

# METAL HALIDE-PHOSPHORUS HALIDE-ALKYL HALIDE COMPLEXES: REACTIONS WITH NIOBIUM AND TANTALUM PENTACHLORIDES

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The reactions of niobium and tantalum pentachlorides with trichlorophosphine and phenyldichlorophosphine have been studied in presence of alkylating agents such as sec-butyl chloride, iso-butyl chloride, tert-butyl chloride, tert-amyl chloride cyclohexyl chloride and triphenylmethyl chloride. Solid products have been isolated and characterised by vibrational spectroscopy as ionic complexes of alkyl- and/or aryl-phosphonium cations with hexachloroniobate and hexachlorotantalate anions.

## INTRODUCTION

BULLOCK *et al.* (1972) isolated the methyl tert-butyl dichlorophosphonium hexachloroniobates and tantalates from the reaction systems,  $\text{CH}_3\text{PCl}_2\text{—MCl}_5\text{—Bu}^t\text{Cl}$  in  $\text{CS}_2$ , where M is Nb or Ta. The present authors (1977 *a, b*) studied the reactions between trichlorophosphine, metal chloride, and alkyl/aryl chlorides and phenyldichlorophosphine-metal chlorides and alkyl/aryl chlorides using anhydrous boron, aluminium, tin(IV) and iron (III) chlorides and secondary butyl, isobutyl, tertiary butyl, tertiary amyl, cyclohexyl and triphenyl-methyl chlorides as alkylating agents. The present investigation is an extension of the earlier work using anhydrous niobium and tantalum pentachlorides. Solid ionic complexes have been isolated and have been characterised by infrared spectroscopy. The vibrational spectra reported here are interpreted in terms of the cations  $\text{RR}'\text{PCl}_2^+$  associated with either of the hexachloro-anions  $\text{NbCl}_6^-$  and  $\text{TaCl}_6^-$ .

## MATERIALS AND METHODS

*Reagents* — Niobium (V) chloride (Fluka), tantalum (V) chloride (Fluka), and triphenyl methyl chloride (Fluka) were used as such. Carbon disulphide (Pfizer) was dried over phosphorus (V) oxide and distilled before use. Trichlorophosphine (BDH) was distilled before use. Phenyl dichlorophosphine was prepared by the method reported by Buchner and Lockhart Jr. (1951). Alkyl chlorides were prepared by known methods, dried over phosphorus (V) oxide and distilled. Since many of the reactants and products are hydrolysed very readily, all manipulations were carried out using all standard joints and glass apparatus with rigorous exclusion of moisture.

*Analysis* — Chlorine was estimated gravimetrically. Niobium and tantalum were determined as oxides. To estimate phosphorus, the compounds were oxidised with nitric acid and potassium permanganate solution (2 per cent), precipitated as

phosphomolybdate, dissolved in dilute ammonia and precipitated again as magnesium ammonium phosphate.

*Preparation of compounds* — To a weighed quantity of metal chloride, dissolved or suspended in carbon disulphide, a slight excess of phosphorus halide was added initially. The contents were shaken vigorously in order to dissolve the metal chloride. Now alkylating agent (alkyl chlorides) was introduced. The order of addition was always kept the same to prevent the formation of hydrocarbon polymers. Excess of reagents were used to minimise the chance of polymeric anions formation. After the additions of the reagents the flask was allowed to stand for some time. After some time the solid started separating and settled down. The mother liquid was removed and the solid product was washed with carbon disulphide by decantation and dried under vacuum at room temperature. Elemental analysis, preparations, and products are listed in Table I. The melting points of the solids were not sharp and the solids melted with decomposition.

*Spectroscopy* — The spectral region 4000–500  $\text{cm}^{-1}$  was examined using Beckman I.R.-20 Spectrophotometer and samples were prepared in nujol mull between potassium bromide plates.

