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ICA Review

Organic Derivatives of Niobium(V) and Tantalum(V)

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Contents

1. Introduction

The chemistry of organic derivatives of niobium(V) and tantalum(V) has progressed at a very fast pace during the last decade (out of 320 references quoted at the end of this review, about 240 pertain to the last 10 years). In addition to the treatise entitled "The Chemistry of Niobium and Tantalum" by F. Fairbrother[1] published in 1967, a few general reviews on topics like alkoxides and dialkylamides[2], alkoxides, mercaptides, dialkylamides and phosphides[3], oxime derivatives of metals and metalloids[4] during recent years have covered some specific aspects of the chemistry of these two metals also. Thus the organic derivatives of Niobium and Tantalum do not appear to have been reviewed at all in a systematic manner. It has, therefore, been attempted in the present article to present a general review of the topic under the following broad headings: Addition compounds, Substitution derivatives, Compounds containing metal–carbon bonds and Cluster compounds.

In order to avoid undue repetition, some of the matters described and discussed in the above treatise and review articles have been included just by references along with any additional matter which has been published since the topic was reviewed.

2. Addition Compounds

Niobium and tantalum pentahalides (MX_5)** exhibit a strong tendency of adduct formation with ligands containing N,O,S and P. As early as 1905, Smith and Hall[5] had reported an addition reaction of $NbCl_5$ with NH_3. In 1924, Linder and Feit[6] published a similar but inconclusive study with $TaCl_5$.

In 1937, several workers[7–10] observed that NH_3 forms an adduct with $TaCl_5$ at low temperature (~ 80° C), but loses it gradually followed by ammonolysis at higher temperatures:

$$\begin{tikzcd} TaCl_5 + NH_3(\text{liquid}) \arrow[r, "-80^\circ C", "\text{vacuum}"'] & TaCl_5\cdot 12NH_3 \arrow[d, "-67.5^\circ C"] \\ TaCl_5\cdot 7NH_3 & TaCl_5\cdot 10NH_3 \arrow[l, "-44^\circ C"'] \end{tikzcd}$$

$$\begin{tikzcd} TaCl_5\cdot 7NH_3 \arrow[r, "0^\circ C"] & Ta(NH_2)_2Cl_3\cdot 3NH_3 + 2NH_4Cl \arrow[d, "170^\circ C"] \\ & Ta(NH_2)_2Cl_3 + 3NH_3 + 2NH_4Cl \end{tikzcd}$$

$$3Ta(NH_2)_2Cl_3 + 8NH_3(\text{gas}) \xrightarrow[\text{6days}]{750^\circ C} Ta_3N_5 + 9NH_4Cl$$

$$Ta_3N_5 \xrightarrow{\sim 1190^\circ C} 3TaN + N_2$$

$$3Ta(NH_2)_2Cl_3 \xrightarrow[300^\circ C]{\text{under vacuum}} Ta_3N_5 + NH_4Cl + 8\ HCl$$

A similar pattern[11] was suggested for the reaction of $NbCl_5$ and NH_3, but only NbN could be isolated on prolonged heating at 800° under reduced pressure.

A. Addition Compounds with Pyridine and Related Ligands

Contradictory results have been reported regarding the reactions of MX_5 with pyridine and other similar

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** For sake of brevity M will be used to represent both the metals, where both Nb and Ta show similar behaviour.

nitrogen containing ligands. NbX_5 (X = Cl, Br or I) forms a 1 : 1 adduct at low temperature with pyridine, which reduces to $NbX_4 \cdot 2C_5H_5N$ even at room temperature. By contrast, TaX_5 (X = Cl or Br) forms a $TaX_5 \cdot C_5H_5N$ adduct[12] only. Adducts with the formulae, $MX_4 \cdot 2L$ (X = Cl, Br or I, L = pyridine or γ-picoline) and $MX_4 \cdot L'$ (L′ = bipyridine or 1,10-phenanthroline) have also been isolated in the reaction of MX_5 with the above ligands[13]. MF_5 under similar conditions yields $MF_5 \cdot 2C_5H_5N$ [14] which undergoes decomposition above 100° C. On treatment with concentrated HF, these give rise to pyridinium salts:

$$NbF_5 \cdot 2C_5H_5N + HF \rightarrow [C_5H_5NH][NbF_6] + C_5H_5N$$

$$3TaF_5 \cdot 2C_5H_5N + 4HF \rightarrow 2[C_5H_5NH][TaF_6] + [C_5H_5NH]_2[TaF_7]$$

Pentahalides on treatment with bipyridyl in anhydrous acetonitrile[15] yield the following products:

$$MCl_5 + \text{bipy} \xrightarrow[\text{MeCN}]{0°\,C} MCl_5(\text{bipy})(\text{MeCN})$$

$$MBr_5 + \text{bipy} \xrightarrow[\text{MeCN}]{0°\,C} MBr_5 \cdot 2\text{bipy}$$

$$NbI_5 + \text{bipy} \xrightarrow[\text{MeCN}]{0°\,C} \text{no pure products}$$

On the basis of i.r. evidence[16], structure of these derivatives, $MX_5(\text{bipy})(\text{MeCN})$ has been shown to be similar to that of their diarsine analogues.

MX_5 (X = Cl or Br) reacts with 2,2′-bipyridyl[17] in dry benzene to give adducts:

$$MX_5 + \text{bipy} \xrightarrow{C_6H_6} MX_5 \cdot \text{bipy}$$

However, in ether the reactants are reported to yield complex adducts:

$$NbCl_5 + \text{bipy} \xrightarrow{\text{ether}} Nb_2OCl_8 \cdot 2\text{bipy}$$

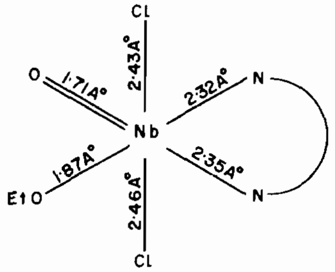
$$TaCl_5 + \text{bipy} \xrightarrow{\text{ether}} Ta_4OCl_{18} \cdot 4\text{bipy}$$

It may be that the latter products are due to hydrolysis. The reactions in alcohol containing traces of moisture yielded $NbOCl_2(OR) \cdot \text{bipy}$ (where R = Et or Pr^n) derivatives[17, 18].

$NbOCl_3$ and $NbOBr_3$ form 1 : 1 adducts[17, 19] with 2,2′-bipyridyl and o-phenonthroline in anhydrous benzene.

Earlier i.r. assignments for $NbOCl_2(OR)\text{bipy}$ derivatives[20] have been confirmed by a study of the same complexes with ^{18}O labelled ligands.

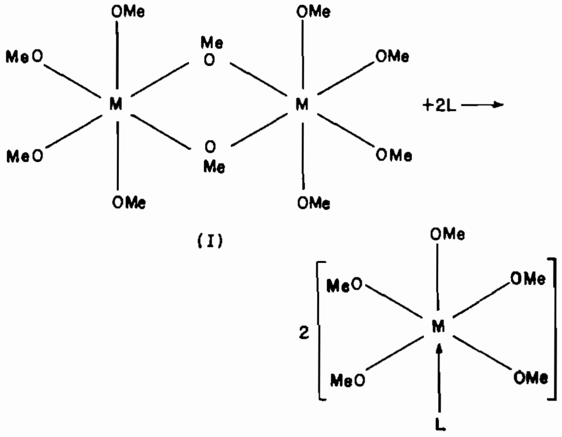
X-ray crystalographic analysis[21] of the compound $NbOCl_2(OEt) \cdot \text{bipy}$[18, 22] shows that Nb occupies the centre of a distorted octahedron with chlorine atoms in *trans*-position:



Adducts having formula $Nb(OR)_3Cl_2 \cdot \text{bipy}$, where R = Me, Et, Pr^i, Pr^n or Bu^n, have also been synthesised[23] by the reaction of $NbCl_5$ with 2,2′-bipyridyl in refluxing alcohol:

$$NbCl_5 + \text{bipy} \xrightarrow{ROH} Nb(OR)_3Cl_2 \cdot \text{bipy} + 3HCl$$

Early transition metal alkoxides auto-associate[2] into dimer, trimer or tetramer in preference to coordination complex formation even with potential ligands. The n.m.r. study of solution mixture of niobium or tantalum penta-methoxide and ligands like amines, amine oxide or phosphine oxide indicate the possibility of dissociation of dimeric species (I) to monomeric species (II)[24]:



(I)

(II)

Although the formation of a few complexes of the type $Ta(OR)_5L$ (where R = Me and L = N_2H_4; R = OPr^i and L = ethylenediamine) were postulated by Bradley *et al.*[25, 26] as early as 1956 yet only recently has the coordination ability of a large numers of potential monodentate and bidentate ligands with niobium and tantalum pentamethoxide been reported[27, 27a]. The i.r. and n.m.r. studies of these derivatives indicate the octahedral geometry[27]. Various factors which are able to play a part in controlling the coordination chemistry of niobium and tantalum methoxide has been discussed[27a].

B. Addition Compounds with Alkyl Cyanides and Related Ligands

1 : 1 soluble addition complexes of MX_5 (X = Cl, Br or I) can be isolated on refluxing the pentahalides with excess RCN (R = Me, Et or Pr^n)[28–31] and stripping off the free ligand under reduced pressure. The soluble adducts $MX_5 \cdot RCN$ are reported to be monomeric in boiling benzene and are thermally stable up to 150° C, above which they tend to be reduced to $MX_4 \cdot 2RCN$.

The nature of complexes formed by MX_5 (X = Cl or Br) with acetonitrile has long been a topic of controversy. Kepert and Nyholm[29] reported complexes of the type $MX_5 \cdot MeCN$, which are monomeric, isomorphous and non-electrolytic in nature. I.r. spectra of these compounds are normal for coordinated acetonitrile. Later workers[32,33], however, suggested that these adducts exist as pseudooctahedral halogen bridged dimers in the solid state. The results of Kepert and Nyholm[29] have now been confirmed by a detailed vibrational study of $NbX_5 \cdot NCCY_3$ (X = Cl, or Br; Y = H or D) in the solid state and in acetonitrile solution by Ozin and Walton[34] which leaves little doubt that these species are six coordinate molecular and monomeric. Based upon their ^{93}Nb n.m.r. spectral studies, Kidd and Spinney[35] recently reported a method for characterising species of the type $NbCl_nBr_{6-n}$ MeCN (n = 0–6) and $NbCl_nBr_{5-n}MeCN$ (n = 0–5) in MeCN solution.

With acetonitrile, metal fluorides form adducts of the type $(MF_5MeCN) \cdot 2MeCN$[36] which are reduced on heating under vacuum to $MF_5 \cdot MeCN$. The i.r. and n.m.r. studies[37,38] of 1 : 2 adduct, $MF_5 \cdot 2MeCN$ show it to be ionic in nature, having the configuration $[MF_4(MeCN)_4]^+[MF_6]^-$, whereas no such ionic species could be detected in 1 : 1 adducts, $MF_5 \cdot MeCN$.

I.r., Raman spectra[34,39,40], conductivity and molecular weights of $MX_5 \cdot MeCN$ complexes show their monomeric nature and the coordination of N to metal. The isotopic shift of about 25 cm^{-1} in the mode of vibration of CH_3CN by replacing CH_3CN with CD_3CN provides additional evidence in this direction. The possibilities of some ionic species at a very low concentration having equilibria of the type,

$$2MX_5 \cdot MeCN \rightleftharpoons (MX_4 \cdot 2MeCN)^+ + MX_6^-$$
$$MX_5 \cdot MeCN + MeCN \rightleftharpoons (MX_4 \cdot 2MeCN)^+ + X^-$$

cannot, however, be ruled out. The X-ray powder diagram[40] reveals C_{4v} symmetry of the molecules.

$MX_5 \cdot MeCN$ when treated with R_4NX gives $(R_4N)MX_6$ derivatives[37]:

$$MX_5 \cdot MeCN + R_4NX \rightarrow (R_4N)MX_6 + MeCN$$
$$X = Cl \text{ or } Br;\ R = Me \text{ or } Et$$

The bromoderivative $(R_4N)MBr_6$ when treated with excess carbon tetrachloride forms an adduct $NR_4MBr_6 \cdot CCl_4$, which when heated to 80° C reforms NR_4MBr_6[41]. These compounds fume in the air, are insoluble in water but are soluble in acetone, and are not hydrolysed even by aqueous ammonia at room temperature. When heated above 230° C under vacuum, these derivatives yield MBr_5.

$NbCl_5$ on treatment with Et_4NBr in MeCN yielded $(Et_4N)NbCl_5Br$[36]. Similarly $(Et_4N)TaCl_5Br$ and $(Et_4N)TaCl_5I$ were also synthesised.

Acrylonitrile, $H_2C{=}CH{-}C{\equiv}N$, forms 1 : 1 adducts with MX_5 (X = Cl or Br) in which the bonding[42] is through N atom rather than with the double bond:

$$MX_5 + C_2H_3CN \rightarrow MX_5 \cdot NCC_2H_3$$

The comparative Raman spectra of the complexes MX_5L (where L is acrylonitrile or dimethyl sulphide) with those of the model species MX_5Y (where X = Cl or Br and Y = Cl, Br or I) show an overall lowering of the symmetry[43] below C_{4v}.

Trichloroacetonitrile oxidises Nb(IV) to Nb(V) and forms a 1 : 1 adduct[44]:

$$NbCl_4 + CCl_3CN \rightarrow NbCl_5 \cdot NCCCl_3$$

Although a series of mixed products are formed in the above reaction, yet the main constituent was reported to be $NbCl_5 \cdot NCCCl_3$ which is readily converted to $NbCl_5 \cdot MeCN$ on treatment with MeCN[44].

Cyanogen chloride forms a 1 : 1 adduct[45] with metal chlorides:

$$MCl_5 + NCCl \rightarrow MCl_5 \cdot NCCl$$

The adducts are solid in nature, soluble in MeCN, $MeNO_2$ and $SOCl_2$. These decompose in benzene and hydrolyse readily in water. I.r. studies show that the coordination[45] occurs through nitrile. These derivatives melt beyond 170° C in a sealed tube but start decomposing from 140° C when heated in contact with air.

C. Thiocyanate Complexes

The complexation of thiocyanate ions with niobium and tantalum chlorides[46,47] in non-aqueous solvents was demonstrated by conductometric and spectrophotometric techniques. Actual synthesis of thiocyanate complexes was effected[48] first in 1966 by the reaction of KSCN with $TaCl_5$ in methanol. On evaporating the volatile fraction and extracting with carbon tetrachloride, thiocyanate complexes were obtained in which the tantalum was bonded with the N atom of the thiocyanate. Soluble hexathiocyanate complexes[49,50] were also synthesised by the following reaction:

$$MCl_5 + 6KCNS \xrightarrow{MeCN} KM(NCS)_6 + 5KCl$$

$KTa(NCS)_6$ on treatment with 2,2′-bipyridine or 4,4′-dimethyl-2,2′-bipyridine[51] yielded complexes having composition $Ta(NCS)_5L$. Compounds having the composition $Ta(NCSe)_5L$ were also synthesised by a similar route[51].

The reaction of MCl_5 with KCNS in varying stoichiometric ratios in MeCN has been reported to yield derivatives[52] having the composition $[NCl_x(NCS)_y \cdot MeCN] \cdot nMeCN$, where $x = 1–4$, $y = 4–1$ and $n = 0,1$ or 2.

$[M(NCS)_5 \cdot MeCN] \cdot nMeCN$ on treatment with pyridine or quinoline (L) yielded a $M(NCS)_5L$. derivative. Similar reactions in ether instead of MeCN yielded $MCl_4(NCS) \cdot Et_2O$ and $MCl_3(NCS)_2 \cdot Et_2O$ derivatives[52,53]. Derivatives of the type $NH_4[M(NCS)_6] \cdot nMeCN$ (where n = 2,5 and 7) have also been obtained by the reaction of NH_4CNS with $[M(NCS)_6] \cdot nMeCN$ in MeCN solution.

On heating $[Nb(NCS)_5 \cdot MeCN] \cdot 2MeCN$ derivative[54] gives $[Nb(NCS)_5 \cdot MeCN]$, $[Nb(NCS)_5] \cdot MeCN$ and $[Nb(NCS)_5]_2$ derivatives at different temperatures. Solvate free tantalum thiocyanate complex[53] was also synthesised in a similar manner.

MeCSN or MeNCS is reported to form 1 : 1 adducts[55] with MCl_5 in n-heptane solution at 20° C. On heating, these adducts undergo a isomerisation equilibrium of the type:

$$MeSCN \cdot MCl_5 \rightleftharpoons MeNCS \cdot MCl_5$$

The above was confirmed by the band shift of the ν (C–N) and ν (C–S) vibrations on heating[55].

D. Addition Compounds with Nitrosyl Chloride

$NbCl_5$, $TaCl_5$, $NbOCl_3$ and $TaOCl_3$ form 1 : 1 adducts[56–58] when allowed to react with excess of NOCl in a sealed tube out of contact with air and moisture. The derivatives $MCl_5 \cdot NOCl$ are thermally stable and can be sublimed in poor yields. The spectral and crystallographic studies[59] show that the adducts $MCl_5 \cdot NOCl$ are ionic $[NO^+][MCl_6^-]$ in nature and MCl_6^- ions have octahedral symmetry.

