7. Niobium

Terence P. Kee

CONTENTS

INTRODUCTION

This review is intended to cover the literature on the inorganic coordination chemistry of niobium for the year 1991. To keep the review to a managable length, we have chosen to limit the study to low nuclearity inorganic coordination systems only; consequently several areas have had to be omitted. Specifically, organic/organometallic chemistry, high-nuclearity cluster chemistry (including polyoxometallates) and solid state and materials science have been excluded unless there was a strong reason to include them from an inorganic/coordination chemistry viewpoint.

This review covers the Chemical Abstracts from volumes 114 (July-Dec), 115 and 116 (Jan-June) respectively.

The layout of the review focuses on the different oxidation states of niobium which range from +5 down to –2. However, most compounds of niobium in oxidation states lower than +5 are found to be stabilised by carbon-based organic ligands and as such lie outside the scope of the present review. Consequently it has proven more efficient to separate the +5 oxidation state from the others since most coordination chemical studies have inevitably dealt with the former state. Within each main section the sub-sections are organised according to the nature of the coordinated ligands; halogens from group 17, chalcogens from group 16 and pnictogens from group 15. Within

0010-8545/93/$24.00

these broad boundaries however, there are areas of overlap where ligands from more than one group are present but these species will be covered in at least one of the relevant sections.

For background material the readers' attention is directed to a comprehensive review of the coordination chemistry of niobium and tantalum covering the years 1985-1987 especially for areas of cluster chemistry, solid state and materials related science [1].

7.1 NIOBIUM (V)

7.1.1 Complexes with group 17 ligands

Niobium(V) is a hard Lewis acid and consequently forms complexes readily with hard Lewis bases such as halide anions. Many such homoleptic halide complexes have been studied in detail previously, but there is still current interest in these species, in for example electrochemical studies, electrosynthetic methods and for their ability to afford highly crystalline complexes with novel cations. Some of these applications are outlined below.

A general method for the electrosynthesis of anionic fluoride complexes has been reported via the oxidation of sacrificial metal anodes in 20% aqueous HF solution at room temperature and at an applied potential of 2-8 V [2]. In this manner, $K_2[NbF_7]$ was synthesised.

The vibrational frequencies of $[NbX_6]^-$ ($X = F, Cl, Br, I$) have been calculated and shown to model closely those observed by experiment [3].

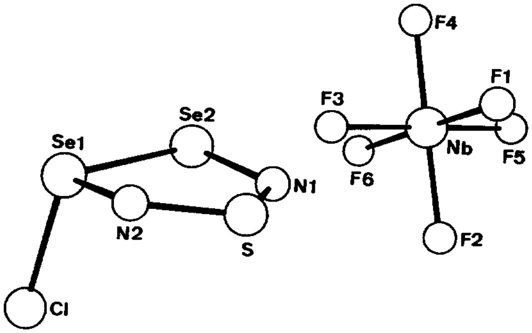
Duff and Heath have studied the M(V)/M(IV) reduction potentials ($E_{1/2}$) for the mixed chloro-acetonitrile complexes $[NbCl_{6-n}(CH_3CN)_n]^m$ and deduced that as more chloride ions are replaced by acetonitrile ligands, so the reduction potentials increase in steps of 0.45 V per ligand replaced [4]. Thus the reduction process becomes easier, a result which seems reasonable on electrostatic grounds as the overall charge on the niobium(V) species becomes progressively less negative as chloride ions are exchanged for acetonitrile ligands.

$$[PPh_4][NbCl_6] + (Me_3Si)_2S \xrightarrow{CH_2Cl_2} [PPh_4]_2[Nb(S)Cl_5].2CH_2Cl_2 \qquad (1)$$

$$[PPh_4][NbBr_6] + (Me_3Si)_2S \xrightarrow{CH_2Cl_2} [PPh_4][Nb(S)Br_4] \qquad (2)$$

Along a more synthetic line, homoleptic halide complexes of niobium(V) have found use as precursors to thiohalide species as shown in equations 1 and 2 [5]. These reactions will be discussed further in Section 1.2, but the study illustrates that halide complexes are often useful synthetic precursors on account of their solubility and structural properties. The same workers, in the same paper, described also the X-ray crystal structure determination of $NEt_4[NbCl_6]$ in the space group $P2_1/n$ [5]. The lattice is composed of discrete cations and anions, the latter having the expected octahedral structure with niobium-chlorine distances ranging from 2.339 (2) Å to 2.349 (2) Å.

