we have isolated the hexachloroprotactinate(v), Me_4NPaCl_6, and the octachloro-compound, $(Me_4N)_3PaCl_8$. The complexes are soluble in thionyl chloride, giving pale yellow solutions, and are precipitated therefrom by carbon disulphide; they are soluble in nitromethane but decompose on contact with methyl cyanide and acetone. The octachloro-complex is bright yellow, in contrast to the almost colourless hexachloroprotactinate(v), presumably a result of the higher co-ordination number, and the metal–chlorine vibrational frequency in the far infrared, ν_3, is lower in the octachloro-salt, as might be expected (Table 1).

TABLE 1.

Colour, and metal–chlorine vibrational frequencies, ν_3 (cm.$^{-1}$).

$PaCl_5$	Yellow	362, 322	$CsNbCl_6$	Yellow	336
$(PaCl_5)_2SOCl_2$	Yellow-orange	—	NH_4NbCl_6	Yellow	333
$CsPaCl_6$	Pale yellow	305	Me_4NNbCl_6	Yellow	334
$Ph_4AsPaCl_6$	Pale yellow	310	$CsTaCl_6$	White	319
Me_4NPaCl_6	Pale yellow	308	NH_4TaCl_6	White	321
$(Me_4N)_3PaCl_8$	Bright yellow	290	Me_4NTaCl_6	White	323

The corresponding tetraethylammonium chloride complexes were soluble in thionyl chloride–carbon disulphide mixtures and could not be isolated. Absorption spectra of thionyl chloride solutions of protactinium pentachloride and the tetra-alkylammonium chloro-complexes were measured between 10,000 and 2,800 cm.$^{-1}$. Peaks were observed at 4683w (inflexions at 4818 and 4914), 3234vs, 3002w, and 2958w cm.$^{-1}$ for $0·8 \times 10^{-2}$M-solutions of protactinium pentachloride. However, for solutions of the hexachloro- and octachloro-complexes the only peaks observed were those of the tetra-alkylammonium cations.

Tetraphenylarsonium hexachloroprotactinate(v), $Ph_4AsPaCl_6$, which gives an orange-red solution in thionyl chloride, is obtained in a similar fashion to the tetra-alkylammonium complexes. It is isostructural with the hexachlorouranate(v) analogue, and the observed *X*-ray reflections are given in Table 2. The compounds are obviously of low symmetry and the powder patterns have not been indexed.

The tetramethylammonium hexachloroniobate(v) and hexachlorotantalate(v), Me_4NNbCl_6 and Me_4NTaCl_6, respectively, crystallise from thionyl chloride solutions at 0° in the presence of excess tetramethylammonium chloride. They are very soluble in methyl cyanide and nitromethane, insoluble in benzene, carbon disulphide, and diethyl ether, and rapidly hydrolyse in acetone, ethanol, and methanol. Attempts to prepare the octachloro-complexes of these elements by the method used for the protactinium(v) compounds yielded only mixtures of the hexachloro-complexes and tetramethylammonium chloride.

All the above compounds are extremely sensitive to moisture but are relatively stable to heat; the tetraphenylarsonium and tetra-alkylammonium hexachloro-complexes decompose at temperatures between 200 and 250° whilst the octachloro-complex becomes paler above 170°, evidently on account of decomposition to the hexachloro-complex.

[9] Martz and Lagemann, *J. Chem. Phys.*, 1954, **22**, 1193.

[10] Casey and Maddock, *J. Inorg. Nuclear Chem.*, 1959, **10**, 58; Brown, Wilkins, and Smith, *J.*, 1959, 1463; Brown, Sato, Smith, and Wilkins, *J. Inorg. Nuclear Chem.*, 1961, **23**, 91.

TABLE 2.

X-Ray diffraction data for tetraphenylarsonium complexes.