E. Addition Compounds with Ethers

Diethyl ether forms soluble 1 : 1 adducts[60] with MX_5 (X = Cl or Br). The complexes are monomeric in boiling benzene, thermally stable up to 150° C and then undergo decomposition with the formation of a mixture of MX_5 and M_2O_5:

$$MX_5 \cdot Et_2O \xrightarrow{150^\circ C} MOX_3 + 2EtX$$

$$5MOX_3 \xrightarrow{250^\circ C} 3MX_5 + M_2O_5$$

Crystalline ether complexes of the type $NbCl_5 \cdot HCl \cdot 2Et_2O$ and $TaCl_5 \cdot HCl \cdot 2Et_2O$ have also been isolated[61] by passing dry HCl in the cold etherial solution of the corresponding metal pentachloride.

F. Addition Compounds with Cyclic Ethers and Thioethers

Cyclic ethers and thioethers form 1 : 1 addition complexes with MX_5 (X = Cl or Br). No reduction or abstration of oxygen or sulphur from the ligand was noticed[62], as had been observed in the reaction of dialkyl or diaryl sulphoxide and MX_5[63]. I.r. studies show the bonding of S to metal rather than O in thioxane complexes and with only one oxygen in dioxane complexes. Little is known about their thermal stability.

G. Addition Compounds with Ketones

Aceto- and benzo-phenones form 1 : 1 adducts[64] with MX_5 (X = Cl or Br). These complexes are soluble in polar solvents like MeCN, CH_2Cl_2 and EtOH, but are insoluble in non-polar solvents like C_6H_6, C_6H_{14} and CCl_4. The adducts are reported to be hydrolytically unstable. $NbCl_5$ shows a strong tendency of O abstraction from acetophenone[64]. No such adduct formation was observed with acetone or other aliphatic ketones.

H. Addition Compounds with Sulphur Containing Ligands

A mixture of niobium or tantalum pentachloride, SCl_2 and Cl_2 on heating in a sealed tube forms an addition complex having the composition $MCl_5 \cdot SCl_4$[65]. These complexes are highly susceptible to hydrolysis.

The pentahalides undergo solubilisation on refluxing with excess alkyl sulphides and form 1 : 1 adduct $MX_5 \cdot Et_2S(Me_2S)$ after evaporating the volatile constituents[66]. Some of these adducts can be sublimed unchanged and others undergo decomposition. Tetrahydrothiophene, $(CH_2)_4S$ forms 1 : 2 adducts under similar conditions:

$$MX_5 + Me_2S(Et_2S) \rightarrow MX_5 \cdot Me_2S(Et_2S)$$

$$MX_5 + (CH_2)_4S \rightarrow MX_5 \cdot 2(CH_2)_4S$$

Tantalum pentachloride reacts with Me_2S in CH_2Cl_2 solution at 45° C to give $TaCl_5 \cdot 2Me_2S$ adduct[67].

It has been established by a comparative relative stability investigation of the adducts obtained by the reactions of ethers, sulphides and nitriles with corresponding pentachloride by n.m.r. method[68] that the electronic factor was found to be predominant for the stability of nitrile complexes and steric factor for the stability of ether and sulphide complexes. Although the steric factor is responsible for the stability of sulphide and ether adducts, yet sulphide adducts are more stable than ether complexes.

The spectroscopic, electrical and chemical evidences for the compounds $NbF_5 \cdot 2Me_2SO_4$, $NbF_5 \cdot 2C_5H_5N$ and $NbF_5 \cdot 2(CH_2)_4S$ indicate the existence of NbF_6^- and $NbF_4L_4^+$ species[37]. The presence of NbF_6^- species is confirmed by ^{19}F and ^{93}Nb n.m.r. studies. Similar NbF_6^- species are observed in the case of $Me_2NCHO \cdot NbF_6$[69] and ethanolic solution of NbF_5[70] by ^{19}F and ^{93}Nb n.m.r. studies and i.r. spectral study of $NbF_5 \cdot 2L$ derivatives[71].

I. Addition Compounds with Aromatic and Heterocyclic Amines

$NbOCl_3$ in benzene reacts with aromatic or heterocyclic amines (L) in absence of moisture to give complexes of the general formula, $NbOCl_3 \cdot L$[72]. The i.r. spectral bands reveal the coordination of N to metal.

Mixing a chloroform solution of $N(CH_2 \cdot Ph)_3$ to a HCl saturated $NbCl_5$ solution in $CHCl_3$ yields a white crystalline solid on standing, which has a composition of the type $[(PhCH_2)_3NH]_2NbOCl_5 \cdot 2CHCl_3$. The complex on heating at 100° C under vacuum changes to $[(PhCH_2)_3NH]_2NbOCl_5$. Similarly, yellow crystals of the composition $[(PhCH_2)_3NH]_2NbCl_7 \cdot 1.5CHCl_3$ are isolated on mixing $NbCl_5$ and $(PhCH_2)_3N \cdot HCl$ in chloroform which in turn loses $CHCl_3$ molecule on heating at about 100° C[61].

J. Addition Compounds with Phosphorus Containing Ligands

Metal pentachlorides and oxytrichlorides form adducts with Ph_3PS[56], Ph_3PO[56, 73, 74], $[N(CH_3)_2]_3PO$[74, 75], $(C_6H_5)_2(C_6H_5CH_2)PO$[74], Bu_3P[76], Ph_3PS, Ph_3PSe, $Ph_2P(S)CH_2(S)PPh_2$ and $Ph_2P(S)CH_2CH_2(S)PPh_2$[77] when allowed to react in a suitable organic solvent:

$$MCl_5 + Ph_3PO \xrightarrow{MeCN} MCl_5 \cdot Ph_3PO$$

$$NbCl_5 + Ph_3PO\ (\text{excess}) \xrightarrow{MeCN} NbOCl_3 \cdot 2Ph_3PO$$

$$\begin{tikzcd}
TaCl_5 + Bu_3P \arrow[r, "\text{room temp.}"] & TaCl_5 \cdot Bu_3P \arrow[d, "225\text{–}445\,°C"] \\
 & TaPCl_2 + 3BuCl
\end{tikzcd}$$

$$NbOCl_3 + 2[N(CH_3)_2]_3PO \rightarrow NbOCl_3 \cdot 2[N(CH_3)_2]_3PO$$

$$TaBr_5 + Ph_3PS \rightarrow TaBr_5 \cdot Ph_3PS$$

$TaPCl_2$ was found to be thermally (up to 700° C) and hydrolytically stable and hydrolyses only on prolonged refluxing with water:

$$TaPCl_2 + H_2O \rightarrow TaPO + 2HCl$$

Some of these soluble derivatives are reported to be monomeric in nature. The i.r. spectral data reveal the coordination of O,S or N with the metal instead of P.

Brown and coworkers[77] reported the synthesis of 1 : 1 adducts of $(NMe_2)_3PO$, Ph_3PO, Ph_3PS and Ph_3PSe with MX_5 ($X = Cl$ or Br) in non-aqueous solvents. Pentabromides form 1 : 1 adducts with $Ph_2P(S)CH_2(S)PPh_2$ and only 1 : 0.33 adducts with $Ph_2P(S)CH_2 \cdot CH_2(S)PPh_2$ but no such adduct formation was reported with pentachlorides.

$NbCl_5 \cdot Ph_3PO$ was also synthesised by the interaction of $NbCl_5$ and $[Ph_3PCl_2O]Cl$ in an inert solvent[78]. The i.r. spectral evidence indicates the solvation of $NbCl_5$ and $TaCl_5$ with Bu_3PO_4 and formation of the adducts $MCl_5 \cdot Bu_3PO_4$ and $MCl_5 \cdot 2Bu_3PO_4$ in which the ligand is bonded through the phosphoryl oxygen[79].

In ethanolic solution, pentahalides of these metals form $M(OEt)_2X_3 \cdot Ph_3PO$ derivatives when treated with Ph_3PO[80]. Under similar conditions, Et_4NX forms $NEt_4M(OEt)_2X_4$[80].

Metal pentachlorides have the tendency to abstract oxygen from diisopropylmethylphosphonate (L) and to form $MOCl_3 \cdot xL$ adducts. The reaction mixtures form different types of polymeric species[81] under different experimental conditions having M=O, M–O–M chelating and bridging phosphonato grouping.

3. Substitution Derivatives

A. Halide Alkoxides

The halide alkoxides of niobium and tantalum have been synthesised by the following routes: (i) By the reaction of metal chlorides with the corresponding alcohols[82]:

$$MCl_5 + nROH \rightarrow M(OR)_nCl_{5-n} + nHCl$$

(where $n = 2$ or 3; $R = CH_3$ or C_2H_5).

(ii) By the reaction of $NbCl_5$ and $Nb(OEt)_5$ in definite stoichiometric ratios in MeCN[83]:

$$NbCl_5 + 4Nb(OEt)_5 \xrightarrow{MeCN} 5Nb(OEt)_4Cl \cdot MeCN$$

In MeCN solution, the product appears to exist in the ionic form $[NbCl_3 \cdot OEt(MeCN)_2]^+[NbCl_5OEt]^-$. On treatment with Et_4NCl, it gives $(NEt_4)NbCl_5 \cdot OEt$:

$$Nb(OEt)_4Cl \cdot MeCN + 4Et_4NCl \rightarrow (Et_4N)(NbCl_5OEt) + 3Et_4N \cdot OEt + MeCN$$

(iii) By the reaction of metal chloride with NaOR in the parent alcohol[84]:

$$MCl_5 + nNaOR \xrightarrow{ROH} MCl_{5-n}(OR)_n + nNaCl$$

(where $n = 1$–4; $R = Me$ or Et).

(iv) $NbCl_5$ on refluxing with $SO(OMc)_2$ in carbon tetrachloride solution gives the $Nb(OMe)Cl_4$ derivative[85]:

$$NbCl_5 + SO(OMe)_2 \rightarrow Nb(OMe)Cl_4 + MeCl + SO_2$$

$Nb(OMe)Cl$ reacts with Et_4NCl or RCl in MeCN solution at 0° C to form an ionic species $[NbCl_5 \cdot OMe]^-$ at room temperature, but on refluxing the reaction mixture a complex $(NEt_4)_4NbOCl_5$ was isolated.

(v) By the reaction of metal ethoxide or isopropoxide with acetyl chloride or acetyl bromide[86–88]:

$$M(OEt)_5 + CH_3COX \rightarrow M(OEt)_4X + CH_3COOEt$$
$$M(OEt)_5 + 2CH_3COX \rightarrow M(OEt)_3X_2 + 2CH_3COOEt$$
$$M(OEt)_5 + 3CH_3COX \rightarrow M(OEt)_2X_3 \cdot CH_3COOEt + 2CH_3COOEt$$
$$M(OEt)_5 + 4CH_3COCl \rightarrow M(OR)Cl_4 \cdot CH_3COOEt + 3CH_3COOEt$$

$$M(OEt)_5 + 4CH_3COBr \rightarrow MOBr_3 \cdot CH_3COOEt + 3CH_3COOEt + EtBr$$

(vi) Alkoxy fluorides are synthesised by the interaction of the corresponding chloromethoxide with KF[89] or by the reaction of $M(OEt)_5$ with MF_5 in required stoichiometric ratios.

The reactions of metal alkoxides with acetyl chloride or bromide are quite facile up to the introduction of two halogen atoms. Substitution of a third and a fourth chlorine atom proceeds with the addition of one mol of the corresponding ester, whereas the substitution of a fourth bromine atom resulted in the formation of $MOBr_3 \cdot CH_3COOR$ derivative. $M(OPr^i)_5$, when treated with CH_3COCl in molar ratio 1 : 4, yields $MOCl_3 \cdot CH_3COOPr^i$ whereas $M(OBu^t)_5$ forms $MO(OOCCH_3)Cl_2 \cdot CH_3COOBu^t$ as final product.

These halide alkoxides vary from coloured solids to viscous liquids, soluble in common organic solvents; they are highly hydrolysable and thermally unstable except monochloro derivatives which could be distilled unchanged under reduced pressure[86–88]. The existence of dimeric species in $Nb_2(OEt)_nCl_{5-n}$ and $Nb(OMe)Cl_4$ derivatives[90] has been shown by mass spectroscopic (70 eV) studies.

EtONa, Et_4NCl and C_5H_6NCl react with $NbCl_4OEt$ and $NbCl(OEt)_4$[91] to yield derivatives having compositions represented by $NaNbCl_5(OEt)$, $Na[NbCl_4(OEt)_2]$, $Et_4N[NbCl_5(OEt)]$, $C_5H_6N \cdot NbOCl_4$ and $NaNb(OEt)_6$. These species also exist in dilute non-aqueous solutions and their formation has been confirmed by conductometric titrations[91] between the reactants.

Metal fluoro-ethoxides, $MF_n(OEt)_{5-n}$, where n = 1, 2 or 3, on treatment with CsF in ethanol solution form $Cs_3Nb_3O_4F_{10}$ and $CsTaOF_4$ derivatives[92]. I.r. spectral studies of these derivatives indicate the existence of M=O as well as M–O–M type bonding, suggesting a complex structure. Buslaev and Kokunov[93], on the other hand, reported the formation of a number of cesium oxyfluoroniobates (tantalates), $CsNbF_2O(OEt)_2$, $Cs_2Nb_2F_5O_3(OEt)$, $Cs_3Nb_3F_9O_4(OEt)$, $Cs_3Nb_3F_{10}O_4$, $Cs_4Ta_4F_{10}O_5(OEt)_4$, $Cs_2Ta_2F_7O_2(OEt)$ in the reactions of Nb (Ta) fluoroethoxides with CsF in ethanolic solution. Formation of other biproducts like Et_2O and HF in the above reactions indicates that the reactions are rather complex and obviously, more detailed work under absolutely anhydrous and rigorously controlled conditions is needed to clarify the nature of the above reactions.

B. Alkoxides

The reactions of niobium and tantalum pentachlorides with alcohols and phenol were studied by Funk and coworkers[82,94] and could be represented by the following equations:

$$MCl_5 + 3ROH \rightarrow MCl_2(OR)_3 + 3HCl$$

$$MCl_5 + 5C_6H_5OH \rightarrow M(OC_6H_5)_5 + 5HCl$$

The reactions can be driven to complete substitution in the cases of alcohols also by the use of ammonia as proton acceptor[95–97].

$$MCl_5 + 5ROH + 5NH_3 \xrightarrow{\text{Benzene}} M(OR)_5 + 5NH_4Cl$$

However, the above simple procedure was successful only for primary and secondary alkoxides. For the tertiary butoxide of tantalum, the method originally adopted for titanium[99] was extended and consisted of treating tantalum pentachloride with tertiary butanol in presence of benzene and pyridine and by completing the reaction with ammonia[100]:

$$TaCl_5 + 5Bu^tOH + 4C_5H_5N + NH_3 \rightarrow Ta(OBu^t)_5 + 4C_5H_5N \cdot HCl + NH_4Cl$$

The advantage in this modified procedure is the presence of pyridine from the beginning so that any HCl produced is neutralised before it can react with the much more reactive tertiary butanol to form tertiary butyl chloride and water, which could hydrolyse the tantalum pentachloride irreversibly. Under the same conditions, niobium pentachloride has been reported to yield the oxide-tertiary butoxide, $O{=}Nb(OBu^t)_3$ only. This difference in behaviour may be due to an even greater tendency of niobium for forming oxy-compounds.

A more convenient method of synthesising higher alkoxides of these metals is by alcoholysis reactions[98] of the type:

$$M(OEt)_5 + 5ROH \rightarrow M(OR)_5 + 5EtOH$$

Mehrotra and coworkers[101] extended the technique of alcoholysis by using a solvent like benzene, with which the ethanol (or isopropanol) formed in the reaction can be easily azeotroped off. Apart from the advantage of a lower temperature of the reaction medium, this simple variation made the synthesis of mixed alkoxides possible by carrying out the reactions in different stoichiometric ratios[102]:

$$M(OEt)_5 + xROH \rightarrow M(OEt)_{5-x}(OR)_x + xEtOH$$

The alcoholysis method has been extended to the synthesis of 2,2,2-trifluoroethoxides[103] and hexafluoroisopropoxides[104] of the two metals also.

Apart from alcoholysis the *trans*-esterification technique has also been exploited for the preparation of higher alkoxides. By carrying out the reaction in the presence of cyclohexane, the ethyl or isopropyl acetate[105,106] produced can be again azeotroped out along with the solvent and the reactions can be carried out in the desired molar ratio:

$$M(OPr^i)_5 + xCH_3COOR \rightarrow M(OPr^i)_{5-x}(OR)_x + xCH_3COOPr^i$$

These alcoholysis and *trans*-esterification reactions are very sensitive to steric factors depending on the nature of the alkyl groups involved. For example, the higher pentaalkoxides of niobium could be obtained with various alkyl acetates where R = Pr^n, Pr^i, Bu^n, Bu^s, Bu^t, pentyl^n and Ph groups whereas only mixed derivatives, $Ta(OEt)(OR)_4$ or $Ta(OPr^i)(OR)_4$ could be obtained in the case of tantalum, except in the reaction of secondary or tertiary butyl acetates, in which cases the formation of pentaalkoxides has been reported. This may be due to formation of more stable bridged dimers in the cases of normal alcohols in which slightly smaller tantalum atoms are so effectively sourrounded that further coordination with the reacting alkyl acetate molecule is sterically hindered.

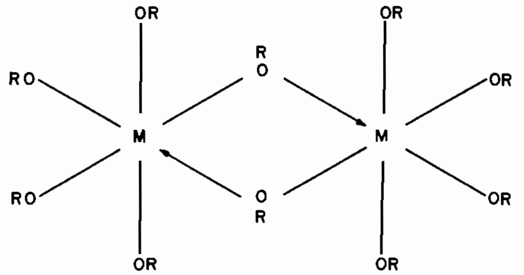
Comparatively much less work has been published[107] on tetraalkoxides of these metals, which can be synthesised by treating the tetradialkylamides with alcohols:

$$M(NR'_2)_4 + 4ROH \rightarrow M(OR)_4 + 4R'_2NH$$

(i). Physical Properties

Similar to the alkoxides of Group III and IV elements, the volatility of these alkoxides also increases and molecular complexity decreases with the increase of the ramification of the alkyl chains[101, 108].