Two papers have dealt with the use of hexahaloniobate anions to stabilise unusual cations. Thus, $[ClF_2]^+[NbF_6]^-$ has been studied by X-ray diffraction [6]. It belongs to the orthorhombic system, space group *Pcca*. The niobate anion has the expected octahedral structure. In a similar fashion, the crystal structure of the complex $[Se_2N_2SCl]^+[NbF_6]$ has been solved [7], containing the unusual 3-chloro-1,3,4,2,5-thiadiselenadiazolium cation (1). Presumably it is a combination of their ability to provide both high crystallinity and high thermodynamic stability that makes hexahaloniobates so useful in stabilising reactive cations.



Crystal structure of $[Se_2N_2SCl][NbF_6]$ (1).
Reproduced with permission from ref. 7

7.1.2 *Complexes with group 16 ligands*

This area of niobium chemistry has continued to be one of major interest with many studies focusing on the chemistry of systems containing the [Nb=O] and [Nb-OR] moieties.

The oxyhalide complex of niobium, $K_2[Nb(O)F_5].H_2O$ has been prepared via the same electrochemical procedure to that used in the synthesis of $K_2[NbF_7]$ as decribed in Section 7.1.1 [2]. Similar oxyfluorides of niobium(V) have been prepared by reaction of Nb_2O_5 with metal fluorides or oxides in NH_4HF_2 or $M'HF_2$ (M' = alkali metal) melts [8]; analogous methods apply also to tantalum systems [9]. Another high-temperature route to oxyhalides has been reported, by heating a stoichiometric mixture of CsX and Nb_2O_5 to 850°C the compounds, $Cs_2[Nb(O)X_5]$ (X = F, Cl) can be prepared [10]. Mixed-metal oxofluoroniobates have been observed by vibrational spectroscopy in a high temperature melt comprising $LiF-NaF-KF-K_2NbF_7-Nb_2O_5$ [11]. The species are believed to be of the form $[Nb(O)F_n]^{(n-3)-}$ where n is probably 5. Vibrational data are consistent with the presence of $[Nb(O)F_5]^{2-}$, (ν(Nb=O) = 921 cm^{-1} observed in the Raman spectrum) [11]. Addition of further quantities of oxide to the melts result in the formation of species believed to be $[Nb(O)_2F_n]^{(n-1)-}$. The vibrational specta of these species show two bands assigned to metal-oxo stretches (symmetric and asymmetric) at 879 and 809 cm^{-1} (in the infrared spectrum) and 878 and 815 cm^{-1} (in the Raman spectrum) [11]. One of the polyoxofluoro complexes present was proposed to contain the $[Nb(O)_2F_4]^{3-}$ anion. Addition of even more oxide results in other polyoxohalo complexes, $[Nb(O)_3F_n]^{(n+1)-}$, which apparently polymerise [11].

The oxalate complexes, $[Nb(O)(C_2O_4)_2(H_2O)_2]$ and $[Nb(O)(C_2O_4)_3]$ have been isolated from acidic solutions of Nb_2O_5 in oxalic acid [12] where it was demonstrated that the equilibrium between the two species is dependent upon the pH, the oxalic acid concentration and the niobium concentration.

The high temperature and electrolytic syntheses for oxyhalide compounds of niobium described above are not the simplest to perform, requiring sophisticated equipment. Consequently, there is a need for convenient, low-temperature solution routes to oxyhalide and thiohalide complexes. One of the most promising and general of these solution methods involves the use of $(Me_3Si)_2O$ and $(Me_3Si)_2S$ as reagents for introducing the [O] and [S] moieties into the metal coordination sphere as illustrated in equation 3 [5]:

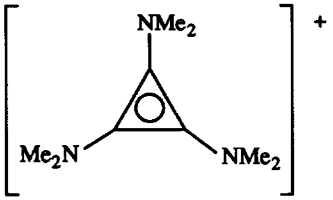
$$NbCl_5 + (Me_3Si)_2S \xrightarrow{CH_2Cl_2} Nb(S)Cl_3 + 2\,Me_3SiCl \qquad (3)$$

Here, the thermodynamics are in favour of the forward reaction since two strong (Si-Cl) bonds are formed at the expense of two weaker (Si-S) bonds and two molecules of Me_3SiCl are released for every molecule of $(Me_3Si)_2S$ that reacts thus providing an entropic driving force. Moreover, since the product thiohalide species are frequently less soluble than the starting pentahalides, the precipitation of the former from solution is another thermodynamic driving force for the forward reaction. The Me_3Si group acts as a proxy for a hydrogen atom in the above reaction, which can also be performed using H_2S although in this case the reverse reaction is likely to be more facile than that using $(Me_3Si)_2S$ and is best accomplished in the presence of a base as HCl acceptor (equation 4) [5].

$$NbCl_5 + NEt_4SH \xrightarrow{CH_2Cl_2} [NEt_4][Nb(S)Cl_4] + [NEt_4][NbCl_6] \qquad (4)$$

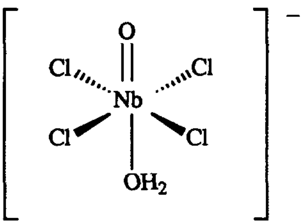
There is reasonable flexibility in the nature of the niobium starting material that can be accommodated by this synthetic method. Thus, equations 1 and 2 show how hexahaloniobates can be used in place of $NbCl_5$. The larger size of the bromine atom results in the formation of a tetrabromothioniobate anion as opposed to the pentahaloniobate as observed in the analogous chloro system [5].

A number of X-ray diffraction studies have been reported on oxyhalide compounds of niobium(V). Thus, $Cs_2[Nb(O)F_5]$ has been shown to possess the $Cs_2[ZrF_6]$ structure and $Cs_2[Nb(O)Cl_5]$ has the same structure as $K_2[PtCl_6]$ on the basis of powder diffraction work [10]. The single-crystal X-ray analysis of $[PPh_4]_2[Nb(S)Cl_5]$. $2CH_2Cl_2$ reveals a positional disorder of the sulfur and chlorine atoms, a phenomenon that makes definitive structure elucidation in thiohalides particularly problematic. However, it is reported that $[PPh_4]_2[Nb(S)Cl_5]$. $2CH_2Cl_2$ has the same structure as β-$[AsPh_4]_2[UCl_6].2CH_2Cl_2$ [5]. As with the hexahaloniobates, mixed oxohaloniobates have been used as stable counter-ions for unusual cations. $[C(NH_2)_3]^+{}_2[Nb(O)F_5]^{2-}$ crystallised in the monoclinic system from an aqueous solution of $[Nb(O)F_5]^-$ and $[C(NH_2)_3]^+$ (2). Infrared spectroscopy located the ν(Nb=O) stretching vibration at 900 cm^{-1} (KBr disc) [13] in a region typical of terminal Nb=O moieties.



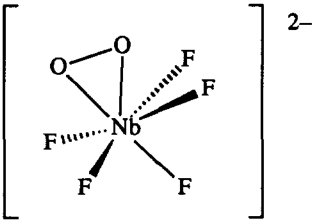
(2)

In a similar manner, the X-ray crystal structure of $[C_3(NH_2)_3]^+[Nb(O)Cl_4(H_2O)]^-$ has been reported [14]. The complex is synthesised from the reaction between MCl and $NbCl_5$ in concentrated aqueous HCl (where M = the 1,2,3-tris(dimethylamino)cyclopropenylium cation). The cation is as shown above (2), whereas the niobate anion (3) has the expected octahedral-based geometry with a coordinated water ligand in a position *trans* to the oxo ligand. The $[Nb\text{-}O(H_2O)]$ distances are quite long, 2.370 (2) Å and 2.382 (2) Å respectively, for the two crystallographically independent molecules in the unit cell, these are similar to values observed for [Nb-O(thf)] in niobium(V)-thf adducts [14]. The Nb=O distances in (3) are 1.702 (2) Å and 1.705 (2) Å [14]. These values are representative of such niobium oxygen distances in niobium(V) systems. The X-ray crystal structure of the complex $[bis(15\text{-}crown\text{-}5)Na]^+[Nb(O)Cl_4(CH_3CN)]^-$ has been shown to be monoclinic with the space group $P2_1/c$ [15]. The niobate anion has the expected pseudo-octahedral structure as illustrated in (3), where the water molecule *trans* to the niobium-bound oxo group is replaced by a molecule of acetonitrile. The niobium-oxygen separtion is 1.682 (7) Å [15].