Ph_4AsUCl_6 $\sin^2\theta$ (obs.)	$Ph_4AsPaCl_6$ $\sin^2\theta$ (obs.)	*I* (est.)	Ph_4AsUCl_6 $\sin^2\theta$ (obs.)	$Ph_4AsPaCl_6$ $\sin^2\theta$ (obs.)	*I* (est.)	Ph_4AsUCl_6 $\sin^2\theta$ (obs.)	$Ph_4AsPaCl_6$ $\sin^2\theta$ (obs.)	*I* (est.)
0·0045	0·0045	M	0·0525	0·0525	W	0·0963	0·0961	W−
0·0073	0·0074	M+	0·0531	—	W−	0·1044	0·1039	W+
0·0107	0·0107	S	0·0569	0·0567	M−	0·1058	—	W−
0·0133	0·0133	S	0·0588	0·0586	M−	0·1077	0·1075	M−
0·0154	0·0153	S	0·0631	0·0627	W	0·1139	0·1135	W−
0·0161	0·0161	M	0·0645	0·0644	M−	0·1148	—	W
0·0183	0·0182	M+	0·0705	—	W−	0·1186	—	W−
0·0231	0·0231	M	0·0718	0·0714	W	0·1204	—	W−
0·0239	0·0239	M	0·0730	0·0728	W+	0·1243	0·1243	W
0·0258	0·0258	M	0·0740	0·0740	M	0·1270	0·1266	M−
0·0281	0·0282	W	0·0787	0·0787	M	0·1285	0·1285	M−
0·0301	0·0298	M	0·0797	0·0794	W	0·1312	0·1312	W
0·0316	0·0316	S	0·0811	0·0811	W+	0·1373	0·1371	W+
0·0368	0·0369	M+	0·0830	0·0828	W	0·1440	0·1436	W
0·0414	0·0415	M+	0·0846	—	W−	0·1470	0·1470	W
0·0444	0·0444	W	0·0924	0·0920	M−	0·1570	—	W−
0·0450	0·0450	W	0·0939	0·0934	W			

Ammonium and alkali-metal chlorides are insoluble in thionyl chloride, which precludes its use for the homogeneous preparation of the chlorocomplexes of these ions. However, the ammonium and cæsium hexachloro-complexes of protactinium(v), niobium(v), and tantalum(v) are readily obtained from the reaction between ammonium or cæsium chloride in iodine monochloride and the pentachlorides in thionyl chloride. The products are soluble in iodine monochloride, less so in iodine monochloride–thionyl chloride mixtures, and completely insoluble in thionyl chloride; they are also slightly soluble in methyl cyanide and nitromethane but insoluble in benzene, carbon disulphide, ethyl acetate, and diethyl ether. Extensive hydrolysis with hydroxide formation occurs in these solvents if they are not anhydrous. Ammonium hexachloroniobate (yellow) and hexachlorotantalate(v) (white) begin to darken in colour at about 240°/1 atm. and melt with decomposition at 285 and 295°, respectively. The cæsium salts of all three elements show no visible signs of decomposition below 360°, the hexachloroniobate(v) exhibiting a reversible colour change (yellow to orange) similar to that observed [5] for cæsium hexachlorouranate(v). *X*-Ray powder photographs show that these hexachloro-complexes and the cæsium salts of uranium(v) and tungsten(v) are isostructural and of low symmetry. Values of $\sin^2\theta$ for the observed reflections are listed with visually estimated intensities (Tables 3 and 4); similar data have been presented previously [5] for cæsium hexachlorotungstate(v) and hexachlorouranate(v). The powder patterns have not been indexed, and single-crystal studies are in progress in an attempt to elucidate the structures.

TABLE 3.

X-Ray diffraction data for ammonium complexes.

NH_4NbCl_6 $\sin^2\theta$ (obs.)	NH_4TaCl_6 $\sin^2\theta$ (obs.)	*I* (est.)	NH_4NbCl_6 $\sin^2\theta$ (obs.)	NH_4TaCl_6 $\sin^2\theta$ (obs.)	*I* (est.)	NH_4NbCl_6 $\sin^2\theta$ (obs.)	NH_4TaCl_6 $\sin^2\theta$ (obs.)	*I* (est.)
0·0138	—	W	0·0715	0·0710	M	0·1336	0·1332	W+
0·0146	—	M	0·0751	0·0755	M−	—	0·1344	W+
0·0168	0·0170	S	0·0768	0·0767	M−	0·1366	0·1360	M−
0·0172	0·0172	S	0·0795	0·0793	M	0·1483	0·1478	W−
0·0221	0·0219	S	0·0807	0·0807	M+	0·1533	—	W−
0·0256	0·0256	S−	0·0817	0·0817	M+	0·1556	—	W−
0·0277	0·0273	S−	0·0887	0·0883	M	0·1613	0·1609	W+
0·0412	0·0412	M+	0·0996	0·0993	W	0·1701	0·1699	W−
0·0424	—	W	0·1004	0·1002	W+	0·1755	0·1751	W+
0·0436	—	M−	0·1021	0·1022	W	0·1856	0·1854	M
0·0526	0·0524	M	0·1081	0·1083	M−	0·1886	0·1881	W+
0·0533	0·0531	M	—	0·1092	W	0·1919	0·1916	W−
0·0638	0·0636	M	0·1191	0·1190	M−	0·2238	0·2239	W−
0·0694	0·0689	W+	0·1307	0·1303	W+	—	0·2255	W−