Normal alkoxides of Nb and Ta have been generally reported to be dimeric in boiling benzene. These elements with the electronic structure $4d^4 5s^1$ and $5d^3 6s^2$ can assume octahedral configuration with d^2sp^3 hybridisation by the two molecules of the alkoxides being bound together through intermolecular coordinate bonds:

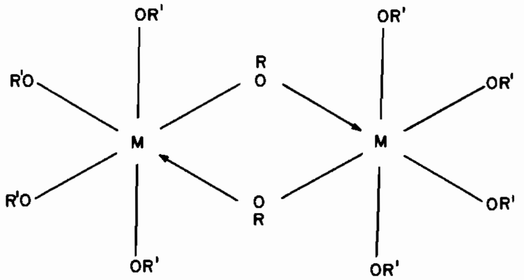


Polymerisation, a consistent feature of normal alkoxides, appears to be prevented in secondary and tertiary alkoxides by steric hindrance to intermolecular association and this leads to a decrease in the degree of polymerisation and an increase in volatility.

Bradley and coworkers[95, 108] reported the molecular weights of a number of tantalum n-alkoxides in different boiling organic solvents and inferred that the variation in their molecular complexities depends on the donor power of the solvent rather than on the difference in dielectric constant (Table I).

A slight decrease in molecular complexities in toluene in comparision to benzene may be due to increased dissociation at elevated temperature.

Some mixed alkoxides, *e.g.*, $Nb(OBu^t)(OMe)_4$, $Nb(OBu^t)(OEt)_4$, $Ta(OEt)(OPr^n)_4$, $Ta(OEt)(OPr^i)_4$, $Ta(OEt)(OBu^n)_4$, $Ta(OBu^t)(OEt)_4$ *etc.* are reported to be dimeric in boiling benzene, having a bridged structure of the type:



However, some other mixed alkoxides like $Nb(OBu^t)(OPr^i)_4$, $Nb(OEt)(OAm^t)_4$, $Ta(OEt)(OBu^s)_4$, $Ta(OEt)(OBu^t)_4$, $Ta(OEt)(OAm^t)$, $Ta(OBu^t)(OPr^i)_4$ *etc.* have a molecular complexity of the order of 1.15, 1.18, 1.38, 1.21 and 1.21 respectively under similar conditions. This difference in degree of association was attributed to the increased steric hindrance which prevents the equilibrium from proceeding towards complete dimerisation.

The i.r. absorption spectra of some primary and secondary alkoxides show two distinct absorption bands[109–111] in solution as well as in Nujol mull, one corresponding to terminal and the other to bridging alkoxide groups. The possible assignments have been made and the dimeric structure has been qualitatively discussed in terms of the relative intensities of terminal to bridging C–O bands.

The variable temperature (–90° C to 50° C) n.m.r. studies[112, 113] of these dimeric pentaalkoxides, $M_2(OR)_{10}$, reveal the alkoxide bridged bioctahedral (edge shared) structure in which a rapid intramolecular exchange of the two types of terminal groups and of the terminal and bridging groups occurs between three nonequivalent sites. Hollaway[114] observed that the activation energy (10.12 Kcal/mol) for the scrambling of the terminal and bridging alkoxide groups is constant and increases by only a small amount on increasing the degree of chain branching in the alkoxide group.

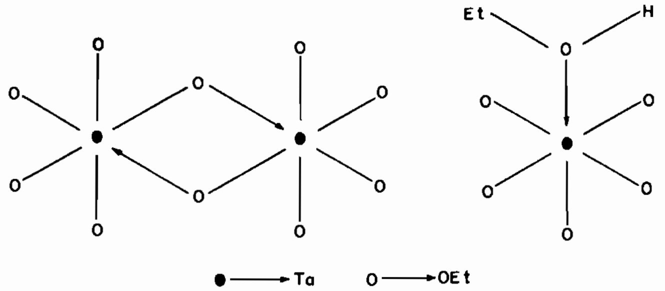
A low temperature n.m.r. study[115] of $Nb_2(OMe)_{10}$ in various solvents shows a significant variation in chemical shifts corresponding to various non-equivalent methoxide groups. This was attributed to the interaction of the solvent with the dissolved methoxide derivative and the preferential solvation of some of the distinct sites.

TABLE I. Molecular Complexity of Alkoxides.

Alkoxides	Solvents					
	Benzene	Toluene	Acetonitrile	Pyridine	Isopropyl ether	Parent alcohol
	b.p. 80°C	110°C	82°C	114°C	68°C	
	D 2.28	2.38	38.8	12.5	3	
$Ta(OMe)_5$	1.98	1.83	1.50	1.01	1.75	1.20
$Ta(OEt)_5$	1.98	1.83	1.50	0.99	1.84	1.78
$Ta(OPr^n)_5$	1.95	1.83	1.50	0.99	1.84	1.70
$Ta(OBu^n)_5$	2.02	1.83	1.48	0.99	1.84	1.40

The monomeric tertiary butoxide shows a rapid intramolecular exchange[112] down to −90° C.

Tantalum pentaethoxide shows a molecular complexity of 1.98 and 1.78 in boiling benzene and ethanol respectively[108]. A molecular complexity of 1.78 in ethanol indicates the presence of two species, *viz.*, dimeric as well as solvated monomeric, in both of which tantalum may attain an octahedral 6-coordination:



Both of these species hydrolyse on addition of water giving polymeric tantalum oxide ethoxides having different compositions depending on the degree of hydrolysis. Plausible structures for some of these polymeric oxide ethoxides[116,117] have been suggested qualitatively on the basis of some infrared spectral evidence. The spectra were found to be quite complex and a continuous decrease in intensity of the ethoxy bands in the region 3.5 μ, 7 μ and 18 μ and increase in the intensity and broadening of a band in the region 19–22 μ corresponding to Ta–O–Ta show the formation of polymeric oxide ethoxide species.

The hydrolysis of $Nb(OEt)_5$ under controlled conditions yielded crystalline niobium oxide ethoxide, $Nb_8O_{11}(OEt)_2O$. The X-ray pattern reveals that the octameric molecule consists of 8 slightly distorted octahedra[118] in which three edge sharing octahedra are linked by two bridging octahedra through corner sharing.

Derivatives like $M(OMe)_5$ and $MCl_2(OMe)_3$ undergo peroxidation[119] on treatment with H_2O_2 in non-aqueous media. The use of labelled H_2O_2* in the above reactions indicates the fixation of the O* atom between M and OMe groups.

C. Double Alkoxides

Niobium and tantalum pentaalkoxides on treatment with the corresponding alkali metal alkoxides in molar ratio 1 : 1 yield double alkoxides having stoichiometry $M'M(OR)_6$, where M′ = Li, Na or K, M = Nb or Ta and R = Me, Et or Pr^i [120]:

$$M'(OR) + M(OR)_5 \xrightarrow{\text{Benzene}} M'M(OR)_6$$

These derivatives are soluble in common organic solvents and are monomeric in boiling benzene. Conductometric titrations[121] of $M(OR)_5$ with the corresponding alkali metal alkoxides in a mixed solvent (alcohol and benzene) provide an additional evidence for the formation of $M'M(OR)_6$ type double alkoxides. The tantalum derivatives tend to have comparatively higher thermal stability compared to the analogous niobium derivatives and the majority of these can be sublimed unchanged under reduced pressure. Rubidium and cesium also form double alkoxides, $RbM(OPr^i)_6$ and $CsM(OPr^i)_6$[122] which are sparingly soluble in benzene and the parent alcohol; these are also thermally stable and can be sublimed under reduced pressure.

Another class of double alkoxides having stiochiometry $M'[M(OR)_6]_2$ where M' = Mg, Ca, Sr or Ba and R = Et or Pr^i have been synthesised by the reactions of the corresponding alkaline earth metal alkoxides with metal ethoxide and isopropoxide[123]. The double ethoxides are completely miscible in parent alcohol and benzene, whereas the isoproxides are soluble in benzene and sparingly soluble in isopropanol. These derivatives are found to be monomeric in boiling benzene.

The thermal stability of the above derivatives increases from Ba to Mg. The ethoxide derivatives, $M'[M(OEt)_6]_2$, M' = Mg, Ca, Sr or Ba, distilled out and isopropoxide derivatives sublimed under reduced pressure, whereas the magnesium analogs disproportionate due to their poor thermal stability.

Only six ethoxide or isopropoxide groups from $M'[M(OR)_6]_2$ could be replaced[123] with tertiary butoxide groups even after prolonged refluxing with tertiary butanol in presence of benzene and simultaneous removal of produced ethanol or isopropanol azeotropically. These mixed double alkoxides are also found to be monomeric in nature.

Aluminium and gallium isopropoxide react with niobium or tantalum isopropoxide in benzene solution forming two classes of double alkoxides[123]:

$$M'(OPr^i)_3 + M(OPr^i)_5 \rightarrow M'M(OPr^i)_8$$
$$2M'(OPr^i)_3 + M(OPr^i)_5 \rightarrow MM'_2(OPr^i)_{11}$$

These double alkoxides are volatile under reduced pressure and soluble in common organic solvents. $M'M(OPr^i)_8$ derivatives have molecular complexity of about 1.6 showing a tendency to dimerisation whereas $MM'_2(OPr^i)_{11}$ derivatives are found to be monomeric in nature.

D. Phenoxides and Allied Derivatives

The formation of polynuclear complexes by the reaction of niobium and tantalum pentaoxide with polyphenols in aqueous solution was studied by Rosenheim and Roehrich[124]. Ligands like phenols, naphthol and anthrol have a tendency to replace chlorine atoms from metal pentachloride in CS_2 solution[125] and compounds of the type $Nb(OPh)_4Cl$, $Ta(OPh)_4Cl$, $Nb(OC_{10}H_7)_3Cl_2$, $Ta(OC_{10}H_7)_3Cl_2$, $Ta(OC_{10}H_7)_5$, $Nb(OC_{14}H_9)_2Cl_3$ and $Ta(OC_{14}H_9)_2Cl_3$ have been synthesised.

All five chlorine atoms were replaced by reacting the corresponding pentachloride with phenol and naphthol[94] in carbon tetrachloride and benzene media.

Mixed ethoxide phenoxide derivatives have been synthesised[126] by the reaction of metal ethoxide with phenol in stoichiometric ratios in refluxing benzene:

$$M(OEt)_5 + nC_6H_5OH \xrightarrow[n\,=\,1\text{–}4]{} M(OEt)_{5-n}(OC_6H_5)_n + nEtOH$$

The final product in the case of niobium was the pentaphenoxide whereas tantalum could yield only the $Ta(OEt)(OPh)_4$ derivative. Similar results were obtained by the *trans*-esterification of the ethoxides[105, 106] with phenyl acetate in cyclohexane.

The phenoxide derivatives are soluble in common organic solvents and some of these can be distilled unchanged under reduced pressure. Their chemical and structural investigations have yet to be made.

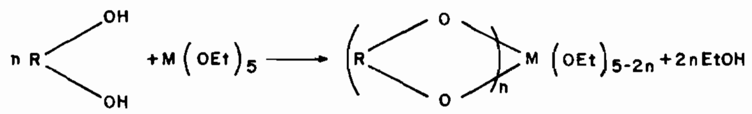
o-Mercaptophenol reacts with metal pentachloride to form the derivatives $HM(SC_6H_4O)_3$ in which the metal is hexacoordinated[127].

Pentathiophenolates of niobium and tantalum have also been synthesised by the reaction of metal pentachloride with $Al(SPh)_3Et_2O$ in benzene solution[128].

E. Glycollates and Catechollates

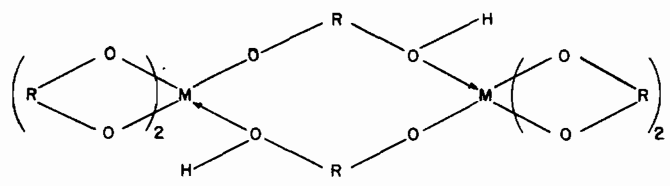
Rosenheim and Roehrich[124] reported the formation of hydroxy derivatives in the reaction of niobium and tantalum compounds with catechol. The formation of polynuclear complexes in psuedo non-aqueous media with catechol and 1,2-diols has been shown by Fairbrother and coworkers[130].

A number of glycollates in non-aqueous media have been synthesised by the reaction of metal ethoxide with various glycols like ethane-1,2-diol, propane-1,2-diol, propane-1,3-diol, butane-2,3-diol, butane-1,4-diol, pentane-1,5-diol, hexylene glycol and pinacol in molar ratios 1 : 1, 1 : 2 and 1 : 3[131–133]:



The triethoxide monoglycollate and monoethoxide diglycollate derivatives are soluble in common organic solvents but undergo decomposition when heated under reduced pressure except the butane-2,3-diol and hexylene glycol derivatives which can be distilled unchanged under reduced pressure.

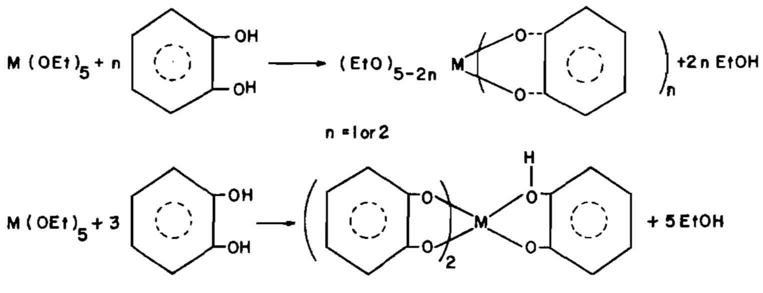
The tris-derivatives undergo decomposition on heating except butane-2,3-diol and hexylene glycol derivatives which lose a glycol molecule intermolecularly, giving derivatives with a composition corresponding to dimetal pentaglycollates:



The tris-derivatives which are soluble in common organic solvents are dimeric in nature.

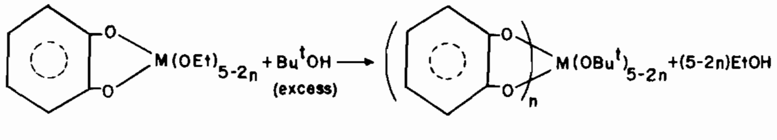
A mixture of MCl_5 and catechol in benzene in 1:5 molar ratio yields $M(C_6H_4O_2H)_5$, whereas $M_2(C_6H_4O_2)_5$ derivatives are obtained on prolonged refluxing of a 2:5 molar mixture[134]. Fusion of o-$C_6H_4(OH)_2$ and $Ta(OMe)_5$ in molar ratio 1:1 gives $Ta(C_6H_4O_2)(OMe)_3MeOH$ which melts with decomposition around 170° C[135]. A crystalline product, $KTa(C_6H_4O_2)_2(OMe)_2$ was isolated on refluxing a reaction mixture of $KTa(OMe)_6$ and o-$C_6H_4(OH)_2$ in methanol. The product was found to be soluble in acetonitrile or acetone and insoluble in ether, benzene or carbon tetrachloride. Species like $M(C_6H_4O_2)(OMe)_4^-$, $M_2(C_6H_4O_2)_2(OMe)_7^-$, $M(C_6H_4O_2)_2(OMe)_2^-$ and $M(C_6H_4O_2)_3(OMe)^{-2}$ have been established[135] in methanol solution and their equilibrium constants have been evaluated.

Catechollates and mixed ethoxide catechollates[136] have been synthesised by the reactions of the corresponding ethoxide with catechol in different molar ratios:



Mono and di-derivatives are soluble and tris-derivatives are sparingly soluble in common organic solvents.

Ethoxide derivatives change to tertiary butoxide derivatives[136] on refluxing with excess tertiary butanol in benzene:



The dihydroxy compounds (LH_2) like 2,3-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,2'-dihydroxybiphenyl and 2,2'-dihydroxybinaphthyl[137] react with metal pentachloride in benzene to form cyclic derivatives, $H(ML_3)$, in which the metal always appears to achieve hexacoordination. Some of these derivatives on treatment with amines, NH_3 or BuLi gives the corresponding salts:

$$HML_3 + RNH_2 \rightarrow RNH_3 \cdot ML_3$$
$$HML_3 + NH_3 \rightarrow NH_4 \cdot ML_3$$
$$HML_3 + BuLi \rightarrow Li \cdot ML_3 + BuH$$

F. *β-Diketonate and β-Ketoester Derivatives*

Rosenheim and Roehrich[124] in 1932 synthesised an inner complex of niobium by the reaction of the water extract of a fused mixture of Nb_2O_5 and $KHSO_4$ with acetylacetone. Funk[138] had successfully isolated dichloride dialkoxide acetylacetonates of niobium and tantalum by the reaction of a solution of the corresponding anhydrous pentachloride in methanol or ethanol with acetylacetone:

$$MCl_5 + Hacac \xrightarrow{ROH} MCl_2(OR)_2(acac) + 3HCl$$

A similar reaction was reported with benzoylacetone[138] also. The compounds are reported to be in the form of rhombic needles and their colour varies from colourless to deep yellow. Djordjevic and Katovic[139] also synthesised the above compounds by a similar route and have confirmed their isomorphous nature by powder X-ray diffraction. These derivatives are quite stable in solid state and undergo interaction with solvent molecules on dissolution:

$$\begin{array}{l} NbX_2(acac)(OR)_2 \overset{ROH}{\rightleftharpoons} NbX_2(OR)_3 + H^+ + acac^- \\ \qquad\qquad\qquad\qquad\quad \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\qquad\quad 1/2Nb_2X_4(OR)_6 \\ NbX_2(acac)(OR)_2 \overset{ROH}{\rightleftharpoons} NbX(acac)(OR)_3 + H^+ + X^- \\ \qquad\qquad\qquad\qquad\quad \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\qquad\quad Nb(acac)(OR)_4 + H^+ + X^- \end{array}$$

The above interaction equilibria were proposed on the basis of molecular weight and specific conductivity data in parent alcohols.