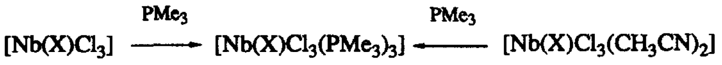
(3)

The unusual niobium(V) peroxo complex, $K_2NbO_2F_5 . H_2O$ has been analysed by single-crystal X-ray diffraction and shown to belong to the monoclinic system (space group *C*2) [16]. The anion has a distorted monocapped octahedral geometry in which one of the peroxo oxygen atoms occupies the capping position (4). The oxygen-oxygen atom separation is, at 1.45 Å, comparable to those of other transition metal peroxo complexes [16].



(4)

Tertiary phosphine complexes of $[Nb(X)Cl_3]$ (X = O, S) have been investigated and a number of complexes prepared which have the general formula $[Nb(X)Cl_3(PMe_3)_3]$ [17]. Interestingly, different coloured products are obtained in these systems depending upon the synthetic method used (equation 5):



$$[Nb(X)Cl_3] \xrightarrow{PMe_3} [Nb(X)Cl_3(PMe_3)_3] \xleftarrow{PMe_3} [Nb(X)Cl_3(CH_3CN)_2] \qquad (5)$$

When base-free $[Nb(O)Cl_3]$ is used in equation 5, the resulting adduct is yellow and when $[Nb(O)Cl_3(CH_3CN)_2]$ is used in the synthesis, the isolated adduct is green. Both products appear to be identical in all but the infrared stretching frequency of the (Nb=O) groups, which are 882 cm^{-1} (yellow) and 871 cm^{-1} (green) respectively. The assignments of these vibrations have been confirmed by ^{18}O labelling experiments (5). It was initially believed that the differences in colour and IR stretching frequencies resulted from different geometries in the solid state but single-crystal

X-ray diffraction analyses of both phases confirmed the same geometrical arrangement, (6), viz. a mono-capped trigonal anti-prismatic structure with the oxygen atom capping the trigonal face formed by the three phosphorus atoms. Although the different coloured materials show the same basic X-ray structure, there is a significant difference in the (Nb=O) bond separations, 1.781 (6) Å (yellow) and 1.929 (6) Å (green). The thiohalide analogues also display the same type of behaviour, with two different coloured products (orange and green) which appear to have the same structure based on single-crystal X-ray diffraction but which have different (Nb=S) distances; 2.196 (2) Å (orange) and 2.296 (1) Å (green). Again, IR spectroscopic analysis of the two materials reveals identical spectra (7) apart from the vibrations assignable to the ν(Nb=S) moieties. Two discrete vibrations are observed in CH_2Cl_2 solution, separated by 34 cm^{-1} [17]. It is not yet clear how these observations can be explained, but the problem of isomorphous replacement of [O] or [S] by [Cl], either intramolecularly or as a result of co-crystallisation of $[NbCl_4(PMe_3)_3]$ with $[Nb(X)Cl_3(PMe_3)_3]$, was discussed by the authors as a potential explanation for the variation in metal-O(S) distances. However, the authors drew attention to the unusual IR spectroscopic behaviour as being incompatible with the isomorphous replacement theory and could not rule out the possibility that the compounds described may be examples of so-called "bond-stretch" isomers [18].

^{19}F and ^{93}Nb NMR spectroscopic studies have been reported for $[Et_3NH]_2[Nb(O)F_5]$ in CH_3CN solvent at temperatures ranging from 270 K to 320 K [19]. Within the temperature range 246-282 K, an exchange process is observable between the fluoride ligands in axial and equatorial sites in the niobate anion.