## RESULTS AND DISCUSSION

The products were fairly moisture sensitive and became sticky upon exposure to the atmosphere. Niobium complexes were yellow while tantalum compounds were white in colour. These were insoluble in common organic solvents but dissolved in acetone with probable dissociation as these can not be recovered as such on removal of the solvent.

In agreement with the conclusions of the vibrational spectra and analytical data of the compounds treated here, they can readily be interpreted in terms of univalent ionic species.

*Cations spectra* — Alkyl trichlorophosphonium cations  $\text{R}^+\text{PCl}_3^+$  should be a distorted tetrahedron having  $\text{C}_{3v}$  symmetry. Pentatomic molecules with general formula  $\text{XY}_3\text{Z}$  are expected to have six vibrational modes,  $3\text{A}_1$  and  $3\text{E}$ , according to the selection rule (Ross 1972), all of which are infrared and Raman active. The infrared spectra of the alkyltrichlorophosphonium cations showed weak absorptions between 790–780  $\text{cm}^{-1}$ , which could be assigned to P-C (alkyl) vibrations. Medium weak absorption between 212–208  $\text{cm}^{-1}$  may be due to  $\text{R}'\text{-P-Cl}$  vibrations. P-Cl vibrations were observed between 495–480  $\text{cm}^{-1}$  and 640–630  $\text{cm}^{-1}$ . Other band at 230–225  $\text{cm}^{-1}$ , can be assigned to Cl-P-Cl and  $\text{PCl}_3$  bonding. Our results were in good agreement with the results obtained by Beattie *et al.* (1968) for  $\text{MePCl}_3^+$ , and Bullock *et al.* (1972) for  $\text{Bu}^+\text{PCl}_3^+$ .

The expected alkyl phenyldichlorophosphonium cation should be further distorted tetrahedrally having symmetry  $\text{C}_s$ , with  $6\text{A}'$  and  $3\text{A}''$  modes. All these modes are infrared and Raman active. The infrared (near and far) spectral study of alkylphenyl dichlorophosphonium cation,  $\text{R}'\text{PhPCl}_2^+$ , in all the complexes showed