Solvolysis of the Nb=O bond was also confirmed by the spectra of alcoholic solutions of $NbOCl_3$ in the presence of acetylacetone:

$$NbOCl_3 + Hacac + 2ROH \rightarrow NbCl_2(acac)(OR)_2 + H^+ + Cl^- + H_2O$$

The polymeric chain[140] present in $NbOCl_3$ appeared to be broken up and the spectra were found to have a close similarity to that of the product obtained from $NbCl_5$ reaction.

The reaction of acetylacetone with powdered $NbOCl_3$ at room temperature gives

$$NbOCl_3 + Hacac \rightarrow NbOCl_2 \cdot acac + HCl$$

The oxychloride derivative was found to be insoluble and decomposed without melting and was, therefore, considered to be polymeric in nature[139].

Pentamethoxides of niobium and tantalum yield $M(OMe)_4(acac)$ on refluxing with acetylacetone in methanol solution[135]. $M(OMe)_4(acac)$ on fusion with $MCl_2(OMe)_2(acac)$ gives $MCl(OMe)_3(acac)$:

$$M(OMe)_4(acac) + MCl_2(OMe)_2(acac) \rightarrow 2MCl(OMe)_3(acac)$$

Johnson[141] synthesised compounds having stoichiometry $MX_2(OMe)_2L$, where X = Cl or Br and L = β-diketone or related ligands by refluxing a mixture of metal pentahalide and ligand in anhydrous methanol.

The i.r. spectral studies of the complexes $MX_2(OR)_2(acac)$ and $NbOCl_2(acac)$ show the presence of Cl and O bridges[142].

A number of β-diketone[148] and β-ketoester[143–146] derivatives having composition $M(OEt)_{5-n}(Lig)_n$ where Lig = acetylacetone, benzoylacetone, methylacetoacetate, ethylacetoacetate or ethylbenzoylacetate and n = 1, 2 or 3, have been synthesised by the reaction of the corresponding ethoxide with ligands in the required stoichiometric ratio:

$$M(OEt)_5 + nHLig \xrightarrow{\text{Benzene}} M(OEt)_{5-n}(Lig)_n + nEtOH$$

These derivatives are light coloured in appearance, soluble in common organic solvents, monomeric in boiling benzene and hydrolysable in nature. All β-ketoester derivatives can be distilled under reduced pressure whereas only mono β-diketone tetra-ethoxide derivatives could be distilled and other derivatives undergo decomposition.

The ethoxide groups in the mixed derivatives, $M(OEt)_{5-n}(Lig)_n$, are readily exchanged with higher boiling alcohols like normal, secondary or tertiary butanol:

$$M(OEt)_{5-n}(Lig)_n + ROH \rightarrow M(OR)_{5-n}(Lig)_n + (5-n)EtOH$$

Kapoor and coworkers[146] synthesised dibenzoylmethane derivatives, $M(OR)_{5-n}(Lig)_n$, where R = Et or Bu^t and n = 1, 2 or 3 by a similar route.

Niobium and tantalum appear to achieve coordination numbers six, seven and eight in mono-, di- and tri- substituted derivatives respectively. The non-formation of tetra- and penta derivatives in the above reactions could be ascribed to the improbability of achieving a coordination number beyond eight by the central metal atoms.

Syamal and coworkers[147] synthesised moisture sensitive, crystalline, monomeric and diamagnetic complexes of stoichiometry $MCl_2(OMe)_2L$, where L = benzoylacetone, *o*-hydroxybenzophenone, 2-hydroxyacetophenone, benzoyl-acetanilide, acetoacetanilide and salicyldehyde. The n.m.r. spectra of complexes suggest a *trans*-dichloro structure having 6-coordinated metal atoms.

A number of fluoro-alkoxy fluoro β-diketo derivatives have been synthesised[148] by the reaction of metal halide with fluoro β-diketone in presence and absence of fluoro alcohols:

$$MX_5 + nCF_3COCH_2COCF_3 + mCF_3CH_2OH \rightarrow M(OCH_2CF_3)_m(CF_3COCHCOCF_3)_nX_{5-(m+n)} + (m+n)HX$$

where m = 1, 2 or 3, n = 1 or 2 and X = Cl or Br.

$$MX_5 + nCF_3COCH_2COCF_3 \rightarrow M(CF_3COCHCOCF_3)_nX_{5-n} + nHX$$

where n = 2 or 3.

$$MX_5 + CF_3CF_2CF_2COCH_2COCF_3 + 3CF_3CF_2CH_2OH \rightarrow M(OCH_2CF_2CF_3)_3(CF_3CF_2CF_2COCHCOCF_3)X + 4HX$$

These derivatives are soluble in organic solvents and volatile in nature except some bromo-derivatives which are non-volatile.

G. Carboxylic and α-Hydroxy Carboxylic Acid Derivatives

Pentachlorides of niobium and tantalum form basic acetates[149] on treatment with acetic acid. Pentaethoxides react with lower and higher carboxylic acids[150] in different stoichiometric ratios to form compounds with composition, $M(OEt)_{5-n}(OOCR)_n$:

$$M(OEt)_5 + nRCOOH \rightarrow M(OEt)_{5-n}(OOCR)_n + nEtOH$$

where n = 1, 2 or 3.

When the reaction was carried out in molar ratio 1:4 or 1:>4, the lower carboxylic acids give the corresponding basic carboxylates and the higher carboxylic acids form monoethoxide tetracarboxylates:

$$M(OEt)_5 + 4RCOOH \rightarrow MO(OOCR)_3 + RCOOEt + 4EtOH$$

$R = CH_3, C_2H_5$ or C_3H_7

$$M(OEt)_5 + 4RCOOH \rightarrow M(OEt)(OOCR)_4 + 4EtOH$$

$R = C_{11}H_{23}, C_{15}H_{31}$ or $C_{17}H_{35}$

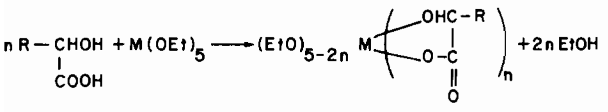
These derivatives are soluble in common organic solvents except the basic carboxylates which are insoluble. The formation of basic carboxylates is not surprising because of the tendency of these metals to form oxy derivatives. For example, penta-chlorides form oxytrichloride adducts on treatment with dimethyl or diphenyl sulphoxide[63]:

$$MCl_5 + 3Me_2SO \rightarrow MOCl_3 \cdot 2Me_2SO + Me_2SCl_2$$

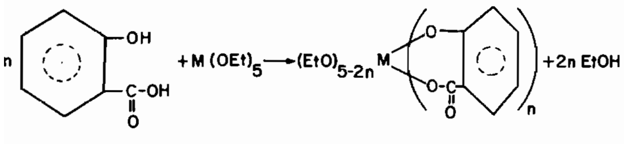
The carboxylate derivatives are thermally unstable and undergo decomposition except the tetraethoxide monoacetate and butyrate derivatives which can be distilled out under reduced pressure.

Salicylic acid forms internal complexes[124] with niobium and tantalum chlorides in pseudo non-aquous media. A mixture of $NbCl_5$ or $TaCl_5$ fused with salicylic acid yielded $Nb_2(OC_6H_5COO)_5$ or $Ta_2(OC_6H_5COO)_5$ deriv-atives[16], whereas only $Nb_2Cl_4(OC_6H_4COO)_3$ was formed when the above reactants were mixed and refluxed in dry ether.

The reactions of metal pentaethoxide with various hydroxy carboxylic acids[151] like lactic, mandelic or salicylic acid form different derivatives according to the ratio of reactants:



n = 1 or 2 and R = CH_3 or C_6H_5



These derivatives are soluble in common organic solvents and undergo decomposition on heating even under reduced pressure. Reactions in molar ratio 1:3 or > 3 yield tris-derivatives which are sparingly soluble in nature. No attempt has been made to investigate the physico-chemical and structural aspects of this class of compounds.

H. Nitrogen Containing Ligand Derivatives

The addition of pyridine hydrochloride or quinoline hydrochloride in HCl solution of $NbCl_5$ or $NbOCl_3$ yielded $(C_6H_5NH)NbOCl_4$ or $(C_9H_7NH)NbOCl_4$ derivatives[152]. The i.r. spectra of these products show the presence of linear Nb–O–Nb–O bonds. Djordjevic and Vuletic[153] synthesised 8-coordinated tri-peroxo-niobates(V) and tantalates(V) by the reaction of potassium niobate or tantalate with ligands like 2,2′-bipyridine and *o*-phenanthroline in H_2O_2 solution. I.r. spectral and other physico-chemical evidence shows the attachment of the peroxo group on the metal as bidentate ligand in addition to 2,2′-bipyridine and *o*-phenanthroline which behave as normal bidentate ligands.

$NbCl_5$ forms a diamagnetic complex, $Li[Nb(Dipy)_3] \cdot 3.5THF$ by the reaction of metal chloride with 2,2′-dipyridyl and Li_2(dipy) under nitrogen atmosphere at −78° C[154], which is soluble in pyridine, slightly soluble in benzene, DMF, ether and decomposes in ethanol and water.

8-Quinolinol has been used[155–157] for the extraction of these metals in the form of oxo-complexes, $MO(Q)_3$. Frazer and coworkers[158] synthesised a series of complexes having the general formula $MX_m(Q)_{5-m}$, where M = Nb or Ta, X = Cl or Br, QH = 8-quinolinol and m = 1–3, by the reaction of the corresponding metal halides with 8-quinolinol. The elemental analysis, i.r. spectral and X-ray powder diffraction studies indicate the existence of the metal in 9-, 8-, 7- and 6-coordination states.

Benzoylphenylhydroxylamine (BPHA) reacts with metal pentachlorides in non-aqueous media and forms in an inert atmosphere an ultimate product $M(BPHA)_4Cl$[159]. The reaction with KSeCN in molar ratio 1:6 in MeCN solution yields complexes[168] having stoichiometry $K[M(NCSe)_6]$ in which the nitrogen is bonded to the metal.

(i). Amino Complexes

Fowles and coworkers[161–163] made a detailed study of the reactions of MX_5 (X = Cl, Br) with primary ($MeNH_2$, $EtNH_2$, Pr^nNH_2 and $BuNH_2$), secondary (Me_2NH, Et_2NH and Pr_2NH) and tertiary (Me_3N and Et_3N) amines. Higher primary amines form $MX_3(NHR)_2 \cdot NH_2R$ type complexes whereas lower amines like $MeNH_2$ and $EtNH_2$ form $MX_2(NHMe)_3$ and $MX_2(NHEt)_3$ derivatives. Secondary amines form $MX_3(NR_2)_2 \cdot NHR_2$ type derivatives having monomeric character in boiling benzene:

$$MX_5 + 5NHR_2 \rightarrow MX_3(NR_2)_2 \cdot NHR_2 + 2NHR_2 \cdot HCl$$

Only insoluble adducts are formed with tertiary amines:

$$MX_5 + NR_3 \rightarrow MX_5 \cdot NR_3$$

These derivatives are diamagnetic in nature and do not show any tendency to reduction.

Metal pentafluorides form adducts[164] like $MF_5 \cdot 2EtNH_2$, $MF_5 \cdot Et_2NH$ and $MF_5 \cdot Et_3N$ with primary, secondary and tertiary amines, whereas adducts like MF_4NEt_2 and $MF_3(NEt_2)_2$[165] are formed with Me_3SiNEt_2; the latter are polymeric in nature with fluorine bridges.

All the five chlorine atoms of metal penta-chlorides can be replaced by reacting with the lithium salts[166] of secondary amines:

$$MCl_5 + 5LiNR_2 \rightarrow M(NR_2)_5 + 5LiCl$$

Some of these derivatives are thermally unstable and decompose. The niobium derivatives appear to undergo the following sequence of decomposition:

$$Nb(NR_2)_5 \rightarrow Nb(NR_2)_4 + NR_2 \text{ (or } HNR_2\text{, imine } etc.\text{)}$$

However, the tantalum derivatives follow a different mode:

$$Ta(NR_2)_5 \rightarrow Ta(NR_2)_4 + R_2N^- \rightarrow RN{=}Ta(NR_2)_3 + HNR_2 + (R\text{–}H\text{, olefin})$$

Only $Ta(NMe_2)_5$ could be sublimed unchanged[167]. Bradley and Gitlitz[168] have attempted to explain the stability and structure of some of these complexes on the basis of their i.r. and n.m.r. spectra.

Dialkylamido derivatives of niobium on refluxing with alcohols or triethyl silanol[107] form penta-derivatives of the type $Nb(OR)_5$ or $Nb(OSiEt_5)_5$, with the liberation of the corresponding dialkyl amine.

Dialkylamido derivatives of tantalum undergo insertion reaction[169] on treatment with MeCN;

$$Ta(NMe_2)_5 + xMeCN \rightarrow Ta[N:C(Me)NMe_2]_x(NMe_2)_{5-x}$$

Reaction with CS_2 gives N,N-dialkyldithiocarbamate, $Ta[S_2C(NMe_2)]_5$[170], whereas the reaction product of CS_2 and $Nb(NMe_2)_5$ was found to be a mixture of $Nb[S_2C(NMe_2)]_5$ and tetramethyldithiuram disulphide. The chemistry of these metal dialkylamides has been recently reviewed in two review[2,3] articles.

The oxyhalides, $NbOX_3$ (X = Cl or Br) undergo aminolysis[171,172] with primary and secondary aliphatic amines. The reactions proceed with the partial displacement of Cl or Br from $NbOX_3$ and lead to the formation of a 1 : 1 adduct:

$$NbOX_3 + H_2NR \rightarrow NbOX_2 \cdot NHR \cdot NH_2R + RNH_2 \cdot HCl$$

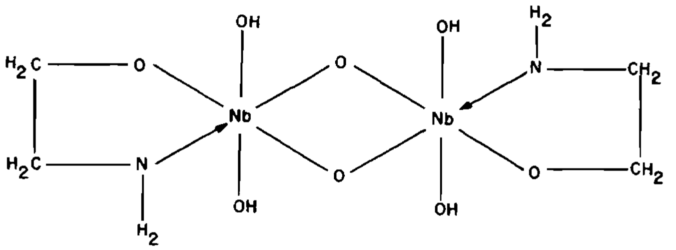
$$NbOX_3 + HNR_2 \rightarrow NbOX_2 \cdot NR_2 \cdot NHR_2 + R_2NH \cdot HCl$$

No aminolysis was observed with tertiary amines even on prolonged refluxing and insoluble adducts precipitate out instantaneously on mixing, except in the reaction of $NbOCl_3$ and $N(C_8H_{17})_3$, where a soluble species[84], $NbOCl_3 \cdot N(C_8H_{17})_3$ was reported. The i.r. spectral data indicate polymeric nature of these products having Nb–O–Nb–O backbone.

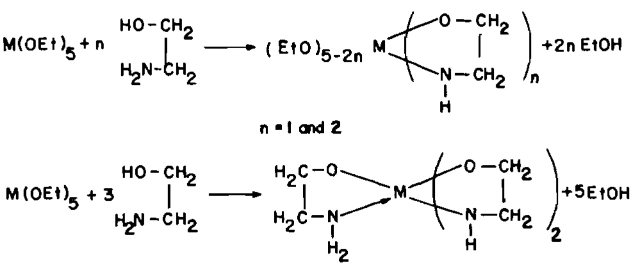
Similar adducts[173] have also been isolated with aromatic and heterocyclic amines, *e.g.*, $PhNEt_2$, 2-methylquinoline, 2-phenylquinoline *etc.*

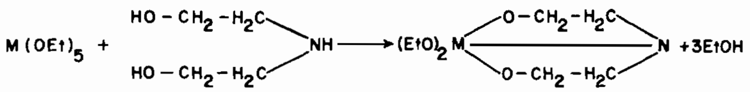
(ii). Alkanolamine Derivatives

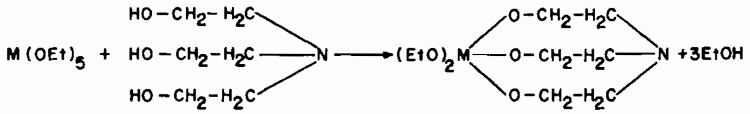
Fairbrother and Taylor[174] reported the solubility of niobic acid in aqueous solution of ethanolamine and had suggested the formation of a five membered chelate ring:

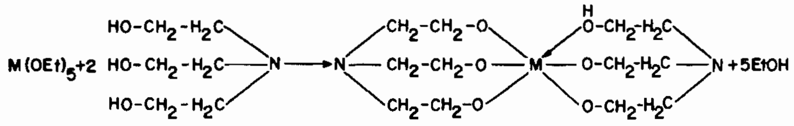


Mehrotra and Kapoor[175,176] studied the reactions of niobium and tantalum pentaethoxides with monoethanolamine, diethanolamine and triethanolamine in non-aqueous media. The following types of reactions have been reported:









Monoethanolamine derivatives are soluble in organic solvents and show a tendency to polymerisation and decomposition on heating under vacuum. The bis- and tris-derivatives are sparingly soluble.

Diethanolamine gives only soluble mono-derivatives. Pure bis-derivatives could not be isolated even after prolonged refluxing.