A thermogravimetric analysis of $[NH_4]_3[Nb(O)F_6].1.5H_2O$ revealed that this complex decomposed in four main stages as illustrated in equations 6-9, where the predominant intermediates are formed by sequential loss of H_2O and NH_4F, to yield ultimately, $[Nb(O)_2F]$ [20].

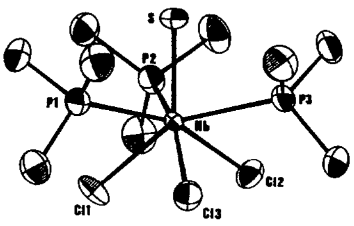
$$[NH_4]_3[Nb(O)F_6].1.5H_2O \longrightarrow [NH_4]_3[Nb(O)F_6].H_2O + 0.5\,H_2O \quad (6)$$

$$[NH_4]_3[Nb(O)F_6]H_2O \longrightarrow [NH_4]_2[Nb(O)F_5].H_2O + NH_4F \quad (7)$$

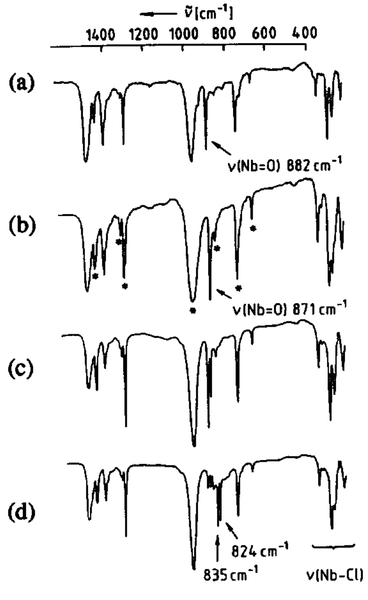
$$[NH_4]_2[Nb(O)F_5]H_2O \longrightarrow [NH_4][Nb(O)F_4].H_2O + NH_4F \quad (8)$$

$$[NH_4][Nb(O)F_4]H_2O \longrightarrow [Nb(O)_2F] + 2\,HF + NH_4F \quad (9)$$

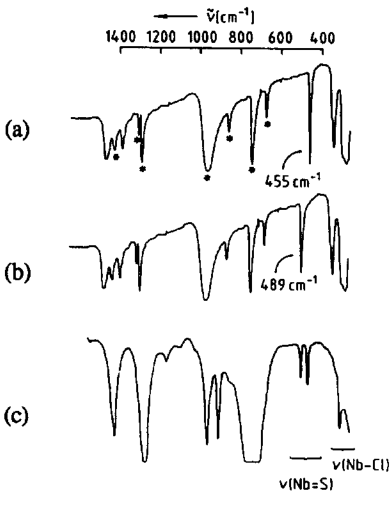
Complexes containing the $[Nb(O)F_5]^{2-}$ anion show high luminescence efficiency due to the high energy position of the UV absorption band. Thus, the complex $Cs_2[Nb(O)F_5]$ absorbs at 260 nm in the UV due to a charge-transfer band and re-emits in the visible region at 470 nm [10].



Structure of the isomorphous series [Nb(X)Cl$_3$(PMe$_3$)$_3$] (6). The one shown here has X = S. Reproduced with permission from ref. 17.



(5)



(7)

(5) IR spectra (Nujol mull, CsI, cm^{-1}) for yellow (a) and green (b) isomers of [Nb(O)Cl$_3$(PMe$_3$)$_3$]. (c) is a mixture of the two forms and (d) a mixture of the ^{18}O labelled forms. The asterisk denotes bands attributed to Nb-PMe$_3$ stretching and bending modes. (7) IR spectra for green (a) and orange (b) isomers of [Nb(S)Cl$_3$(PMe$_3$)$_3$]. c) is a mixture of the two forms. Reproduced with permission from ref. 17.

