

## Phosphorus chloride-metal chloride-alkyl chloride complexes : Reactions with vanadium(III) chloride and vanadium(V) oxychloride

SNEH LATA, SORAN SINGH, S N DUBEY and D M PURI\*  
Department of Chemistry, Kurukshetra University, Kurukshetra 132 119, India

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**Abstract.** The reactions of anhydrous vanadium(III) chloride and vanadium(V) oxychloride with trichloro- and phenyl dichloro-phosphine have been studied in the presence of alkylating agents such as *tert*-butyl chloride, *tert*-amyl chloride, cyclohexyl chloride and triphenyl methyl chloride. Solid products have been obtained. The structures of the complexes have been assigned on the basis of elemental analyses, infrared spectra, magnetic susceptibility and conductivity data.

**Keywords.** Organophosphonium ; polychloro metallates ; vanadium.

### 1. Introduction

Synthesis of organophosphonium polychloroaluminates have earlier been used for the preparation of new organophosphorus compound by either their hydrolysis or alcoholysis (Kinnear and Perren 1952). However, it was only Bullock *et al* (1972, 1973) who initiated the synthesis and structural study of such polychlorometallates. Puri and Saini (1977, 1978, 1979) also studied the reaction systems, metal chloride-phenyldichloro- or trichlorophosphine-alkyl chloride. The systems have also been studied using antimony(V) chloride by Sneh *et al* (1980). Synthesis and structural studies of  $(C_2H_5)_4N_3V_2Cl_9$  and  $[(C_2H_5)_4N][VCl_4]$  (Casey and Clark 1969) and  $[pyH][VOCl_4]$   $[(C_2H_5)_4N][VOCl_4]$  (Drake *et al* 1969) and  $[PCl_4][VOCl_4]$  (Griffiths and Nycholls 1971) have been made. However, the organophosphonium derivatives of the polychloro vanadium(III) and oxovanadium(V) do not seem to have been studied. In view of this it was thought worthwhile to study the reaction systems, vanadium(III) or oxovanadium(V) chloride-phenyl dichloro- or trichlorophosphine-alkyl chloride.

### 2. Experimental

Anhydrous vanadium(III) chloride (BDH) and vanadium oxychloride (Fluka) triphenyl methyl chloride (Riedel) and trichlorophosphine (BDH) were used as

\* To whom correspondence should be made

Table 1. Characterisation data of complexes.

MCl <sub>3</sub>	Amount of reactants (in g) R/Cl	R	R'	Product colour any yield (in g)	Found (Calc.), (%)		M.P.* (° C)	Molar-conductance (in Mho-cm <sup>2</sup> /g) of 10 <sup>-3</sup> M soln in nitro- benzene
					Cl	P		
0.73	0.63	0.42	Cl	Bu <sup>t</sup> [Bu <sup>t</sup> PCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid (1.24)	63.38 (63.95)	7.70 (7.98)	175	11.2
0.34	0.29	0.22	Cl	Am <sup>t</sup> [Am <sup>t</sup> PCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid (0.68)	60.72 (61.79)	7.18 (7.71)	172	13.4
0.32	0.28	0.36	Cl	C <sub>6</sub> H <sub>11</sub> [C <sub>6</sub> H <sub>11</sub> PCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid (0.79)	58.74 (59.96)	6.98 (7.48)	178	11.6
0.28	0.24	0.49	Cl	Ph <sub>3</sub> C [Ph <sub>3</sub> CPCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid (0.83)	44.13 (43.26)	5.85 (5.38)	170	12.4
0.40	0.45	0.29	Ph	Bu <sup>t</sup> [Bu <sup>t</sup> PhPCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid (0.94)	51.06 (49.79)	7.80 (7.24)	180	10.8
0.39	0.44	0.26	Ph	Am <sup>t</sup> [Am <sup>t</sup> PhPCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid (0.88)	49.71 (48.64)	5.90 (6.11)	168	13.6
0.32	0.36	0.56	Ph	Ph <sub>3</sub> C [Ph <sub>3</sub> CPhPCl <sub>3</sub> ] [VCl <sub>4</sub> ] Light green solid	33.20 (34.57)	4.68 (5.03)	178	12.54

*Vanadium(III) complexes*

Vanadium (V) Complexes

0.78	0.62	0.42	Cl	Bu <sup>t</sup>	[Bu <sup>t</sup> PCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Brown solid	60.49 (61.62)	6.40 (7.25)	112	18.44
0.91	0.72	0.49	Cl	Am <sup>t</sup>	[Am <sup>t</sup> PCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Brown solid	58.58 (59.54)	7.16 (7.44)	114	16.88
0.47	0.37	0.30	Cl	C <sub>6</sub> H <sub>11</sub>	[C <sub>6</sub> H <sub>11</sub> PCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Brown solid	57.61 (58.57)	6.48 (7.15)	120	20.84
0.40	0.32	0.64	Cl	Ph <sub>3</sub> C	[Ph <sub>3</sub> PCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Greenish brown solid	41.82 (42.16)	4.89 (5.26)	123	19.63
0.48	0.49	0.26	Ph	Bu <sup>t</sup>	[Bu <sup>t</sup> PhPCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Brown solid	48.39 (48.85)	6.54 (7.12)	117	24.67
1.75	1.84	1.074	Ph	Am <sup>t</sup>	[Am <sup>t</sup> PhPCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Brown solid	45.48 (46.50)	6.43 (6.78)	121	22.88
0.43	0.44	0.28	Ph	C <sub>6</sub> H <sub>11</sub>	[C <sub>6</sub> H <sub>11</sub> PhPCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Brown solid	44.23 (45.17)	6.13 (6.57)	124	18.58
0.44	0.45	0.70	Ph	Ph <sub>3</sub> C	[Ph <sub>3</sub> CPhPCl <sub>3</sub> ] [VOCl <sub>4</sub> ] Yellowish brown solid	33.09 (33.84)	4.18 (4.92)	114	27.04

\* Melt with decomposition and colour change.

such *tert*-butyl *tert*-amyl and cyclohexyl chloride were prepared by the known methods and distilled before use. Phenyl dichlorophosphine was prepared by known method (Buchner and Lockart 1951). Solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$  and nitrobenzene) were purified by known methods.