Triethanolamine forms mono- and bis-derivatives which are soluble and monomeric in nature. Monoderivatives can be distilled under reduced pressure whereas bis-derivatives undergo decomposition.

Physico-chemical and structural aspects of this class of derivatives do not appear to have been investigated.

(iii). Oxime Derivatives

Keto- and aldoximes (LH) like acetoxime, ethylmethylketoxime, diethylketoxime, acetaldoxime, benzaldoxime and cyclopentanoneoxime react with niobium and tantalum pentaethoxide or isopropoxide in different stoichiometric ratios yielding derivatives having the composition $M(OR)_{5-n}(L)_n$[177, 178].

$$M(OR)_5 + nLH \rightarrow M(OR)_{5-n}(L)_n + nROH$$
$$n = 1\text{–}5;\ LH = \text{Oxime.}$$

The pentaoximates are also synthesised by the reaction of metal pentachloride with the corresponding oxime in presence of triethylamine:

$$MCl_5 + 5LH + 5Et_3N \rightarrow M(L)_5 + 5Et_3N \cdot HCl$$

These derivatives vary from solids to viscous liquids. These are hydrolytically unstable, soluble in common organic solvents and monomeric in boiling benzene. Tetra- and triethoxide derivatives of lower oximes can be distilled under reduced pressure but higher oxime derivatives show appreciable decomposition. The ethoxide groups of $M(OEt)_{5-n}(L)_n$ can be replaced by higher alcohols like n-butanol, *sec*-butanol and *tert*-butanol[171].

The pentaoximate derivatives form hydrated oxides on exposure to the atmosphere and chloride oximates on treatment with acetyl chloride:

$$M(L)_5 + 2CH_3COCl \rightarrow MCl(L)_4 + CH_3COL$$
$$ML_5 + 2CH_3COCl \rightarrow NCl_2L_3 + 2CH_3COL$$

The reactions appear to become quite complex after the substitution of two oxime groups by chlorine atoms.

The chemistry of oxime derivatives of metals in general has been extensively reviewed in a recent review article[4].

(iv). Schiff Base Derivatives

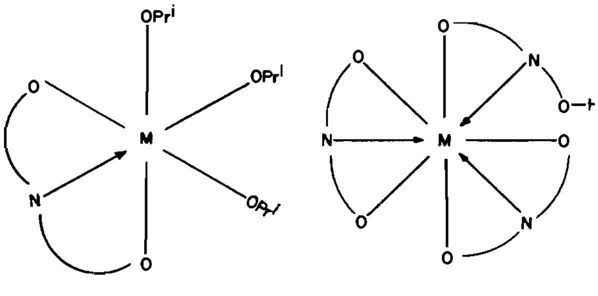
The first attempt at the synthesis of Schiff base derivatives of niobium and tantalum was made in 1960 by the reaction of the corresponding metal pentachlorides with bis-salicylidene-ethylenediamine[180]. Compounds having composition $[MCl(Salen)]Cl_2$ were isolated. Tandon and coworkers[181–184] synthesised a number of Schiff base derivatives by the reaction of metal isopropoxides with various bifunctional tridentate ligands (SBH_2) like salicylidene-2-hydroxyethylamine ($C_9H_{11}NO_2$), salicylidene-2-hydroxy-n-propylamine ($C_{10}H_{13}NO_2$), *o*-hydroxy-acetophenone-2-hydroxyethylamine ($C_{11}H_{13}NO_2$), *o*-hydroxy-acetophenone-2-hydroxy-n-propylamine ($C_{12}H_{15}NO_2$), β-hydroxy-naphthylidene-2-hydroxyethylamine ($C_{13}H_{13}NO_2$), acetylacetone-2-hydroxyethylamine ($C_7H_{13}NO_2$), acetylacetone-2-hydroxy-n-propylamine ($C_8H_{15}NO_2$), acetylacetone(2-oxyanil) ($C_{11}H_{13}NO_2$), benzoylacetone-(2-oxy-anil) ($C_{16}H_{15}NO_2$) and salicylidene-*o*-aminophenol ($C_{13}H_{11}NO_2$); monofunctional bidentate ligands (SBH) like benzylidene-2-hydroxyethylamine ($C_9H_{11}NO$), benzylidene-2-hydroxy-n-propylamine ($C_{10}H_{13}NO$), benzylidene-*o*-aminophenol ($C_{13}H_{11}NO$), salicylidene-aniline ($C_{13}H_{11}NO$) and β-hydroxy-naphthylidene-aniline ($C_{17}H_{13}NO$); bifunctional tetradentate ligands ($S'B'H_2$) like bis-acetylacetone-ethylenediamine ($C_{12}H_{20}N_2O_2$), bis-benzoylacetone-ethylenediamine ($C_{22}H_{24}N_2O_2$) and bis-salicylidene-ethylenediamine ($C_{16}H_{16}N_2O_2$) Schiff bases in benzene.

The reactions may be represented as follows:

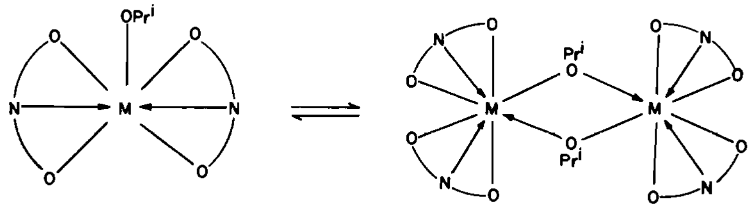
$$\mathrm{M(OPr^i)_5 + nSBH_2 \rightarrow M(OPr^i)_{5-2n}(SB) + 2nPr^iOH}$$
$$\mathrm{n = 1\ or\ 2}$$
$$\mathrm{M(OPr^i)_5 + 3SBH_2 \rightarrow M(SB)_2(SBH) + 5Pr^iOH}$$
$$\mathrm{M(OPr^i)_5 + nSBH \rightarrow M(OPr^i)_{5-n}(SB)_n + nPr^iOH}$$
$$\mathrm{n = 1\text{–}4}$$
$$\mathrm{M(OPr^i)_5 + S^1B^1H_2 \rightarrow M(OPr^i)_3(S^1B^1) + 2Pr^iOH}$$
$$\mathrm{M(OPr^i)_5 + 2S^1B^1H_2 \rightarrow M(OPr^i)_2(S^1B^1)(S^1B^1H) + 3Pr^iOH}$$

The isopropanol produced during the reaction was distilled off azeotropically. The pattern of the reaction has been reported to involve S_N2 type mechanism. The central metal atoms acquire coordination numbers six, seven and eight respectively, depending on the nature and number of ligand molecules in these derivatives.

The derivatives, $M(OPr^i)_3(SB)$, $M(OPr^i(SB)_2$ and $M(SB)_2(SBH)$ are moisture sensitive, coloured, varying from solid to liquid, soluble in common organic solvents and thermally unstable. $M(OPr^i)_3(SB)$ and $M(SB)_2(SBH)$ derivatives are monomeric and the following structures have been proposed by Tandon and Prashar[181,182] on the basis of certain i.r. spectral evidence:



$M(OPr^i)(SB)_2$ derivatives show a molecular complexity between 1.2 to 1.6 indicating the probability of an equilibrium between monomeric and dimeric species:



Monofunctional bidentate Schiff bases can replace only four isopropoxide groups from $M(OPr^i)_5$ whereas bifunctional tetradentate Schiff bases can replace only three isopropoxide groups even after prolonged refluxing in benzene. This may be due to larger steric hindrance and supersaturation of coordination sites in the metal atoms.

(v). Hydroxylamine Derivatives

N,N-Diethylhydroxylamine reacts with metal ethoxides or isopropoxides in different stoichiometric ratios to form complexes[177–179] having the composition $M(OR)_{5-n}(ONEt_2)_n$:

$$\mathrm{M(OR)_5 + nEt_2NOH \xrightarrow{Benzene} M(OR)_{5-n}(ONEt)_{2n} + nROH}$$
$$\mathrm{n = 1\text{–}5}$$

The products are generally liquids, miscible with organic solvents, monomeric in boiling benzene, highly susceptible to hydrolysis; they can be distilled unchanged in quantitative yield under reduced pressure.

I. Trialkylsilyloxide Derivatives

A number of compounds having M–O–Si bonds, where M = V, Nb, Ta, Cr, W, P, Sn, Zr *etc.* have been synthesised[185,186] to study the stability of this linkage to chemical and thermal degradation in order to build inorganic polymers having a Si–O–M backbone. The derivatives, $M(OSiR_3)_5$[187,188] have been synthesised by the reaction of metal alkoxides with the corresponding trialkylsilyl acetate or trialkylsilanol:

$$\mathrm{M(OR)_5 + 5R_3SiOOCCH_3 \rightarrow M(OSiR_3)_5 + 5CH_3COOR}$$
$$\mathrm{M(OR)_5 + 5R_3SiOH \rightarrow M(OSiR_3)_5 + 5ROH}$$

The mixed derivatives $(EtO)_{5-n}Ta(OSiR_3)_n$ where n = 1–5, have been synthesised[189] by refluxing the reaction mixtures of $Ta(OEt)_5$ and $R_3SiOOCCH_3$ in different molar ratios in cyclohexane and continuous fractionation of the liberated ester with the solvent cyclohexane:

$$\mathrm{Ta(OEt)_5 + nR_3SiOOCCH_3 \rightarrow (EtO)_{5-n}Ta(OSiR_3)_n + nEtOOCCH_3}$$

These derivatives are liquids or crystalline solids, soluble in common organic solvents, monomeric in nature and susceptible to hydrolysis. The liquids are distillable whereas solids undergo decomposition under reduced pressure. Mixed alkoxide trialkylsilyloxide derivatives undergo disproportionation[189]. The i.r. spectra show absorption bands[109] for M–O and M–O–Si bonds.

Hydrolysis of $Ta(OSiMe_3)_5$ in dioxane–cyclohexane mixtures yields a product containing coordinated dioxane and trimethylsilanol[190]. This product when heated to 120° C under vacuum yields polymers having composition $[TaO_x(OSiMe_3)_{5-2x}]_n$ where $X = 0.469$ to 1.202, which are soluble in cyclohexane. The polymers having molecular complexity in the range 1.8–10.04 have been identified. Similar polymers have also been characterised in the hydrolysis of tetramethylsilyloxide of zirconium[191] and titanium[192].

J. Reactions with Phosphorus Containing Ligands

Metal pentachlorides react with methyl phosphonic acid in absolute acetone to form $M_2O(O_3PMe)_4$ derivatives[193], which are amorphous, insoluble in water and common organic solvents and polymeric in nature. The reactions with sodium salts of dimethyl dithiophosphate, diethyl dithiophosphate and dicyclohexyl dithiophosphate (LNa) in methanol solution[194] form $NbX(OMe)_2L_2$, where X = Cl or Br, derivatives. These derivatives are soluble, monomeric and diamagnetic in nature.

Difluorodithiophosphinic acid, HS_2PF_2, which itself is a strong acid[195, 196], forms difluorodithiophosphinates with several metals and metal oxides[197, 198]. The reaction of niobium or tantalum pentachloride[199] with this ligand gives:

$$MCl_5 + 2HS_2PF_2 \rightarrow Cl_3M(S_2PF_2)_2 + 2HCl$$

The products are air and moisture sensitive, volatile, thermally stable and diamagnetic. ^{19}F.N.m.r. and i.r. spectra indicate the bidentate nature of F_2PS^- ion. Some of these niobium derivatives undergo rearrangement during volatilization with the formation of SPF_2Cl:

$$Cl_3Nb(S_2PF_2)_2 \rightarrow Cl_2Nb(S)S_2PF_2 + SPF_2Cl$$

$Cl_3Nb(S_2PF_2)_2$ on dissolution in pyridine gives SPF_3 and a complex product:

$$3Cl_3Nb(S_2PF_2)_2 \rightarrow 3Cl_3NbS + 4SPF_3 + P_2S_5$$
$$Cl_3NbS + 2Cl_2NbS + 4PyHCl + 2Py \rightarrow [PyH]^+_4[S_3Nb_3Cl_{11}]\cdot 2Py^{-4}$$

The tantalum complexes do not either show any tendency of such decomposition during volatilization or complex formation on dissolution in pyridine.

Metal pentachlorides form ionic complexes[200] when mixed and refluxed with tertiary butyl and alkylphosphorus chloride:

$$Me_3CCl + RPCl_2 + MCl_5 \rightarrow [Me_3CPRCl_2]^+[MCl_6]^-$$

Some hydride complexes[201] of tantalum with $Me_2PCH_2CH_2PMe$ (L) were synthesised by the reaction of tantalum pentachloride with the above ligand in the presence of hydrogen and metallic potassium:

$$TaCl_5 + 5H + 5K + 2Me_2PCH_2CH_2PMe \rightarrow H_5Ta\cdot 2Me_2PCH_2PMe + 5KCl$$

This complex reacts with CO under pressure in benzene solution to form a new complex $HTa(CO)_2L_2$.

K. Reactions with Tri-n-butyl Boron

Tri-n-butyl boron reacts with niobium pentachloride in boiling cyclohexane to form $NbCl_3BBu$[202] which when heated under vacuum or in an argon atmosphere at about 260° C changes to $NbBCl_2$:

$$\begin{tikzcd} NbCl_5 + Bu_3B \rightarrow NbCl_3\cdot BBu + 2BuCl \arrow[d, "260^\circ C"', "Argon"] \\ NbBCl_2 + BuCl \end{tikzcd}$$

Both the products, $NbCl_3\cdot BBu$ and $NbBCl_2$, are polymeric in nature and show an absorption at 685 cm^{-1} which may be assigned to NbBNbB chains.

A mixture of $NbOCl_3$ and excess of Bu_3B on heating in the absence of air near 110° C form $NbOCl\cdot BBu$ which, when heated beyond 320° C, is converted to NbOB:

$$NbOCl_3 + Bu_3B \xrightarrow{110^\circ C} NbOCl\cdot BBu + 2BuCl$$

$$NbOCl\cdot BBu \xrightarrow{320^\circ C} NbOB + BuCl$$

NbOB is quite stable up to 600° C but on heating at about 800° C in contact with air is convertes to Nb_2O_5 and B_2O_3[203, 204]. NbOB was reported to be chemically and structurally analogous to NbON and, therefore, polymeric in nature.

BF_3 reacts with MF_6^- (M = Nb or Ta) derived from tetra-n-butylammonium hexafluoroniobate or tantalate in CH_2Cl_2 solution to form a series of complex ionic species[205]:

$$BF_3 + MF_6^- \rightleftharpoons BF_4^- + MF_5$$
$$MF_5 + MF_6^- \rightleftharpoons M_2F_{11}^-$$
$$BF_3 + BF_4^- \rightleftharpoons B_2F_7^-$$
$$M_2F_{11}^- + BF_3 \rightleftharpoons BM_2F_{14}^-$$

These ionic species have been predicted by fluorine resonance n.m.r. spectroscopy of the solutions at low temperature and vapour pressure measurements.

The reaction with MF_5 was found to be very slow and therefore, no equilibrium could be detected.

L. Insertion Reactions

The insertion across M–N bonds in amino complexes of Group Vth elements, As(III), Sb(III), Nb(V) and Ta(V), by a variety of multiply bonded acceptor molecules like carbon disulphide, ketones, carbon dioxide *etc.* has been reported[206, 207] and included in two recent review articles[208, 209]. The formation of these derivatives was indicated by the disappearance of the characteristic i.r. bands due to the multiply bonded groups accompanied by the appearance of a new band in their i.r. spectra. Bradley and Gitlitz[170, 210] observed an exothermic reaction on dissolution of $M(NR_2)_5$, where R = Me or Et, in carbon disulphide and successfully isolated two different derivatives, *viz.*, $Nb(S_2CNR_2)_4$ and $Ta(S_2CNR_2)_5$ showing insertion of carbon disulphide across M–N bonds:

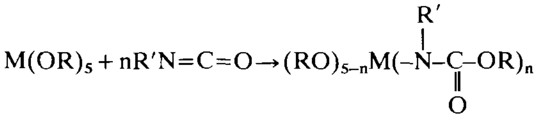
$$Nb(NR_2)_5 + 5CS_2 \rightarrow Nb(S_2CNR_2)_4 + 1/2(R_2NCS_2)_2$$
$$Ta(NR_2)_5 + 5CS_2 \rightarrow Ta(S_2CNR_2)_5$$

The isolation of tetraalkylthiuran disulphide in the first reaction suggests that the unstable pentakis-NN-dialkyldithiocarbamatoniobium is formed first and then this decomposes to give niobium(IV) derivative due to steric reasons. Similar derivatives are isolated by the reaction of metal pentahalides with sodium N,N-diethyldithiocarbamate[211].

Johanson and Pantaleo[141,212] synthesised complexes having composition $MX(OCH_3)_2(S_2CNR_2)_2$ where $X = Cl$, Br or NCS and $R = CH_3$, C_2H_5 or $CH_2C_6H_5$, by the reaction of the corresponding pentahalides with sodium salt in methanolic solution. The $-OCH_3$ group could not be replaced by any other alkoxide group. The conductance, electronic, i.r. and p.m.r. studies indicate a monomeric nature of these products in which the metal is coordinated to seven donor atoms. The X-ray data suggest a pentagonal bipyramid structure in which $-OCH_3$ groups occupy trans-axial position with the halogen and the four S atoms forming a five membered plane which contains the metal[213].

The reactions of MX_5 ($X = Cl$, Br or I) with the sodium salt[214] (NaS_2CNR_2) in different stoichiometric ratios in non-aqueous solvents yield derivatives having composition ML_2X_3 and ML_4X, where $L = R_2NCS_2^-$.