In addition to the studies conducted on systems containing [Nb=O] groups, there have been several that concern the [Nb-OH$_2$] and [Nb-OR] moieties. The former are unusual for early transition metals such as niobium in that the oxophilicity of the metal often results in condensation to terminal [Nb=O] or bridging [Nb-O-Nb] oxo units. One example has already been mentioned above, $[C_2(NH_2)_3][Nb(O)Cl_4(OH_2)]$ [14]. Other reported examples include the cluster compounds, $[(Nb_6X_{12})(H_2O)_4X_2].4H_2O$ (X = Cl, Br) [21] which contain relatively labile water molecules; they are displaced by the more strongly basic alcohols, ROH (R = Me, Et, ^{i}Pr, ^{i}Bu). Among the compounds which contain the [Nb-OR] unit, the most common are those where R is an organic residue. However, hydroxo complexes (R = H) have been reported as the products of isolating Nb(V) from aqueous HCl and H_2SO_4 solutions by extraction into a chloroform solution containing the complexing ligand 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY). In solutions of low chloride concentration, the species extracted is presumed to be $Nb(OH)_3Y_2$ and at high chloride concentrations the species produced is $Nb(OH)_3YCl$ [22].

There have been several reports dealing with alkoxo complexes of niobium(V), many of which come from the Mehrotra group. These workers have isolated and characterised a wide variety of complexes, homo- and hetero-polymetallic alkoxides in which niobium is present invariably as a hexaalkoxometallate anion. Characterisation has been provided by elemental analysis, IR, UV-VIS spectroscopies, magnetic and molecular weight measurements. The following materials have been prepared; $Fe[Al(OR)_4][Nb(O^iPr)_6]$ [23], $[FeNbCl_2(O^iPr)_6]$, $[FeNb_2Cl(O^iPr)_{12}]$, $[FeNb_2(O^iPr)_{13}]$, $[FeNb(O^iPr)_8]$, $[Al_2FeNb(O^iPr)_{14}]$, $[AlFeZr_2Nb(O^iPr)_{19}]$, $[AlFeNbTa(O^iPr)_{16}]$, $[Al_2FeNb(OMe)_{14}]$, $[Al_2FeNb(O^iPr)_6(O^tBu)_8]$ [24], $[Ni(OR)][Nb(O^iPr)_6]$, $Ni[Al(O^tBu)_4][Nb(O^iPr)_6]$, $Ni[Al(OR)_4][Nb(O^iPr)_6]$ (R = ^{i}Pr, Et), $Ni[Zr_2(O^iPr)_9][Nb(O^iPr)_6]$ [25], $[Al(OEt)_4]\{Co[Nb(O^iPr)_6]\}$, $[Zr_2(O^iPr)_9]\{Co[Nb(O^iPr)_6]\}$, $[Ga(O^iPr)_4]Co[Al(O^tBu)_4]$, $[Zr_2(O^iPr)_9]\{Co[Al(O^tBu)_4]\}$ and $[Nb(O^iPr)_6]\{Co[Al(O^tBu)_4]\}$ the latter five compounds have been prepared by reaction of either $ClCo[Nb(O^iPr)_6]$ or $ClCo[Al(O^tBu)_4]$ with the reagents $K[Al(OEt)_4]$, $K[Zr_2(O^iPr)_9]$, $K[Ga(O^iPr)_4]$ and $K[Nb(O^iPr)_6]$ [26]. Other groups have investigated the reactions of $Nb(O)Cl_3$ with alcohols to prepare mixed oxo-alkoxides of niobium (equations 10 and 11).

$$Nb(O)Cl_3 + 3\,NaOEt \longrightarrow Nb(O)(OEt)_3 + 3\,NaCl \qquad (10)$$

$$Nb(O)(OEt)_3 + 3\,ROH \longrightarrow Nb(O)(OR)_3 + 3\,EtOH \qquad (11)$$

$$(R = Me, {}^iPr, Bu)$$

The crystal structures of these species have not been investigated but $Nb(O)(OMe)_3$ was reported to be amorphous and the others to be gelatinous materials. All of these materials dismutate upon heating in the gas phase to afford $Nb(OR)_5$ and $Nb(O)_2(OR)$ and decompose with the formation of R_2O [27]. During an attempt to grow crystals of $Nb(O)(OEt)_3$ suitable for X-ray analysis, the mixed oxo-alkoxide cluster $Nb_8O_{10}(OEt)_{20}$ was isolated and its crystal structure determined. This compound is monoclinic, space group $P2_1/n$ with a cyclic oligomeric structure containing bridging oxo and alkoxo ligands. This product is also the known hydroysis product of $Nb(OEt)_5$ [27].