TABLE I  
Preparation and analysis

Sr. No.	Reagents (g)			R'	Product	Analysis						
	MCl <sub>5</sub>	R'PCl <sub>2</sub>	R'Cl			Found % of			Calculated % of			
						M	P	Cl	M	P	Cl	
Niobium Complexes												
1.	3.572	1.815	1.223	Cl	sec-butyl	[Bu <sup>n</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	18.02	6.27	62.95	18.57	6.19	63.80
2.	3.015	1.532	1.033	Cl	iso-butyl	[Bu <sup>i</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	18.08	6.02	63.50	18.57	6.19	63.80
3.	4.123	2.095	1.412	Cl	tert-butyl	[Bu <sup>t</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	18.69	6.34	62.90	18.57	6.19	63.80
4.	4.632	2.354	1.827	Cl	tert-amyl	[Am <sup>t</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	18.00	5.81	61.54	18.07	6.02	62.06
5.	3.789	1.926	1.663	Cl	cyclohexyl	[C <sub>6</sub> H <sub>11</sub> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	17.75	5.35	59.90	17.66	5.89	60.65
6.	2.412	1.226	2.488	Cl	triphenylmethyl	[Ph <sub>3</sub> CPCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	13.41	4.50	46.59	13.53	4.51	46.49
7.	3.846	2.547	1.317	Ph	sec-butyl	[PhBu <sup>n</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	17.28	5.58	52.07	17.15	5.72	52.35
8.	3.192	2.114	1.093	Ph	iso-butyl	[PhBu <sup>i</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	17.04	5.82	51.93	17.15	5.72	52.35
9.	2.789	1.847	0.955	Ph	tert-butyl	[PhBu <sup>t</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	16.92	5.41	52.23	17.15	5.72	52.35
10.	2.813	1.863	1.109	Ph	tert-amyl	[PhAm <sup>t</sup> PCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	16.70	5.38	50.85	16.72	5.57	51.03
11.	3.427	2.270	1.504	Ph	cyclohexyl	[C <sub>6</sub> H <sub>11</sub> PhPCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	16.42	4.36	49.73	16.36	5.45	49.95
12.	2.781	1.842	2.869	Ph	triphenylmethyl	[Ph <sub>3</sub> CPhPCl <sub>3</sub> ] <sub>2</sub> [NbCl <sub>6</sub> ]	12.84	4.12	39.03	12.76	4.26	38.96
Tantalum Complexes												
13.	3.657	1.389	0.942	Cl	sec-butyl	[Bu <sup>n</sup> PCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	30.48	5.34	54.00	30.71	5.26	54.16
14.	3.127	1.195	0.805	Cl	iso-butyl	[Bu <sup>i</sup> PCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	30.26	5.20	54.20	30.71	5.26	54.16
15.	2.875	1.099	0.740	Cl	tert-butyl	[Bu <sup>t</sup> PCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	30.66	5.14	53.95	30.71	5.26	54.16
16.	3.345	1.278	0.992	Cl	tert-amyl	[Am <sup>t</sup> PCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	30.04	5.01	52.48	30.00	5.13	52.90
17.	2.972	1.136	0.981	Cl	Cyclohexyl	[C <sub>6</sub> H <sub>11</sub> PCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	29.33	5.12	51.46	29.41	5.04	51.87
18.	2.862	1.094	2.221	Cl	triphenylmethyl	[Ph <sub>3</sub> CPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	23.30	4.00	40.87	23.34	3.99	41.15
19.	3.844	1.915	0.990	Ph	sec-butyl	[Bu <sup>n</sup> PhPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	28.55	5.01	44.48	28.68	4.91	44.96
20.	3.147	1.568	0.810	Ph	iso-butyl	[Bu <sup>i</sup> PhPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	28.70	4.82	44.76	28.68	4.91	44.96
21.	3.212	1.600	0.827	Ph	tert-butyl	[Bu <sup>t</sup> PhPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	28.66	4.92	44.67	28.68	4.91	44.96
22.	2.469	1.230	0.732	Ph	tert-amyl	[Am <sup>t</sup> PhPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	27.95	4.78	43.67	28.06	4.80	43.99
23.	3.400	1.694	1.122	Ph	cyclohexyl	[C <sub>6</sub> H <sub>11</sub> PhPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	27.34	4.59	42.71	27.55	4.72	43.18
24.	2.734	1.362	2.121	Ph	triphenylmethyl	[Ph <sub>3</sub> CPhPCl <sub>3</sub> ] <sub>2</sub> [TaCl <sub>6</sub> ]	22.11	3.82	34.29	22.15	3.79	34.71

weak absorption between 795–785  $\text{cm}^{-1}$  which could be assigned to P–C(R') vibrations. Very strong absorption at 1440–1435  $\text{cm}^{-1}$  and 1000–995  $\text{cm}^{-1}$  could be attributed to P–Ph vibrations in comparison with similar bands reported by Seal *et al.* (1961) at 1439 and 998  $\text{cm}^{-1}$  respectively. P–Cl vibrations were observed in the form of very strong and shoulder absorptions between 615–600  $\text{cm}^{-1}$  and between 508–495  $\text{cm}^{-1}$  may probably be an overtone or combination band. Medium weak absorptions between 210–208  $\text{cm}^{-1}$  may be due R'–P–Cl vibrations. Some deformation modes at 227–225  $\text{cm}^{-1}$  and 250–247  $\text{cm}^{-1}$  were also observed. In agreement with the results obtained earlier (Puri *et al.* 1977) the alkylphenyl phosphonium ions seem to have  $C_s$  symmetry.