Insertion across M–O bonds in niobium and tantalum alkoxides has recently been observed[215,216] by treating these alkoxides with isocyanates like phenylisocyanate and α-naphthylisocyanate in different molar ratios in benzene solution:

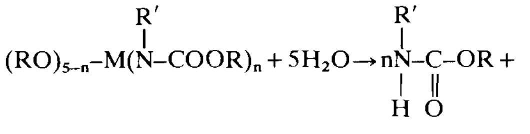


$$M(OR)_5 + nR'N{=}C{=}O \rightarrow (RO)_{5-n}M(-\overset{R'}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-OR)_n$$

(where M = Nb or Ta, R = Me, Et or Pr^i; R' = Ph or Np, n = 1.5)

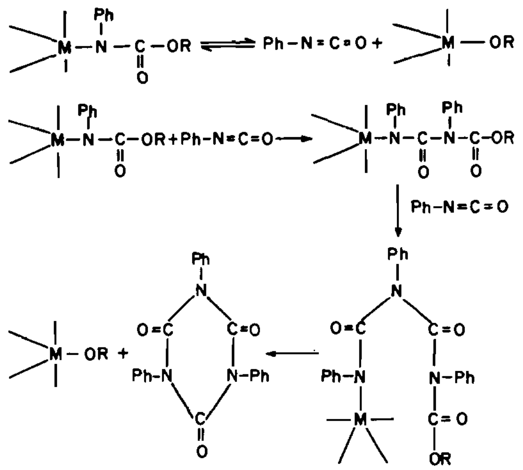
Tetraalkoxide monoureido derivatives could be distilled under reduced pressure whereas higher ureido derivatives undergo disproportionation or decomposition.

These insertion products are extremely susceptible to moisture and form urethane on hydrolysis:



$$(RO)_{5-n}\text{-}M(\overset{R'}{\overset{|}{N}}\text{-}COOR)_n + 5H_2O \rightarrow n\underset{\underset{H}{|}}{\overset{R'}{\overset{|}{N}}}\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR +$$
$$1/2M_2O_5 + (5-n)ROH + 2H_2O$$

These derivatives undergo some rearrangements on storing for long periods even in sealed glass containers and a polymeric isocyanurate sparates out. The following mechanism was suggested[215]:



No insertion reaction across M–O bonds in metal alkoxides was observed even after considerable refluxing with isothiocyanates.

Insertion of methyl isonitrile across Nb–Cl and Ta–Cl bonds was reported by Crociani and Richards[217]. The reaction takes place in ether solution after keeping for about 48 hours at 20° C and a product having composition $MCl_4(Cl\text{–}C{=}NMe)\cdot CNMe$ has been isolated. This compound is dimeric in nature. The reaction of the product $NbCl_4(Cl\text{–}C{=}NMe)\cdot CNMe$ with CNMe and PPh_3 in CH_2Cl_2 solution gives $NbCl_3(Cl\text{–}C{=}NMe)_2\cdot CNMe$ and $NbCl_3(Cl\text{–}C{=}NMe)_2\cdot PPh_3$ derivatives respectively.

4. Compounds Containing Metal–Carbon Bonds

This section deals with the synthesis and reactivity of organometallic compounds in which niobium or tantalum is either σ-bonded to a carbon radical or π-bonded to an arene ring. Prior to 1960, there were practically no known organometallic compounds of either of these metals. Although many unsuccessful attempts had been made[218–221] to prepare organometallic compounds of these metals, the only evidence of any interaction under anhydrous conditions between pentachlorides and aromatic hydrocarbons was based upon the formation of a solution[221]. During the last decade the organometallic chemistry of these metals also has developed rapidly and a few organometallic compounds of these metals are known although these are still far fewer in number compared to those of other transition metals[222–226]. The organometallic compounds of niobium and tantalum can be arranged under the following headings:

A. Cyclopentadienyl Niobium and Tantalum Halide and Sulphide Complexes

Wilkinson and Birmingham[227] were the first to report the synthesis of bis-cyclopentadienylhalides of niobium(V) and tantalum(V) by the reaction of cyclopentadienylmagnesium chloride or bromide with metal chloride or bromide respectively in benzene-ether solution:

$$2(C_5H_5)MgX + MX_5 \xrightarrow{\text{Benzene–ether}} (C_5H_5)_2MX_3 + 2MgX_2$$

(X = Cl, Br; M = Nb, Ta)

These diamagnetic compounds, $(C_5H_5)_2MX_3$, are soluble in polar solvents and could also be prepared[227] in high yields by the following reactions:

$$2(C_5H_5)Na + MX_5 \xrightarrow[\text{1,2-dimethoxyethane}]{\text{THF or}} (C_5H_5)_2MX_3 + 2NaX$$

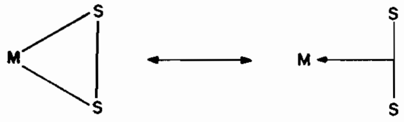
(X = Cl, Br; M = Nb, Ta)

Brantley[228] patented the synthesis of bis-(cyclopentadienyl)niobium chlorides R_2NbX_n (n = 3–2,0) and claimed that these compounds can be used as polymerisation catalysts for drying oils, alkylated resins and curable silicones. $(\pi\text{-}C_5H_5)_2NbBr_3$ hydrolysed readily in air to give the corresponding monohydroxy bromide $(\pi\text{-}C_5H_5)_2Nb(OH)Br_2$[227]. Controlled hydrolysis of $(\pi\text{-}C_5H_5)_2NbCl_3$ yielded $(\pi\text{-}C_5H_5)_2Nb(OH)_mCl_n$ $(m + n = 3)$[228].

Crystalline bis-(cyclopentadienylniobium)triiodide $(\pi\text{-}C_5H_5)_2NbI_3$ has been synthesised by Treichel and Werber[229] by halide ion exchange reactions from $(\pi\text{-}C_5H_5)_2NbCl_2OH$ and NH_4I in aqueous solution. In contrast to chloride and bromide complexes, this compound shows no tendency to hydrolyse. Paramagnetic and air sensitive black crystals of $(\pi\text{-}C_5H_5)_2NbI_2$ have also been reported, when $(\pi\text{-}C_5H_5)_2NbCl_2OH$ is reduced by benzylmercaptan in methanol–benzene solution in presence of NH_4I. Models for $(\pi\text{-}C_5H_5)_2NbI_3$ have been proposed[229] and the i.r. spectra support a structure involving parallel or near parallel cyclopentadienyl rings. Mixed halide complexes of the type $(\pi\text{-}C_5H_5)_2NbI_2Cl$ have been synthesised[230] by the reaction of CH_3I and $(\pi\text{-}C_5H_5)_2NbS_2Cl$ in presence of dichloromethane:

$$(\pi\text{-}C_5H_5)_2NbS_2Cl + CH_3I \xrightarrow{CH_2Cl_2} (\pi\text{-}C_5H_5)_2NbI_2Cl + CH_3SSCl$$

A second compound $(\pi\text{-}C_5H_5)_2NbOCl$, was also formed in the above reaction[230]. Red to violet monomeric complexes of the type $(\pi\text{-}C_5H_5)_2NbS_2X$[230] (X = Cl, Br, I, SCN) have been reported to be formed by the reaction of $(\pi\text{-}C_5H_5)_2NbCl_2(OH)$ and H_2S in methanol in the presence of an ionic halide or pseudohalide (KCl, KBr, NH_4I, KSCN). These diamagnetic complexes are analogus to oxygen complexes[230] and contain the molecular unit S_2 as a ligand. Polymeric compounds having the same formula $[(\pi\text{-}C_5H_5)_2NbS_2X]_n$ have also been reported in the reaction of $(\pi\text{-}C_5H_5)_2NbX_2OH$ (X = Cl, Br) with H_2S. These complexes contain a disulphide bridging group between metal atoms:



M = $(\pi\text{-}C_5H_5)_2NbX$

Siegert and Meijer[231,232] reported the synthesis and properties of the complexes $(\pi\text{-}C_5H_5)_2NbCl_2$ and $(\pi\text{-}C_5H_5)_2Nb(C_6H_5)_2$ by the following reactions:

$$NbCl_5 + 5C_5H_5Na \rightarrow (\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2 + C_5H_5 + 5NaCl$$

$$(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2 + 2HCl \rightarrow (\pi\text{-}C_5H_5)_2NbCl_2 + 2C_5H_6$$

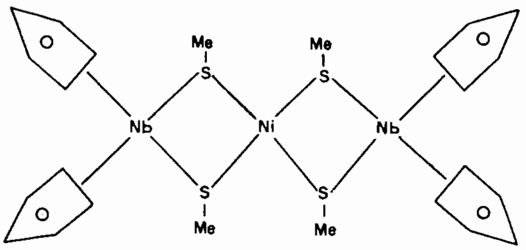
Douglas and Green[233] carried out reaction of $NbCl_5$ with thallium cyclopentadienide in $MeO(CH_2)_2OMe$. Extraction in air with HCl and reduction with $SnCl_2$ resulted in the formation of $(\pi\text{-}C_5H_5)_2NbCl_2$[233]. The complex reacts with MeSH and PhSH in alcoholic base to yield paramagnetic $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ and $(\pi\text{-}C_5H_5)_2Nb(SPh)_2$ respectively[234].

$(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ readily adds salts of Ni, Pd and Pt to give bimetallic derivatives of niobium[234]. The following sequence of reactions was carried out:

$$(C_5H_5)_2NbCl_2 + 2SMe^- \rightarrow 2Cl^- + (C_5H_5)_2Nb(SMe)_2$$

$$2(C_5H_5)_2Nb(SMe)_2 + NiCl_2 \rightarrow (C_5H_5)_2Nb(SMe)_2Ni(SMe)_2 + 2Nb(C_5H_5)_2 + 2Cl^-$$

Similar reactions with $PdCl_2(PhCN)_2$ and $PtCl_2(PhCN)_2$ were also carried out[234]. The cation $[(C_5H_5)_2Nb(SMe)_2Ni(SMe)_2Nb(C_5H_5)_2]^{+2}$, which may be formally considered to contain a niobium (V)–nickel(0)–niobium(V) sequence, was shown to have the structure depicted below:



Nickel is tetrahedrally coordinated to sulphur atoms and the methyl groups attached to sulphur are in transoid conformation[234].

The complex $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ also reacts with [bicyclo2,2,1heptadieneMo(CO)$_4$] to give $[(\pi\text{-}C_5H_5)_2$

Nb(SMe)$_2$Mo(CO)$_4$]^{234}. The diamagnetic complex [(π-C$_5$H$_5$)$_2$Nb(SMe)$_2$Ni(MeS)$_2$Nb(π-C$_5$H$_5$)$_2$]$^{+2}$(BF$_4^-$)$_2\cdot$2H$_2$O has been shown by crystal structure determination to be tetrahedrally coordinated about the metal Ni.

Amine elimination reaction occurs when cyclopentadiene and pentakis(dimethylamino)niobium were reacted together^{235}:

$$\mathrm{Nb(NMe_2)_5 + CpH \rightarrow CpNb(NMe_2)_3 + HNMe_2}$$

The n.m.r. spectrum of the complex in benzene is consistent with the formula CpNb(NMe$_2$)$_3$. The complex decomposes when it is subjected to distillation.

Reaction^{236} of thionylchloride with (π-C$_5$H$_5$)Nb(CO)(PhC:CPh)$_2$ in benzene yielded (π-C$_5$H$_5$)NbCl$_4$. King^{237} reported the synthesis of compounds of the type (π-C$_5$H$_5$)$_2$NbCl$\cdot$BH$_4$ by the reaction of pentachloride and cyclopentadienylsodium in an atmosphere of CO in presence of hydridic reducing agents.

B. Cyclopentadienyl Niobium and Tantalum Carbonyls and Substituted Carbonyl Derivatives

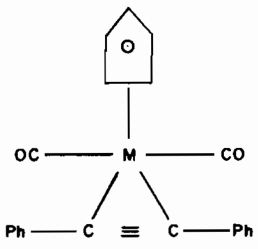
Oxidation of the complexed sodium hexacarbonyl metallates(1–) with mercuric chloride in presence of cyclopentadienylsodium in dimethoxyethane at room temperature converts them to tetracarboxylcyclopentadienyl metallates(1+)$^{238-240}$. These complexes, (π-C$_5$H$_5$)M(CO)$_4$, could be sublimed at 80–100° C/0.05 mm. Similarly, corresponding methylcyclopentadienyl complexes were also prepared^{240,241}. These complexes are soluble in organic solvents and are also thermally stable. N.m.r. spectra of such complexes showed widening of the proton signals. Bonding in (π-C$_5$H$_5$)Nb(CO)$_4$ has been interpreted in terms of seven coordinated metal atoms having the NbF$_7^{-2}$ configuration with the cyclopentadienyl group occupying three coordination sites^{242}.

The complexes, (π-C$_5$H$_5$)M(CO)$_4$ (M = Nb, Ta) undergo a variety of reactions$^{243-245}$ with triphenylphosphine, arsine and stibine under ultraviolet irradiation to give products of the type (π-C$_5$H$_5$)M(CO)$_3$(M^{1}Ph$_3$) and (π-C$_5$H$_5$)M(CO)$_2$(M^{1}Ph$_3$)$_2$ (where M^1 = P, As or Sb in case of M = Nb and M^1 = P in case of M = Ta)$^{243-244}$. These reactions are reversible and can be represented by the following equations:

$$\mathrm{CpNb(CO)_4 + PPh_3 \xrightarrow{uv} CpNb(CO)_3PPh_3}$$

$$\mathrm{CpNb(CO)_3PPh_3 + CO \xrightarrow{uv} CpNb(CO)_4 + PPh_3}$$

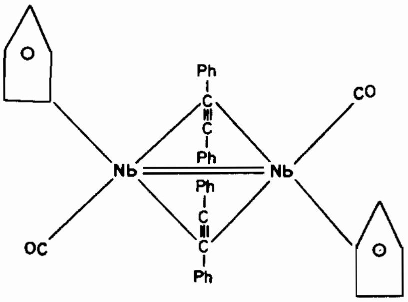
(π-C$_5$H$_5$)M(CO)$_4$ gives with diphenylacetylene, compounds of the type (π-C$_5$H$_5$)M(CO)$_2$(PhC≡CPh)^{245,246}, (π-C$_5$H$_5$)M(CO)(PhC≡CPh)$_2$^{247,248} (M = Nb, Ta) and (π-C$_5$H$_5$)Nb(CO)(PhC≡CPh)$_3$^{247}. (π-C$_5$H$_5$)Nb(CO)(Ph$_2$C$_2$) probably has the structure:



M=Nb,

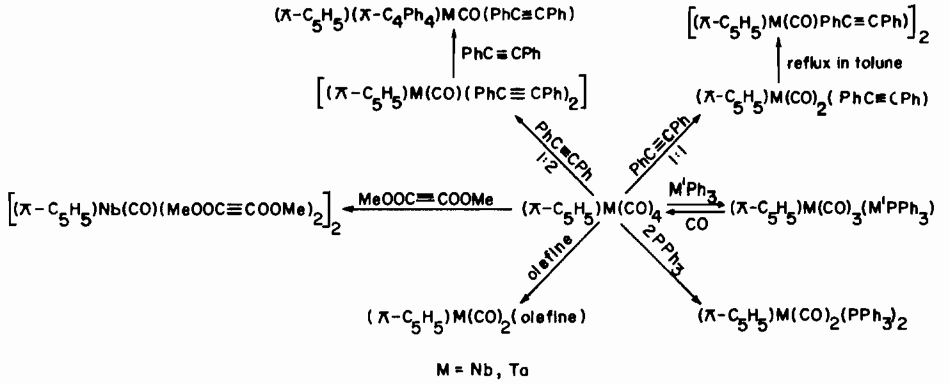
The complex is diamagnetic and monomeric in benzene solution. When it is heated in toluene in the absence of ultraviolet radiation, the dimer [(π-C$_5$H$_5$)Nb(CO)(Ph$_2$C$_2$)]$_2$ is obtained. The crystal structure of [(π-C$_5$H$_5$)Nb(CO)(Ph$_2$C$_2$)]$_2$^{249} has been determined and both these complexes possess triclinic symmetry.

[(π-C$_5$H$_5$)Nb(CO)(Ph$_2$C$_2$)]$_2$^{250} is the first known example of an organometallic compound containing a Nb–Nb bond; the crystal structure of the complex suggests that it contains two bridging acetylenic ligands (PhC≡CPh), which are approximately parallel and lie at right angles to the Nb–Nb vector and the acetylenic bonds have been lengthened to 1.35 Å. The mass spectrum^{250} and diamagnetic character of the complex indicates the presence of a Nb=Nb double bond:



The crystal structure of (π-C$_5$H$_5$)Nb(CO)(PhC≡CPh)$_2$ indicates that two diphenylacetylene molecules are equivalent and are independently coordinated to each niobium atom and there is a partial interaction between π-orbitals of the triple bonds with vacant orbitals of the niobium atoms^{249}. The tantalum compound is isostructural. Reaction of Nb(π-C$_5$H$_5$)(CO)(PhC≡CPh)$_2$ with diphenylacetylene gives the complex Nb(π-C$_5$H$_5$)(π-C$_4$Ph$_4$)(PhC≡CPh)^{251}. The i.r. spectrum of this complex shows one strong band at 2000 cm^{-1} due to terminal carbonyl and one weak band at 1780 cm^{-1} due to ν(C≡C) of coordinated triple bond. The crystal structure of (π-C$_5$H$_5$)Nb(CO)(π-C$_4$Ph$_4$)(Ph$_2$C$_2$)^{252} indicates that the coordinated triple bond is roughly parallel to an edge of the π-bonded tetraphenylcyclobutadiene and it is shorter than that of (π-C$_5$H$_5$)Nb(CO)(PhC≡CPh) complex^{249}. It reflects that Nb–triple bond is weak in cyclobutadiene complex which may be due to the fact that diphenylacetylene in the complex (π-C_5H_5)(π-C_4Ph_4)Nb(CO)(PhC≡CPh) is a two electron donor whereas in (π-C_5H_5)Nb(CO)(PhC≡CPh)$_2$ it is a three electron donor. When the complex (π-C_5H_5)(π-C_4Ph_4)Nb(CO)(PhC≡CPh) is heated, it decomposes to give hexaphenylbenzene[253]. The spacial arrangement of diphenylacetylene and π-tetraphenylcyclobutadiene is favourable for cyclization into hexaphenylbenzene[251]. This reaction supplies evidence for a cyclobutadiene intermediate in some polymerisations of acetylenes to benzene.