The reactions of $Nb(OEt)_5$ with salicylic acid hydrazide (H_2Sa) and anthranilic acid hydrazide (HAa) in different stoichiometric ratios in refluxing benzene have been reported to afford $[Nb(OEt)_{6-2n}(Sa)_n]$ (n = 1, 2) and $[Nb(OEt)_{6-n}(Aa)_n]$ (n = 1-3) respectively [28]. Subsequently, $[Nb(O^tBu)_{6-2n}(Sa)_n]$ (n = 1, 2) and $[Nb(O^tBu)_{6-n}(Aa)_n]$ (n = 1-3) were isolated by alcohol group exchange. In all cases characterisation was provided by elemental analysis, IR and NMR spectroscopies. X-ray diffraction studies were not reported and no attempt was made to assign structures to these compounds.

Both ^1H and ^{93}Nb NMR spectroscopies have been used to probe the nature of the substitution reaction between $NbCl_5$ and MeOH in non-coordinating solvents [29]. These investigations reveal evidence for all possible substitution products although in mixed methanol-aromatic solvents it was shown that $[NbCl_4(OMe)]_2$ and $[NbCl_2(OMe)_3]_2$ are favoured over $[NbCl_3(OMe)_2]_2$. In acetonitrile solvent, ^{93}Nb NMR spectroscopic measurements distinguish between the non base-coordinated dimeric $[NbCl_{5-x}(OMe)_x]_2$ species and the adducts $NbCl_{5-x}(OMe)_x.MeCN$. Therefore, ^{93}Nb monitoring of the solvolysis of $NbCl_5$ by ROH (R = Me, Et, ^iPr) is capable of identifying all $NbCl_{5-x}(OR)_x$ species present and reveals that the solution composition depends upon both the concentration of reagents and the temperature [29].

The use of sterically demanding aryloxides as vehicles for promoting unusual reactivity and structures has continued to be explored. The reaction of $NbCl_3(OC_6H_3Ph_2\text{-}2,6)_2$ with $Mg(BzMe\text{-}p)_2$ where BzMe-*p* represents para-methylbenzyl, results in the isolation of $Nb(BzMe\text{-}p)_3(OC_6H_3Ph_2\text{-}2,6)_2$ in which the two aryloxo ligands occupy mutually *trans* positions [30]. Heating this material to 150°C results in the displacement of one equivalent of *p*-xylene and the formation of a cyclometallated product due to insertion of the metal into one of the ortho-phenyl groups on the aryloxo ligand.

A more inorganic approach has been taken by Sullivan et. al. by studying the reactions of $NbCl_5$ with sterically demanding triarylsiloxides of the form $[OSi(C_6H_4Me\text{-}2)_3]^-$ (equation 12) [31].

$$NbCl_5 + Li[OSi(C_6H_4Me\text{-}2)_3] \xrightarrow{Et_2O} NbCl_4[OSi(C_6H_4Me\text{-}2)_3]1.5Et_2O \qquad (12)$$

Few studies on the coordination chemistry of sulfur containing ligands have been reported during 1991, but one has dealt with cluster species of the form Nb_6I_9S which have been synthesised by reaction of Nb_6I_{11} or Nb_3I_8 with a mixture of niobium and sulfur in a sealed niobium container. The product, Nb_6I_9S reacts with hydrogen to afford $Nb_6[H]I_9S$ in which the hydrogen atom is proposed to occupy an interstitial site within the cluster [32]. Sulfur complexes of lower nuclearity have been reported by Mehrotra and co-workers as products of the reactions between $NbCl_5$ and alkali-metal thiophosphates (equation 13) [33].

$$NbCl_5 + [(RO)_2P(S)S]Na \longrightarrow NbCl_3[S_2P(OR)_2] \qquad (13)$$

In the above equation, sodium can be replaced by $[NH_4]^+$ and R = Ph, ^{i}Pr, ^{i}Bu. The products of these reactions are all orange-yellow viscous liquids which are soluble in polar organic solvents. Characterisation has been provided by IR and NMR spectroscopies; in particular, a single resonance is observed in the ^{31}P NMR spectra in the range δ 77.6-86.8 ppm. Structural studies were not performed on these compound but the authors believed the ligands to coordinate in a chelating fashion [33].