The metal–chlorine vibrational frequencies, observed in the far infrared (Table 1), were all broad, intense bands; slight indications of splitting have been attributed to instrumental aberrations, and the frequencies listed were measured at the centres of the bands. The protactinium–chlorine vibrations occur at approximately the same wavelengths as those observed previously [5] in chlorouranates(V), and the positions of the bands in the hexachloroniobates(V) and hexachlorotantalates(V) are close to those reported [2] for their tetraethylammonium hexachloro-complexes. Protactinium pentachloride has two peaks in this region (322m and 362s cm.$^{-1}$) probably due to the presence of bridging and non-bridging chlorine atoms, respectively. In contrast, the spectrum of the complex with thionyl chloride shows a broad band, more characteristic of the $PaCl_6^-$ ion, stretching from 310m to the limit of the instrument at 275s cm.$^{-1}$.

TABLE 4.

X-Ray diffraction data for cæsium complexes.

$CsNbCl_6$ $\sin^2\theta$ (obs.)	$CsTaCl_6$ $\sin^2\theta$ (obs.)	*I* (est.)	$CsPaCl_6$ $\sin^2\theta$ (obs.)	*I* (est.)	$CsNbCl_6$ $\sin^2\theta$ (obs.)	$CsTaCl_6$ $\sin^2\theta$ (obs.)	*I* (est.)
—	0·0161	M−	0·0101	W−	—	0·1138	W
0·0166	0·0165	M−	0·0111	M	—	0·1232	M−
0·0187	0·0186	M	0·0138	M−	—	0·1248	M−
0·0210	0·0210	S−	0·0150	W	—	0·1264	M−
0·0245	0·0245	S	0·0180	W−	0·1282	0·1275	M+
0·0259	0·0259	S	0·0202	W+	0·1314	0·1307	M
0·0316	0·0314	M	0·0231	S	0·1387	0·1384	W−
0·0383	0·0382	W	0·0242	M−	0·1411	0·1407	M−
0·0395	0·0395	S−	0·0263	M−	0·1429	0·1422	W−
0·0503	0·0499	S	0·0306	M	0·1454	0·1448	M−
0·0510	0·0508	S	0·0324	W−	0·1497	0·1489	W
0·0519	0·0519	W−	0·0329	W−	0·1524	0·1518	W
0·0588	0·0593	W	0·0338	M−	—	0·1549	W
0·0606	0·0606	M	0·0361	M	0·1589	0·1583	W
0·0649	0·0649	M+	0·0391	M	0·1604	—	W
0·0664	0·0662	M+	0·0444	M+	0·1635	0·1625	W
—	0·0727	W	0·0475	M+	0·1786	0·1774	M+
—	0·0747	W	0·0562	W	0·1827	—	W
0·0762	0·0757	S−	0·0603	W	—	0·1830	M
0·0772	0·0767	S−	0·0724	M+	0·1862	0·1858	W
0·0786	0·0782	S−	0·0811	W	—	0·1901	M−
0·0829	0·0824	W	0·0878	W	—	0·2008	W
0·0850	0·0844	M	0·1020	W	—	0·2034	W
0·0954	0·0948	W−	0·1171	W	0·2062	0·2056	W
—	0·0957	W−	0·1204	M+	0·2088	0·2076	W
—	0·0972	W	0·1330	W−	0·2107	0·2100	W
0·1020	0·1013	W−	0·1369	W−	0·2144	0·2135	M−
0·1042	0·1039	M+	0·1602	W−	0·2181	0·2175	M−
—	0·1115	W−	0·1699	M	0·2344	0·2339	W−

EXPERIMENTAL

The preparative work was carried out without any precautions against atmospheric moisture because of the protection afforded by thionyl chloride, but the moisture-sensitive products were handled in a dry-box after isolation. All protactinium handling was carried out in glove-boxes on account of the radioactive hazards associated with weighable amounts of protactinium-231, the isotope used in this work.

Niobium, Tantalum, and Protactinium Pentachlorides.—The metal hydroxide was precipitated from acid solution by ammonium hydroxide, washed with water, 0·5M-nitric acid solution to remove adsorbed ammonium ion, then with acetone, and vacuum-dried at room temperature. An excess of thionyl chloride was slowly added to the dried solid, and the mixture set aside at room temperature for several days, or, in the case of niobium, until the hydroxide had completely dissolved. The pentachlorides were obtained on vacuum-evaporation of the resulting solution and purified by vacuum-sublimation.

Protactinium Pentachloride–Thionyl Chloride Complex.—A thionyl chloride solution of protactinium pentachloride, obtained as above, was evaporated to dryness under a vacuum and the residue heated to about 50°, to give the *product* [Found: Pa 49·8; Cl, 45·0; S, 1·2. $SO^{2+}(PaCl_6)_2^-$ requires Pa 49·4; Cl, 45·45; S, 3·4%].