Analogous photochemical reactions of (π-C_5H_5)M(CO)$_4$ with cyclopentadiene monomer, butadiene, isoprene, cyclohexadiene, cycloheptadiene were reported to yield complexes of the type (π-C_5H_5)M(CO)$_2$(Olefin)[254,255]. A dimeric complex [(π-C_5H_5)Nb(CO)(MeOOCC≡COOMe)$_2$]$_2$ was obtained from the reaction of (π-C_5H_5)Nb(CO)$_4$ and dimethylacetylenedicarboxylate[256]. In the crystal structure[256] of [(π-C_5H_5)Nb(CO)(MeOOCC≡CCOOMe)$_2$]$_2$, the geometry of the molecule and coordination of the bridge of the acetylene ligand is the same as was found in [(π-C_5H_5)Nb(CO)(PhC≡CPh)]$_2$[250].



C. *Niobium and Tantalum Carbonyl and Substituted Carbonyl Derivatives*

The hexacarbonyl metallate ions of niobium and tantalum have been known since the last ten years[257–263] but neither Nb(CO)$_5$ nor Ta(CO)$_5$ has been characterised. Although no neutral hexacarbonyls are properly established, $M_2(CO)_{12}$ (M = Nb, Ta) have been reported in the patent literature[264]. Dekock[265] in his recent publication has reported the identification of all six carbonyls of tantalum, Ta(CO)$_{1-6}$, by infrared spectroscopy in argon matrices at 4.2° K. These carbonyls have been prepared by vaporization of tantalum atoms at 2800° K and subsequent annealing in a carbon monoxide and argon mixture. The infrared spectra showed the presence of bands in the 1819–1967 cm^{-1} range, which have been attributed to CO frequency for Ta(CO)$_n$ species. The assignments are based on the growth and disappearance of bands with annealing and hence cannot be considered as conclusive evidence for each species, particularly for more complex infrared spectra of tantalum species. The same author[265] reports that the metal–carbon bonding decreases with increased coordination number and also predicted the geometry for Ta(CO), Ta(CO)$_3$ and Ta(CO)$_6$ as linear, trigonal planar and octahedral, respectively. Since tantalum has only five valency electrons, the monomeric tantalum carbonyls will be paramagnetic. The "effective atomic numbers" rule predicts that no more than six carbonyl ligands can bond to tantalum and this leads to dimerisation[264]:

$$2Ta(CO)_6 \rightarrow Ta_2(CO)_{12}$$

In contrast to neutral metal carbonyls, salts containing the hexacarbonyl groups such as $M^1M^V(CO)_6$[260–263] (M^1 = alkali metal, M^V = Nb or Ta) and $[NaL_x][M^V(CO)_6]$[238,239,257] (L = bisethyleneglycol dimethylether, x = 2 and L = dimethoxyethane, x = 3) have been well characterized. These air sensitive ionic compounds have been prepared by the reductive carbonylation of niobium and tantalum pentahalides in presence of carbon monoxide with alkali and alkaline earth metals in diglyme (bisethyleneglycol dimethylether) or dimethoxyethane.

Kelbys and Dubeck[253] synthesised diamagnetic compounds of the type RHgTa(CO)$_6$ (where R = Me, Et or Ph) by the reaction of organomercuric halides with sodium trisdimethoxyethanetantalum hexacarbonyl(−1) in benzene or ether. These compounds are believed to contain Ta–Hg bonds and only methyl and ethyl derivatives could be sublimed under vacuum.

Davison and Ellis[266] reported the first photolytically induced carbonyl substitution reactions of hexacarbonyl metallates(−1) of niobium and tantalum with donor molecules like triphenylphosphine and 1,2-bis(diphenylphosphino)ethane in tetrahydrofuran. The substitutions were as follows:

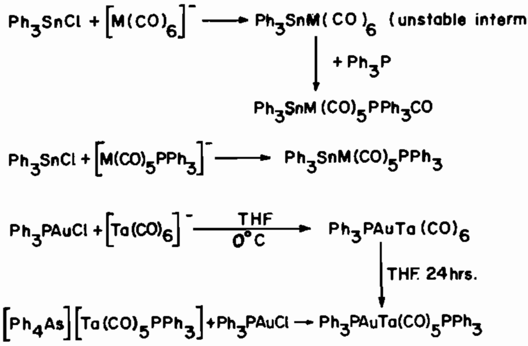
$$[M(CO)_6]^- + PPh_3 \xrightarrow[6h.\,40-60^\circ]{THF,\,h\nu} CO + [M(CO)_5\,PPh_3]^{-1}$$

$$[M(CO)_6]^- + Ph_2PCH_2CH_2PPh_2 \xrightarrow{h\nu,\,THF} 2CO + [M(CO)_4(PPh_2CH_2CH_2PPh_2)^{-1}]^{-1}$$

M = Nb,Ta

Complexes derived from $[M(CO)_5PPh_3]^-$ ions are generally thermally and oxidatively more stable than the one obtained from unsubstituted ions.

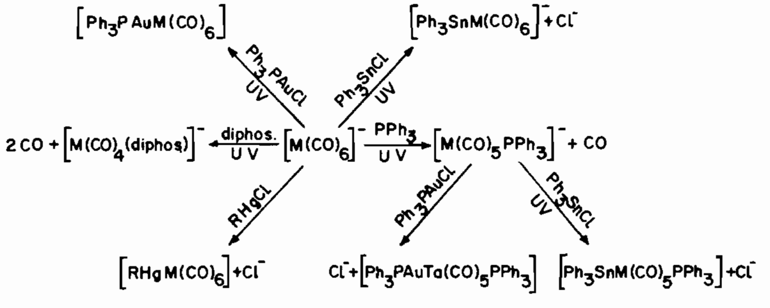
Davison and Ellis[267] also reported the method of isolation of some seven-coordinate derivatives of niobium and tantalum. Complexes of the type $Ph_3SnM(CO)_6$, $Ph_3SnM(CO)_5PPh_3$ (M = Nb, Ta), $Ph_3PAuTa(CO)_5PPh_3$ and $Ph_3PAuTa(CO)_6$ have been prepared by the following routes:



These products are air sensitive; compared to $Ph_3SnNb(CO)_5PPh_3$, the complex $Ph_3SnTa(CO)_6$ is thermally unstable and decomposes slowly in an inert atmosphere at −10° C. The phosphine substituted derivatives are stable in THF while unsubstituted derivatives are heterolytically cleaved to generate the hexacarbonyl salts. The gold–tantalum hexacarbonyl species, unlike the tin–tantalum hexacarbonyl, does not undergo rapid heterolytic cleavage in THF solution and the reaction between $Ph_3PAuTa(CO)_6$ and Ph_3P in this solution yielded $[Ta(CO)_6]^-$ ions rather than the expected substitution product[267].

Infrared spectra of $[LM(CO)_5]^-$ show[267] three line patterns in the carbonyl stretching frequency region expected for the monosubstituted octahedral molecules (L = PPh_3, $Ph_2PCH_2CH_2PPh_2$). The solution spectra of $[LM(CO)_4]^-$ ions show four line patterns expected for an octahedral *cis*-disubstituted metal tetracarbonyl species[267].

Tebbe[268] reported the synthesis of the seven-coordinate hydride $TaH(CO)_2[(CH_3)_2P.CH_2CH_2P(CH_3)_2]_2$ from a very reactive species $TaH_5[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ in benzene at 80° C under carbon monoxide pressure. Crystal structure and stereochemical nonrigidity of the complex has been very recently determined[269] from a combination of X-ray and n.m.r. studies. The tantalum atom is seven-coordinate and bonded to two chelate diphosphine ligands, two carbonyl ligands and a hydride ligand:



M = Nb, Ta

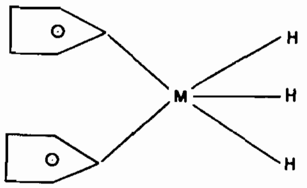
D. Cyclopentadienyl Niobium and Tantalum Hydride Complexes

The first well characterised tantalum di-cyclopentadienyl trihydride, $(\pi\text{-}C_5H_5)_2TaH_3$, has been obtained by the reaction of tantalum(V) chloride with a solution of cyclopentadienylsodium in tetrahydrofuran containing an excess of sodium borohydride[270,271]. The corresponding niobium compound[272,273] has been prepared more recently under hydrogen pressure (800 atm) in toluene as solvent:

$$(\pi\text{-}C_5H_5)Na + MCl_5 + NaBH_4 \rightarrow (\pi\text{-}C_5H_5)_2MH_3$$
$$(M = Nb, Ta)$$

The crystalline air sensitive complexes, $(\pi\text{-}C_5H_5)_2MH_3$, are soluble in light petroleum ether and benzene.

From the physico-chemical studies the trihydrido-derivatives of niobium and tantalum have been shown[273,274] to have the following structure:



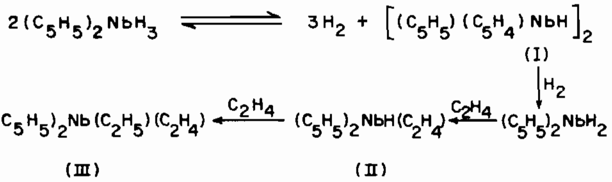
The n.m.r. spectra of these complexes indicate that two types of metal–hydrogen bonds are present, two of the hydrogen atoms being equivalent and bonded to the metal differently from the third.

Binuclear organometallic compounds of the type $(\pi\text{-}C_5H_5)_2Ta(H)_2SnMe_3$ have been recently reported by Lappert *et al.*[275] by the following reactions:

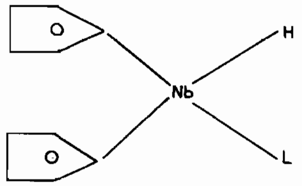
$$Me_3SnNMe_2 + (\pi\text{-}C_5H_5)_2TaH_3 \xrightarrow[\text{reflux}]{\text{THF}} (\pi\text{-}C_5H_5)_2Ta(H)_2SnMe_3 + NHMe_2$$

The product $(\pi\text{-}C_5H_5)_2Ta(H)_2SnMe_3$ is the only example of a d^0 high oxidation state (formally +5) complex[276]. In this complex the possibility of metal–metal bonding does not arise and it was expected that the Ta–Sn bond would also be very long[275].

It is interesting to note that niobium hydrido species are much more reactive than the corresponding tantalum complexes, *e.g.*:



The compounds (I) to (III) were isolated and identified by spectral and analytical data. The structure of (I) has been investigated by X-ray analysis[273,277,278]. The bis(cyclopentadienyl) complexes of niobium and tantalum do not have the simple π-bonded sandwich structure as in ferrocene (parallel staggered rings) or ruthenocene (parallel eclipsed rings). The molecular structure of (I) is that of a dimeric metal hydride containing Nb–Nb bonds, terminal hydride hydrogens and cyclopentadienyl groups, and bridging C_5H_4 groups[278]. Similar structure for tantalocene was also suggested by the same workers[277]. The ethylene hydrido complex (III), $Nb(C_5H_5)_2H(C_2H_4)$ is one member of a class of compounds of general formula $Nb(C_5H_5)_2H$ (L) in which L is a σ donor with π acid character. The following structure has been suggested:



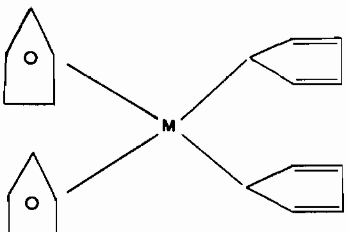
Reduction of $(\pi\text{-}C_5H_5)_2NbCl_2$ with $NaBH_4$ yielded a product, $(\pi\text{-}C_5H_5)_2NbBH_4$, which reacted with R_3P to give $(\pi\text{-}C_5H_5)_2NbH(PR_3)$[279]. Butyl bromide reacts with $(\pi\text{-}C_5H_5)_2NbH(PMe_2Ph)$ according to the following equation:

$$(\pi\text{-}C_5H_5)_2NbH(PMe_2Ph) + BuBr \rightarrow (\pi\text{-}C_5H_5)NbBr(PMe_2Ph) + BuH$$

In dilute aqueous hydrochloric acid, the complex $(\pi\text{-}C_5H_5)_2NbH(PR_3)$ dissolved to give salts of the type $[(\pi\text{-}C_5H_5)_2NbH_2(R_3P)]^+[PF_6^-$ or $BF_4^-]$ after base treatment[279]. Tebbe[280] recently carried out the reactions of dicyclopentadienyl niobium and tantalum hydrides with alkyls of aluminium, gallium, zinc, cadmium and hafnium. The products are either simple Lewis acid base adducts of the type $[(C_5H_5)(C_5H_4)NbHAlEt_3]_2$, $[(C_5H_5)_2Nb(L)HAlEt_3]$ (L = C_2H_4, CO,Me_3P), and $(C_5H_5)_2TaH_3AlEt_3$, or stable compounds which have been formed by alkane evolution, $(C_5H_5)_2NbH_2AlEt_2$ and $[(C_5H_5)_2NbH_2]_2Zn$. Structures[267,280] of some of these products have been suggested on the basis of hydride shifts in n.m.r. spectra. In the compound $(C_5H_5)_2Nb(C_2H_4)HAlEt_3$, insertion of ethylene into the metal–hydride bond is inhibited by Et_3Al.

E. Some π-Bonded Complexes of Niobium and Tantalum

Reactions of pentahalides of niobium and tantalum with excess sodium cyclopentadiene in ether or benzene in a nitrogen atmosphere yield the monomeric moisture sensitive complexes $(\pi\text{-}C_5H_5)_2M(\sigma\text{-}C_5H_5)_2$[281,282] in which two of the cyclopentadienyl groups are σ-bonded and two are π-bonded:



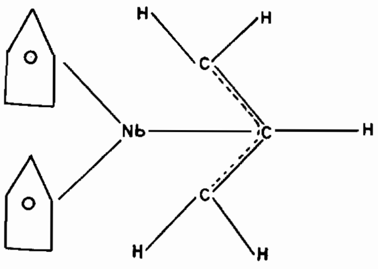
(M = Nb, Ta)

These compounds could not be sublimed and the niobium compound reacts with anhydrous hydrogen chloride to yield $(\pi\text{-}C_5H_5)_2NbCl_2$[231,232]. This chloride complex, which according to Brantley[228] occurs as a by-product of the reaction between niobium pentachloride and NaC_5H_5 in dimethoxyethane, reacts[232,281] with phenyllithium or alkylmagnesium bromide according to the following equation:

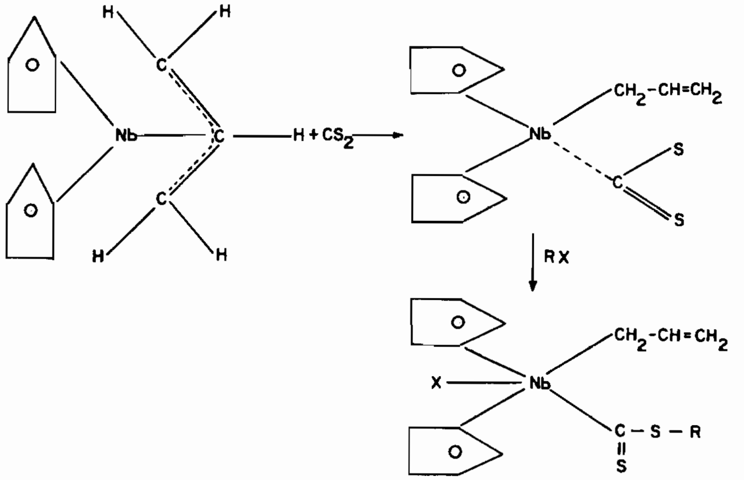
$$(\pi\text{-}C_5H_5)_2NbCl_2 + 2C_6H_5Li \rightarrow (\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_6H_5)_2 + 2LiCl$$

$$(\pi\text{-}C_5H_5)_2NbCl_2 + 2C_3H_5MgBr \rightarrow (\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5) + C_3H_5 + 2MgBrCl$$

Both compounds are air sensitive and show a striking analogy with the corresponding complexes of titanium. Physico-chemical studies show that these complexes are in agreement with a di-π-cyclopentadienyl type structure. N.m.r. and i.r. spectra of the allyl complex are in agreement with the given structure, indicating that the allyl group is π-bonded to niobium:



From i.r. and n.m.r. studies it has been shown that π→σ allyl rearrangement occurs when $(\pi\text{-}C_5H_5)_2Nb(\pi\text{-}C_3H_5)$ reacts with CS_2 to yield $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_3H_5)(CS_2)$[282]:



The compound $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_3H_5)(CS_2)$ further reacts with alkyl halides to give $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_3H_5)I(CSSR)$.

