

## Metal derivatives of organoantimony compounds : reactions of anhydrous Zr(IV), Nb(V) and W(VI) chlorides with arylantimony compounds

HEMANT K SHARMA, 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 Zr(IV), Nb(V) and W(VI) chloride with tetraphenylstibonium chloride and triphenylantimony dichloride have been studied. Tetraphenylstibonium chloride was found to form ionic complexes with the anhydrous chlorides of metals whereas triphenylantimony dichloride formed adducts involving chlorine bridges. The complexes have been characterized by elemental analyses, IR spectra, conductivity and magnetic susceptibility measurements. Only tungsten(V) chloride was reduced when reacted with triphenylstibine.

**Keywords.** Stibonium-metal chloride complexes.

### 1. Introduction

Reactions of alkylantimony compounds with titanium tetrachloride have been studied by Takashi (1967) systematically and isolation of various organometallic complexes have been reported. Anionic complexes of the type  $[R_4M][R_3M'X_2]$  or  $[R_4M]_2[R_2M'X_4]$  (where  $R, R' = CH_3, C_4H_9$  or  $C_6H_5$ ;  $M = N, P, As$  or  $Sb$ ;  $M' = Sn$  or  $Te$  and  $X =$  halo or pseudohalo anion) have been studied both from structural and biological activity point of view (Srivastava *et al* 1979; Bhattacharya and Saxena 1980; Bhattacharya *et al* 1980; Bertazzi *et al* 1972; Netherland Patent 1966; German Patent 1966). A few of them possess a high degree of biocidal activity (Richardson 1973). Study of the reactions between organoantimony compounds and titanium(IV) chloride has also been carried out in our laboratories and the formation of  $[Ph_4Sb][TiCl_5]$ ,  $[Ph_4Sb]_2[TiCl_6]$ ,  $Ph_3SbCl_2 \cdot TiCl_4$  and  $Ph_3SbCl_2 \cdot TiCl_3$  has been reported. Titanium(IV) chloride is reduced to titanium(III) chloride, when reacted with triphenylstibine (Sharma *et al* 1981). The work has been extended to the reactions of zirconium(IV), niobium(V) and tungsten(VI) chlorides.

### 2. Experimental

Anhydrous metal chlorides (Riedel) and triphenylstibine (E. Merck) were used after checking their purity. Tetraphenylstibonium chloride and triphenylanti-

\*To whom correspondence should be made.

mony dichloride were prepared by the known methods (Chatt and Mann 1940; Goddard 1923). Solvents (benzene, *n*-hexane and nitrobenzene) were dried and deoxygenated before use. Because of the hygroscopic nature of some of the reactants, all preparations were carried out under anhydrous conditions. Dry nitrogen gas was flushed through the reaction mixture to keep an inert atmosphere.

### 2.1 Preparation of ionic complexes and the adducts

A general method, reported earlier from these laboratories (Sharma *et al* 1981) was employed for preparing the quaternary stibonium complexes and adducts of Zr(IV), Nb(V) and W(VI) chlorides using the stoichiometric amounts of the reactants.

### 2.2 Reaction of anhydrous tungsten(VI) chloride with triphenylstibine

To a benzene solution of anhydrous tungsten(VI) chloride was added a benzene solution of triphenylstibine slowly and with stirring under dry nitrogen atmosphere. The nitrogen gas was passed for 20-24 hr with occasional shaking. The residue was filtered off after giving 2-3 washings with dry benzene. The filtrate on evaporation of the solvent under reduced pressure yielded a crude product of triphenylantimony dichloride which was recrystallized from benzene, m.p. 142° (Lit. m.p. 143° C). The residue was also dried and analysed.

### 2.3 Physical measurements

Infrared spectra of the compounds (4000-600  $\text{cm}^{-1}$ ) were taken in nujol on Beckman IR-20 spectrophotometer. Far IR spectra of the compounds (600-250  $\text{cm}^{-1}$ ) were recorded using polythene sheets. The conductivity of dilute solutions ( $1 \times 10^{-3}$  M) in nitrobenzene were measured on an Elico-conductivity bridge type CM-82T. The magnetic susceptibility measurements were carried on Gouy's balance.

## 3. Results and discussion

The analytical data of the quaternary complexes of niobium(V) and tungsten(VI) indicated the formation of  $[\text{Ph}_4\text{Sb}][\text{MCl}_6]$  from tetraphenylstibonium chloride and the anhydrous metal chlorides in the molar ratio of 1:1. The lower stability of tungsten(VI) chloride has been reported by Parry (1970) and Fowles and Frost (1966) who observed that even when tungsten hexachloride is exposed to 100 watt light bulb or dissolved in benzene or carbon tetrachloride, it gets reduced to tungsten(V) chloride and it is actually the pentachloride of tungsten which reacts with tetraphenylstibonium chloride to form  $[\text{Ph}_4\text{Sb}][\text{WCl}_6]$ . Observations of reduction of tungsten(VI) to tungsten(V) have been reported in many earlier reactions also (Saini and Puri 1979; Adam *et al* 1963). Zirconium(IV) formed the quaternary complex of the type  $[\text{Ph}_4\text{Sb}]_2[\text{ZrCl}_8]$ .