Ammonium and Cæsium Hexachloroniobate(v), *Hexachlorotantalate*(v), *and Hexachloroprotactinate*(v).—A thionyl chloride solution of the appropriate pentachloride was added to excess ammonium or cæsium chloride dissolved in the minimum quantity of iodine monochloride–thionyl chloride solution (20% thionyl chloride; v/v). The resulting *precipitate* was washed with a small volume of a 1 : 1 mixture of iodine monochloride–thionyl chloride to remove excess ammonium or cæsium chloride, followed by thionyl chloride (3 × 5 ml.) to remove the iodine monochloride, and vacuum-dried at room temperature.

Found: N, 4·25; Nb, 28·6; Cl, 65·35. NH_4NbCl_6 requires N, 4·3; Nb, 28·7; Cl, 65·7%.
Found: N, 3·35; Ta, 43·9; Cl, 51·7. NH_4TaCl_6 requires N, 3·4; Ta, 43·95; Cl, 51·7%.
Found: Cs, 30·4; Nb, 21·1; Cl, 48·25. $CsNbCl_6$ requires Cs, 30·3; Nb, 21·2; Cl, 48·5%.
Found: Cs, 25·15; Ta, 34·2; Cl, 40·4. $CsTaCl_6$ requires Cs, 25·2; Ta, 34·35; Cl, 40·4%.
Found: Pa, 40·15; Cl, 36·6. $CsPaCl_6$ requires Pa, 40·05; Cl, 36·9%.

Tetramethylammonium Hexachloroniobate(v) *and Hexachlorotantalate*(v).—A saturated solution of tetramethylammonium chloride in thionyl chloride (30 mg./ml.) was added to a concentrated solution of niobium or tantalum pentachloride in the same solvent and the mixture cooled to 0°. The complexes, which crystallised slowly as long *needles*, were washed once with ice-cold thionyl chloride (3 ml.) and vacuum-dried at room temperature.

Found: Nb, 24·4; Cl, 55·85. NMe_4NbCl_6 requires Nb, 24·5; Cl, 56·0%.
Found: Ta, 38·85; Cl, 45·3. NMe_4TaCl_6 requires Ta, 38·7; Cl, 45·45%.

Tetramethylammonium and Tetraphenylarsonium Chloroprotactinates(v).—Carbon disulphide (5 ml.) was added to 1 : 1 or 3 : 1 mixtures of the anhydrous tetraalkylammonium chloride or tetraphenylarsonium chloride and protactinium pentachloride in thionyl chloride (3 ml.) at 0°, and the *product* vacuum-dried at room temperature.

Found: Pa, 44·4; Cl, 41·15. NMe_4PaCl_6 requires Pa, 44·6; Cl, 41·1%.
Found: Pa, 27·9; Cl, 25·65. $Ph_4AsPaCl_6$ requires Pa, 27·95; Cl, 25·7%.
Found: Pa, 31·25; Cl, 38·7. $(NMe_4)_3PaCl_8$ requires Pa, 31·35; Cl, 38·5%.

Analysis.—Niobium, tantalum, and protactinium were weighed as the pentoxides, after air-ignition of the double salt or of the hydroxide, precipitated with aqueous ammonia. Chloride was determined potentiometrically against silver nitrate after removal of the metals as hydroxides, and nitrogen was determined directly by the Kjeldahl method.[11a] Cæsium was precipitated from acid solution,[12] after removal of the metal hydroxide with calcium hydroxide, and weighed as cæsium hexachlorostannate(IV). Sulphur [11b] was converted into sulphate by oxidation with ammoniacal hydrogen peroxide, and weighed as barium sulphate after removal of protactinium hydroxide.

Physical measurements.—Infrared spectra were measured on a Hilger H. 800 spectrometer, for Nujol mulls between silver chloride or Polythene plates (3—40 μ region), or solutions in thionyl chloride ($0·8 \times 10^{-2}$M) contained in 2-cm. quartz cells (1—3·5 μ region). *X*-Ray powder photographs were obtained using a Debye–Scherrer 19-cm. camera and a Guinier focusing camera with filtered CuK_α radiation ($\lambda = 1·54051$ Å).

We are indebted to Mr. P. J. Jones for nitrogen analyses and Mr. A. M. Deane for the use of the Hilger spectrometer.

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[*Received, January* 24*th*, 1964.]

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[11] Vogel, " A Textbook of Quantitative Inorganic Analysis," Longmans, London, 2nd edn., 1951, (*a*) p. 248; (*b*) p. 401.
[12] Treadwell and Hall, " Analytical Chemistry," Wiley, New York, 1945, Vol. II, p. 286.