Tetra-allyl complexes of niobium and tantalum were obtained[283] by the reaction of allylmagnesium bromide with niobium and tantalum pentachlorides at very low temperatures. Little is known concerning the properties of these compounds, which are thermally unstable and decompose at 0° C. However, the reaction of $(C_3H_5)_4Ta$ at room temperature with PF_3 under pressure (20 atm) yielded an allyl–trifluorophosphine derivative[284] according to the following reaction:

$$2(\pi\text{-}C_3H_5)_4Ta + 10PF_3 \rightarrow 2Ta(\pi\text{-}C_3H_5)Ta(PF_3)_5 + 3C_6H_{10}$$

The ruby-red compound is moderately stable at room temperature under nitrogen in the solid state. Unsuccessful attempts[284] were made to displace all the allyl groups from tetraallyltantalum. Metallic tantalum was produced when $(\pi\text{-}C_3H_5)Ta(PF_3)_5$ was treated with excess of PF_3 under H_2 pressure to isolate $[Ta(PF_3)_6]$ or $[HTa(PF_3)_5]$[284]. The n.m.r. spectrum of $(\pi\text{-}C_3H_5)Ta(PF_3)_5$ indicates three types of protons in the ratio of 1 : 2 : 2 at 5.47, 7.5, 8.68 τ.

A dimeric π-hexamethylbenzene chloroniobium complex, $Nb_2[\pi\text{-}C_6Me_6]_2Cl_4$, was obtained by the reaction of hexamethylbenzene, aluminium powder, aluminium trichloride and niobium pentachloride in molten state[285]. The n.m.r. spectrum of the diamagnetic complex indicates methyl resonance at 1.77 ppm from tetramethylsilane. A structure of the complex has been proposed[285] on the basis of magnetic measurements and molecular weight determinations.

F. σ-Bonded Complexes of Niobium and Tantalum

The first reported σ-bonded alkyl compounds of these metals were obtained by the low temperature exchange of methyl groups and chlorine atoms between dimethylzinc and niobium(V) or tantalum(V) chlorides[286] respectively:

$$2MCl_5 + 3Me_2Zn \xrightarrow[\text{reduced pressure}]{-78^\circ C} 2Me_3MCl_2 + 3ZnCl_2$$

Both niobium and tantalum compounds can be purified by sublimation under reduced pressure. These complexes are sensitive towards air and moisture and are stable at –78° C, but slowly decompose at room temperature. Compared to the niobium compound the tantalum compound is less stable. The mass spectrum of the niobium compound[287] indicates that it is monomeric and the n.m.r. spectrum in carbon tetrachloride solution gave evidence of the presence of protons attached to a carbon atom which in turn is directly attached to the niobium. Similar observations for the tantalum compound could not be obtained on account of its decomposition at –10° C.

Fowles *et al.*[287,288] carried out the reactions of Me_2Zn with MCl_5 in pentane solution. N.m.r. spectroscopy was used to establish species of the type $Me_n MCl_{5-n}$ (n = 1,3), in the equilibrium between dimethylzinc and pentachlorides of the metals. $MeMCl_4$ and Me_2MCl_3 form complexes with mono- and bidentate ligands with N,O and S donors. For example, the following complex stoichiometries could be categorized: $MeMCl_4L$ and $2MeMCl_4L$ (M = Nb, Ta); $Me_2TaCl_3\cdot L$, $2Me_2TaCl_3\cdot L$ and $4MeTaCl_4\cdot 3L$ (L = 1,4-dioxane). Six-coordinate structures were assigned from i.r. and n.m.r. spectra in most cases, but seven-coordination was also considered quite practicable in some bidentate ligand complexes (*e.g.*, 1,4-dioxane)[287,288].

Methylniobium chlorides were also reported[286] by the reaction of methylmagnesium chloride with $NbCl_5$ at –70° C in THF solution. Mowat and Wilkinson[289] reported the synthesis of a neopentyl derivative of tantalum, $Ta(CH_2CMe_3)_2Cl_2$.

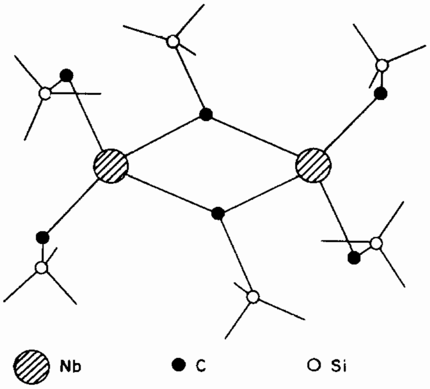
σ-Phenyl compounds of niobium and tantalum containing phenyllithium[290] were obtained by the reactions of metal pentabromides with phenyllithium in ether solution:

$$MBr_5 + 9LiC_6H_5 \xrightarrow{Et_2O} M(C_6H_5)_2(LiC_6H_5)_4 + 5LiBr + 3/2H_5C_6{-}C_6H_5$$

(M = Nb, Ta)

Both of these compounds contain ether molecules and are paramagnetic, air sensitive and thermally unstable in nature.

Mowat and Wilkinson[291] carried out the reaction of MCl_5 with $MgCl(CH_2SiMe_3)$ in diethylether to obtain the binary organometallic derivatives of the type $[M(CSiMe_3)(CH_2SiMe_3)_2]_2$. These diamagnetic compounds are air sensitive and dimeric in nature. The X-ray structure of the niobium compound is shown below:



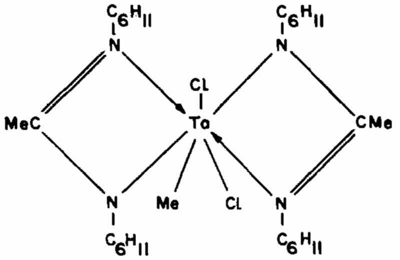
Each niobium atom in the dimer is joined by bridging $CSiMe_3$ groups, which form part of a four-membered quasi aromatic $\overline{M{-}C{-}M{-}C}$ ring and bears two terminal CH_2SiMe_3 groups. The Nb–Nb distance is 2.90 Å. The tantalum analog is isostructural with the niobium complex[291].

Reaction between $TaCl_5$ and $(Me_3SiCH_2)_2Zn$ gives a mixture of $(Me_3SiCH_2)_2TaCl_3$ and $(Me_3SiCH_2)_3TaCl_2$ whereas $NbCl_5$ gives mainly $(Me_3SiCH_2)_3NbCl_2$ which can be purified[292] by vacuum sublimation at 50° C/10^{-4} mm.

Moorhouse and Wilkinson[293] successfully synthesised $(Me_3SiCH_2)TaCl_4$, $(Me_3SiCH_2)_2TaCl_3$ and $(Me_3SiCH_2)_3TaCl_2$ by the reaction of bis(trimethylsilyl)methylzinc and tris(trimethylsilyl)methylaluminium–diethylether (1/1) with $TaCl_5$ under specific experimental conditions. Under similar conditions these workers could isolate only the $(Me_3SiCH_2)_3NbCl_2$ derivative on treatment with $NbCl_5$.

The alkylation of $TaCl_5$ with bis(neopentyl)zinc leads to the formation of a mixture which could not be separated and purified. The formation of tris(neopentyl)tantalum dichloride was detected by comparing the spectra of the reaction mixture with the authentic spectra of the sample synthesised by a different route[294].

$(Me_3SiCH_2)_3MCl_2$ derivatives form 1 : 1 insoluble adducts with 1,10-phenanthroline[293] having a seven-coordinate structure similar to $Me_3TaCl_2\cdot bipy$[294]. On the basis of crystallographic evidence Drew and Wilkins[295,296] reported the structures of $[N(Me)C(Me)S]_2NbCl_3$ and $[Pr^iNC(Me)NPr^i]_2TaCl_3$ derivatives as seven-coordinate monomers having distorted pentagonal bipyramidal geometries with two chlorine atoms in the axial positions and one in equatorial position along with two bidentate ligands. Similar structure[297] was also proposed for dichlorobis(NN-dicyclohexylacetateamidinato)methyltantalum, $MeTaCl_2[C_6H_{11}NC(Me)NC_6H_{11}]_2$, in which the chlorine was replaced with methyl group and bulky cyclohexyl groups attached to nitrogen:



Scampucci and Riess[298] synthesised a number of methylniobium oxichloride complexes like $MeNbCl_2$ 2L, where L = Me_2SO, $(NMe_2)_3PO$, $(MeO)_3PO$ and PPh_3 by the reaction of the above ligands with the reaction product of the reactants MeMgI and $NbOCl_3$ in toluene–ether mixture at −15° C:

$$NbOCl_3 + MeMgI \xrightarrow{-15^\circ C} MeNbOCl_2 + MgICl$$

$$MeNbOCl_2 + 2L \xrightarrow{-10^\circ C} MeNbOCl_2 \cdot 2L$$

Similar complexes were obtained from the reaction of $MeNbCl_4$ and $MeNbBr_4$ with excess ligands:

$$\begin{tikzcd} MeNbCl_4 + L(excess) \arrow[r, "-35^\circ C"] & MeNbCl_4L \arrow[d, "\text{room temp.}"] \\ & MeNbOCl_2 \cdot 2L \end{tikzcd}$$

where L = Me_3NO, C_5H_5NO, Me_3PO, Ph_3PO, $(Me_2N)_3PO$, $(Me_2N)_2(OMe)PO$, $(NMe_2)(OMe)_2PO$, $(MeO)_3PO$, $[(Me_2N)_2PO]_2O$, Ph_3AsO and Me_2SO

$$MeNbBr_4 + Ph_3PO(excess) \xrightarrow{\text{room temp.}} MeNbOBr_2 \cdot 2OPPh_3$$

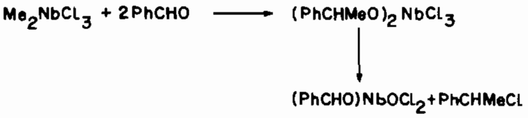
Such oxygen abstraction, halogen exchange reactions were well known with niobium pentahalides[63, 73, 75, 77].

The reaction of $MeNbCl_4$ with acetone and $MeTaCl_4$ with $(Me_2N)_3PO$ gave only 1 : 1 complexes, $MeMCl_4 \cdot L$.

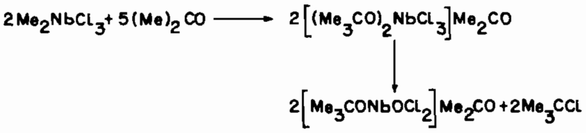
All these complexes are reported to be thermally stable. The i.r. and n.m.r. spectral studies indicate the weaker acceptor property of $MeNbOCl_2$ than $NbOCl_3$ and the stability of the metal–carbon bond during these oxygen abstraction and halogen exchange reactions.

Unsaturated ligands like RNC, RNCO, RNCS, RNCNR and NO undergo insertion[299–302] across metal–carbon bonds in methylniobium and methyltantalum chlorides under specific conditions, whereas the reactions with oxygen donor ligands like tetrahydrofuran, 1,2-dimethoxyethane, 1,4-dioxan and triphenylphosphine form donor–acceptor complexes[287, 288].

Ketones like RR^1CO, where $R = R^1$ = cyclohexyl, R = Me, R^1 = *tert.*-butyl, R = Me, R^1 = neopentyl, form complexes having stoichiometry $Me_xMCl_{5-x} \cdot RR^1CO$, where x = 1 and 2, below 0° C in pentane solution[303]. Benzaldehyde and acetone undergo insertion across the metal–carbon bond in Me_2NbCl_3 under similar conditions. These derivatives are unstable and transform to oxy-derivatives on ageing even at 0° C:



$$\begin{tikzcd} Me_2NbCl_3 + 2PhCHO \arrow[r] & (PhCHMeO)_2NbCl_3 \arrow[d] \\ & (PhCHO)NbOCl_2 + PhCHMeCl \end{tikzcd}$$



$$\begin{tikzcd} 2Me_2NbCl_3 + 5(Me)_2CO \arrow[r] & 2[(Me_3CO)_2NbCl_3]Me_2CO \arrow[d] \\ & 2[Me_3CONbOCl_2]Me_2CO + 2Me_3CCl \end{tikzcd}$$

Although the reaction of Me_2NbCl_3 with pure oxygen was reported to be explosive[287], the reaction of Me_2NbCl_3 and Me_3MCl_2 (M = Nb or Ta) with a mixture of N_2 and O_2 (50v/50v) at −80° C in pentane solution forms products which approach in stoichiometry to $(MeO)_2NbCl_3$ and $(MeO)_3NCl_2$, having a lower M/Cl ratio. The i.r. spectra reveal the insertion of oxygen into the metal–carbon bond as reported for $MeTiCl_3$[304, 305] and other related compounds[306].

Amine N-oxides convert trialkylborane to trialkoxyborane[307] in quantitative yield whereas the reaction of Me_2NbCl_3 with ν-picoline N-oxide at 0° C gives a solid complex, $Me_2NbCl_3 \cdot C_6H_7NO$, which undergoes decomposition above 0° C[303].

Carbodiimides, RNCNR, where R = isopropyl, tertiary butyl, cyclohexyl and *p*-tolyl, also undergo insertion across metal–carbon bonds in methyl metal chlorides, Me_3MCl_{5-x}, where x = 1, 2 or 3 and form products[308] having composition $MCl_4NR\text{–}C(Me)\text{=}NR_2$, $MeMCl_3[NR\text{–}C(Me)\text{=}NR]$, $MCl_3[NR\text{–}C(Me)\text{=}NR]_2$, $Me_2MCl_2[NR\text{–}C(Me)\text{=}NR]$ and $MeMCl_2[NR\text{=}C(Me)\text{=}NR]$. These products have been characterised by i.r. and n.m.r. spectra.

Similar insertion reactions were also attempted with diphenylketone, allene, azobenzene and an imine but no insertion products could be isolated.

Mowat and Wilkinson[296a] reported the synthesis of $Ta[CH_2C(CH_3)_3]_3Cl_2$ by the reaction of $TaCl_5$ with $(CH_3)_3CCH_2MgCl$ in diethylether. This species reacts with neopentyllithium according to the following reaction:

$$Ta[CH_2C(CH_3)]_3Cl_2 + 2LiCH_2C(CH_3)_3 \xrightarrow[\text{1–2 hr at room temp.}]{\text{Pentane}} Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3] + 2LiCl + (CH_3)_4C$$

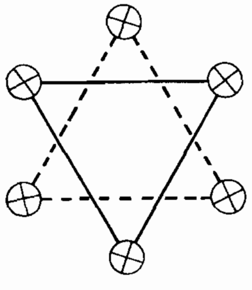
Schrock[309] synthesised the neopentyldiene complex of tantalum $Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$ by intramolecular α-hydrogen abstraction and discussed the results of some preliminary studies concerning the mechanism of its formation.

5. Niobium and Tantalum Cluster Compounds Containing Organic Ligands

Although cluster compounds of niobium and tantalum are well known since the last two decades, only a few compounds containing organic species are known[285, 310]. Fischer and Rohrscheid[285] reported the first organic cluster complexes of niobium and tantalum, $(Me_6C_6)_3MCl_6^+$, from the reaction of the corresponding metal chlorides with a mixture of hexamethylbenzene, aluminium and aluminium chloride. The n.m.r. spectrum of the niobium complex has a sharp resonance line due to methyl protons, indicating that the complex is diamagnetic. An osmometric molecular weight determination suggested some association of the cluster and made a trimetallic formulation more probable than a hexametallic one. Trimetallic formulations of these complexes are also supported by conductivity data.

Recently, King *et al.*[316–318] have shown that the $[(Me_6C_6)_3M_3Cl_6^+]_n$ ions can be easily oxidized to the cations of the stoichiometry $[(Me_6C_6)_3M_3Cl_6^{2+}]_{2n}$; since the latter "oxidized" ions are also diamagnetic[316, 320] they must contain an even number of electrons, the simplest formula thus being $(Me_6C_6)_6M_6Cl_{12}^{+4}$. These workers further suggested that the "non-oxidized" $[(Me_6C_6)_3M_3Cl_6^+]_n$ ions also had a hexanuclear structure of the type $[(Me_6C_6)_6M_6Cl_{12}^{+2}]$ like M_6X_{12} clusters[310, 312–315].

More recently, Churchill and Chang[319] carried out a single crystal X-ray diffraction study of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ which shows a trinuclear formulation to be correct. The molecular symmetry approximates to D_{3h} and the cluster is disordered, the metal cluster lying on a site of crystallographic C_{6h}symmetry:



The pattern of disorder of the trinuclear species (Nb_3 clusters only).

Very recently, King *et al.*[320] have reported the oxidation of the hexamethylbenzene niobium and tantalum clusters $[(Me_5Cl_6)_3M_3X_6]$ (M = Nb, X = Cl and Br; M = Ta, X = Cl) with reagents such as Ce(IV), N-bromosuccinimide, iodide or air in acid solutions or by elektrochemical methods and isolated the corresponding clusters $[(Me_6C_6)_6M_6X_{12}^{+4}]$ as their hexafluorophosphate or thiocyanate salts. A hexametallic formulation has been suggested for the "oxidized" forms of hexamethylbenzene niobium and tantalum clusters, since their diamagnetism excludes the simpler trimetallic formulation. All of these clusters exhibit characteristic maxima in their electronic spectra which could be used for their identification in solution[320].

The dodeca-μ_2-chlorohexaniobium[310] $[Nb_2Cl_{12}]^{+2}$ forms a number of novel electron deficient multicentered complexes of the type $[(Nb_6Cl_{12})Cl_2 \cdot L_4]$ (where L = Me_2SO, $HCONMe_2$, Ph_3ASO, Ph_3PO, pyridine oxide and substituted pyridine oxide[311], $Z\text{-}C_6H_4NO$, Z = H,NO_2, Cl, Me, Me_2N, MeO, PhCH). The metal–oxygen stretching frequencies[311] in the cluster compounds, however, indicate that the cluster ligand bonding is not really important.

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