The adducts of the type  $\text{Ph}_3\text{SbCl}_2 \cdot \text{MCl}_x$  ( $x = 4$  or 5) were formed, when triphenylantimony dichloride and anhydrous chloride of Zr(IV), Nb(V) and W(VI) were taken in the molar ratio of 1:1. The stibonium complex as well as adduct of zirconium(IV) are dirty white solids, those of niobium(V) are yellow solids while the tungsten derivatives are dark green and brown solids respectively. The adducts

did not melt even upto 250° and the melting points of stibonium complexes of zirconium, niobium and tungsten are 260°, 140° and 118° respectively. The elemental analyses (C, H and chlorine) of the ionic complexes as well as of the adducts were in conformation to the required composition.

The conductance measurements of  $1 \times 10^{-3}$  M solution of the stibonium compounds in nitrobenzene indicated the formation of ionic complexes. The molar conductance values of 27.1, 20.2 and 52.3 mhos  $\text{cm}^2 \text{mole}^{-1}$  for  $[\text{Ph}_4\text{Sb}][\text{NbCl}_6]$ ,  $[\text{Ph}_4\text{Sb}][\text{WCl}_6]$  and  $[\text{Ph}_4\text{Sb}]_2[\text{ZrCl}_6]$  respectively suggested the 1:1 electrolytic nature of the former two complexes and 2:1 electrolytic behaviour for the latter. The conductivity of  $\text{Ph}_3\text{SbCl}_2 \cdot \text{MCl}_6$  compounds could not be determined as they were insoluble in nitrobenzene, nitromethane or acetonitrile.

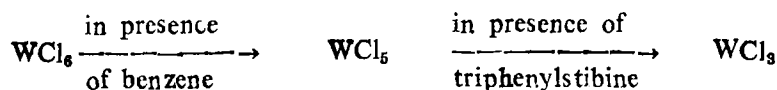
The infrared spectra of the cations showed bands in the regions 440–420  $\text{cm}^{-1}$  for  $\nu \text{Sb-C(Ph)}$  vibrations (Doak and Freedman 1970).

The IR spectra of the hexachlorometallate anion,  $[\text{MCl}_6]^-$  ( $M = \text{Zr, Nb or W}$ ) were in agreement with octahedral species. Of the total six modes, only two fundamentals,  $\nu_3$  and  $\nu_4$  are IR active for octahedral species. The IR spectrum of the anion,  $[\text{ZrCl}_6]^{2-}$  showed a sharp band at 290  $\text{cm}^{-1}$  due to  $\nu_3$  vibrations as observed by Adam and Newton (1968) in  $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{ZrCl}_6]$ . A very sharp band was observed at 330  $\text{cm}^{-1}$  ( $\nu_3$ ) in the spectrum of  $[\text{NbCl}_6]^-$ . The result is in agreement with the one obtained by Horner *et al* (1968) in  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{NbCl}_6]$  and  $[(\text{C}_2\text{H}_5)_4\text{As}][\text{NbCl}_6]$  at 333 and 331  $\text{cm}^{-1}$  respectively. A band at 325  $\text{cm}^{-1}$  ( $\nu_3$ ) was observed for  $[\text{WCl}_6]^-$ , which is in conformation with the earlier results of Adam *et al* (1963).

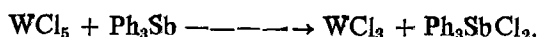
The adducts were found to be insoluble in most of the common organic solvents and their melting points were also very high. The IR bands of the ligand assigned to phenyl ring (Doak *et al* 1965) did not undergo any change on adduct formation. The bands at 420–435  $\text{cm}^{-1}$  assigned to  $\nu \text{Sb-C(Ph)}$  frequency also did not show any shift. The  $\nu (\text{M-Cl})$  vibrations in case of Zr(V), Nb(V) and W(V) have been shifted to lower frequency region at 360, 325 and 310  $\text{cm}^{-1}$  respectively. Therefore, a hexa-coordinated structure involving chlorine bridges could be assigned to these adducts.

Magnetic moment of  $[\text{Ph}_4\text{Sb}]^+[\text{WCl}_6]^-$  was found to be 0.56 B.M. at room temperature. The value is lower than the required for  $d^1$  system. Similar results have been observed by Bullock *et al* (1973), Brisdon and Walton (1965), Bagnall *et al* (1964), Hargreaves and Peacock (1958) and Saini and Puri (1979) for  $[\text{WCl}_6]^-$  anion. This lower value of magnetic moment, may be attributed to spin-orbit coupling (antiferromagnetism) though this may not be the only reason.

Reactions of tungsten (VI), niobium(V) and Zirconium(IV) chlorides with triphenylstibine were also studied in dry benzene. In case of  $\text{WCl}_6$ , after 24 hr, a brown residue was obtained which on analysis was found to be tungsten(III) chloride. On removal of the solvent from the filtrate, a solid was obtained which was found to be triphenylantimony dichloride. The compound was also confirmed by melting point and IR data. Following sequence of the reaction could be proposed:



In the actual reaction with triphenylstibine, it is the tungsten(V) chloride which takes part as follows :



Similar reductions with triphenylstibine have been observed in case of  $\text{CuCl}_2$  (Bhattacharya and Singh 1979; Ondrejovic *et al* 1973),  $\text{FeCl}_3$  (Manulkin and Tatarenko 1951) and  $\text{TiCl}_4$  (Takashi 1967; Sharma *et al* 1981).

In case of Zr(IV) and Nb(V) chlorides neither any adduct formation nor the reduction of the metal chloride occurred, when the reactions of triphenylstibine with zirconium(IV) chloride and niobium(V) chloride was carried out in dry benzene.

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