### 2.1. Syntheses of complexes

To a weighed quantity of metal chloride dissolved in anhydrous solvent (acetonitrile for vanadium (III) chloride and methylene chloride for oxovanadium(V) chloride) phosphorus chloride and alkyl-chloride were added in the order mentioned above. All the additions were carried out under anhydrous conditions. After a few minutes, the precipitation of the solid compound started and it took from few minutes to one month, depending upon the use of alkylating agents. After the reactions were complete, the mother liquor was decanted to another flask and the solid was washed 2-3 times with anhydrous methylene chloride and dried *in vacuo* for about an hour at room temperature. Careful handling of the compounds was required in view of their sensitivity to moisture. The amount of the reagents used, colour of the products and yields are given in table 1. The compounds did not exhibit sharp melting points, decomposition accompanied by change in colour occurred.

### 2.2. Analyses

Chlorine and phosphorus were estimated by known methods (Sneh *et al* 1980). The analytical data are given in table 1.

### 2.3. Physical measurements

The infrared spectra were recorded in the region  $4000\text{--}250\text{ cm}^{-1}$  using Beckman IR-20 spectrophotometer. The samples were prepared in nujol mull between potassium bromide plates to examine  $4000\text{--}600\text{ cm}^{-1}$  spectral region. Polythene sheets were used to examine  $600\text{--}250\text{ cm}^{-1}$  spectral region.

Magnetic susceptibility was recorded by Gouy's method. Conductivity was measured on Elico conductivity bridge CM-82T in dry nitrobenzene.

## 3. Results and discussion

On the basis of elemental analyses of the complexes and their infrared spectral study, the complexes may be formulated as  $[\text{R}'\text{R}'\text{PCl}_2]^+ [\text{MCl}_4]^-$  [ $M = \text{V(III)}$  or  $\text{VO(III)}$ ].

The molar conductance of the complexes ( $1 \times 10^{-3}\text{ M}$ ) in nitrobenzene was found to be in the range of  $10.8$  to  $27.04\text{ mhos cm}^2\text{ mol}^{-1}$ . Such low conductance values are in conformity with 1:1 composition of cation and anion (Fergusson *et al* 1965).

### 3.1. Cation spectra

The infrared spectra of alkyl trichlorophosphonium  $[\text{R}'\text{PCl}_3]^+$  and alkyl phenyl dichlorophosphonium species  $[\text{R}'\text{PhPCl}_2]^+$  show weak absorption at  $800\text{--}780\text{ cm}^{-1}$

which could be assigned to P-C (alkyl) vibrations (Bullock *et al* 1972, 1973; Puri and Saini 1977, 1978, 1979). P-Cl vibrations were observed in the form of very strong bands between 600–590  $\text{cm}^{-1}$  and 540–530  $\text{cm}^{-1}$ . Very strong bands at 1440  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  could be assigned to P-Ph vibrations in comparison with similar bands observed at 1430  $\text{cm}^{-1}$  and 998  $\text{cm}^{-1}$  respectively in  $\text{Ni}(\text{PF}_2\text{C}_6\text{H}_5)_4$ ,  $\text{PCL}_2\text{C}_6\text{H}_5$ ,  $\text{Ni}(\text{PCL}_2\text{C}_6\text{H}_5)_4$  (Seel *et al* 1961) and at 1440  $\text{cm}^{-1}$  and 998  $\text{cm}^{-1}$  in  $[\text{RPhPCL}_2]$   $[\text{SbCl}_6]$  (Sneh *et al* 1980).

### 3.2. Anion spectra

In the anion  $\text{VCl}_4^-$ , absorption at 360–350  $\text{cm}^{-1}$  could be assigned to V-Cl which is comparable with the bands reported in the region 366–356  $\text{cm}^{-1}$  for  $\text{VCl}_4\text{bipy}$  and  $\text{VCl}_4\text{phen}$  (Clark 1963).

In the infrared spectra of the anion  $\text{VOCl}_4^-$ , bands are observed at 1,010–975  $\text{cm}^{-1}$  which could be assigned to  $\nu(\nu=0)$  and are comparable with the bands observed earlier in the complexes containing vanadyl group (Selbin and Holmes 1962; Drake *et al* 1969). The bands observed at 370–360  $\text{cm}^{-1}$  could be due to V-Cl as expected for  $\text{VOCl}_2\text{phen}$  (Clark 1963).

The magnetic moments of complexes containing tetrahedral anion  $\text{VCl}_4^-$  were found to be in the range of 0.3 to 0.2 B.M. This reduction in the value from 2.83 B.M. for two unpaired electrons is probably due to metal-metal interaction. Our results agree with those expected by Casey and Clark (1968) for  $(\text{C}_2\text{H}_5)_4\text{N VCl}_4$  complex.

The compounds containing the anion  $\text{VOCl}_4^-$  were diamagnetic as expected for  $d^0$  system (Drake *et al* 1969).

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