*Anion spectra* — Ross (1972) has pointed out that a heptatomic molecule  $\text{MX}_6$  has octahedral structure with  $O_h$  point groups, and has six fundamentals of which only two  $\nu_3(T_{1u})$  and  $\nu_4(T_{1u})$  are infrared active. Bagnall and Brown (1964) have reported that  $\text{CsNbCl}_6$  and  $\text{CsTaCl}_6$  are isostructural and of low symmetry. Preiss (1971) studied the crystal structures of  $\text{PCl}_4^+\text{NbCl}_6^-$  and  $\text{PCl}_4^+\text{TaCl}_6^-$ . The structures were ionic consisting of tetrahedral cations  $\text{PCl}_4^+$  and octahedral anions  $\text{NbCl}_6^-$  and  $\text{TaCl}_6^-$  respectively.

The infrared and Raman spectra of  $\text{MCl}_6^-$  ( $M = \text{Nb} \& \text{Ta}$ ) have been extensively reported by Adams *et al.* (1963j), Brown *et al.* (1970) and Bullock *et al.* (1973). The vibrational spectra of the metal chloride anions were all consistent with octahedral hexachloro-species. Some stronger bands in niobium complexes at 340–335  $\text{cm}^{-1}$  and at 320–310  $\text{cm}^{-1}$  in tantalum complexes could be assigned to  $\nu_3T_{1u}$  combinations, in agreement with the earlier reported results.

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#### REFERENCES

- Adams, D. M., Chatt, J., Davidson, J. M., and Gerrett, J. (1963). The far-infrared spectra (190–460  $\text{cm}^{-1}$ ) of tetraethylammonium salts of some complex chlorides and bromides. *J. chem. Soc., A*, Part II, 2189–2194.
- Bagnall, K. W., and Brown, D. (1964). Some chloro-complexes of quinquevalent protactinium, Niobium and Tantalum. *J. chem. Soc., A*, Part III, 3021–3025.
- Beattie, I. R., Livingston, K., and Gilson, T. (1964). The vibrational spectrum of methyl tetrachlorophosphorus (V). *J. chem. Soc., A*, No. 1, 1–3.
- Brown, T. L., McDugle, W. G., and Kent, L. G. (1970). Vibrational and pure nuclear quadrupole resonance spectra of hexahalometalates. *J. Am. chem. Soc.*, **92**, No. 12, 3645–3653.
- Buchner, B., and Lockhart, L. B. (Jr) (1951). An improved method of synthesis of aromatic dichlorophosphines. *J. Am. chem. Soc.*, **73**, No. 2, 755–756.
- Bullock, J. I., Perrett, F. W., and Taylor, N. J. (1972). Some metal halide + phosphorus halide + alkyl halide complexes, Part I: Reactions with Boron, Aluminium, Silicon, Germanium and Tin halides. *J. chem. Soc. Dalton*, **17**, 1843–1846.

- (1973). Some metal halide + phosphorus halide + alkyl halide complexes, Part II : Reaction with Niobium and Tantalum pentachlorides and Tungsten Hexachlorides. *J. chem. Soc. Dalton*, **5**, 522-524.
- Preiss, H. (1971). Die Kristallstrukturen der Verbindungen  $FCl_5$ ,  $NbCl_5$  and  $PCl_5TaCl_5$ . *Z. anorg. allgem. Chem.*, **380**, No. 1, 56-64.
- Puri, D. M., and Saini, M. S. (1977a). Reactions of  $BCl_3$ ,  $AlCl_3$ ,  $SnCl_4$  and  $FeCl_3$  with Phenyl dichlorophosphine and t-butyl chloride: Isolation of solid complexes. *J. Indian chem. Soc.*, **15A**, No. 4, 362-363.
- Puri, D. M., Dubey, S. N., Saini, M. S., and Gupta, D. C. (1977b). Metal halide-phosphorus halide-alkyl halide complexes: Reactions with Iron (III) chloride. *J. Indian chem. Soc.*, (In press).
- Ross, S. D. (1972). *Inorganic Infrared and Raman Spectra*, Ch. 7 & 9. McGraw Hill, London.