The complexes $[Nb(S)Cl_3(PMe_3)_3]$ have been described above.

7.1.3 Complexes with group 15 ligands

Most studies have involved either nitrogen or phosphorus based ligands. Some of these have been metioned in other sections above such as $[bis(15\text{-crown-}5)Na]^+[Nb(O)Cl_4(CH_3CN)]^-$ which contains a nitrogen-coordinated acetonitrile ligand [15] and the complexes, $Nb(X)Cl_3(PMe_3)_3$ where X = O, S [17] in which three coordinated trimethylphosphine ligands occupy the vertices of a trigonal face in a mono-capped trigonal anti-prismatic structure (6). However, since nitogen donor ligands are frequently harder donors than phosphorus based ligands most studies with niobium(V) have been concerned with the former ligand types.

In the separation and detection of niobium(V) by reversed-phase HPLC with spectrophotometric detection at 540 nm, 4-(2-pyridylazo)resorcinol was used as a pre-column chelating agent [34]. Although it was not reported exactly how this compound coordinates to niobium, it was reasoned that nitrogen-ligantion *via* the 2-pyridylazo moiety was involved.

It has been reported that reaction of $PhN{=}CPhCMe{=}CPhNH(SiMe_3)$ with $NbCl_5$ affords the compound $[PhN{=}CPhCMe{=}CPhNH]NbCl_4$ in which one equivalent of Me_3SiCl is eliminated [35]. Structural studies were not reported but it is likely that the complex involves ligation from at least two sites on the amido ligand.

Given the current level of interest in the chemistry of systems containing [M=O] and [M=NR] moieties as models for metal-mediated oxidation and amination processes, much effort has been directed towards the chemistry of group 5 compounds containing the imido group [=NR]. A number of different synthetic routes to imido complexes of niobium(V) have been investigated including the elimination of two equivalents of Me_3SiCl between a niobium poly-chloro species and a reagent containing a $[N(SiMe_3)_2]$ unit (equation 14) [36].

$$2\text{-}NC(C_6H_4)N(SiMe_3)_2 + NbCl_5 \longrightarrow [2\text{-}NC(C_6H_4)N{=}]NbCl_3 \qquad (14)$$

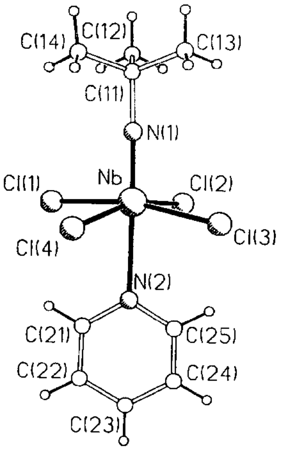
Unfortunately, X-ray crystallographic studies on the product of this reaction have not been reported, but a dimeric or oligomeric structure was considered probable [36]. A similar strategy has been used to prepare the complex, $[Me_2NC(\mathit{S})SN{=}]NbCl_3$ from $NbCl_5$ and $Me_2NC(S)SN(SiMe_3)_2$ [37]. Again, no structural investigations were performed on $[Me_2NC(\mathit{S})SN{=}]NbCl_3$ but it was proposed that the imido group engaged in bidentate ligation througth the thio group marked in italics [37]. A somewhat different, although related σ-metathesis, strategy has been used to sythesise $Nb[=NSiMe_3][N(SiMe_3)_2]_2[OSiMe_3]$ according to equation 15. The yield of this product is only 36% but it obviously involves a novel rearrangement in which a trimethylsilyl group is transferred from nitrogen to oxygen. The product has been characterised by standard spectroscopic techniques [38].

$$Nb(O)Cl_3 + 3\,Li[N(SiMe_3)_2] \longrightarrow Nb[NSiMe_3][N(SiMe_3)_2]_2[OSiMe_3] \quad (15)$$

A related imido complex has been synthesised according to equation 16 [39]. In this case, the product is isolated as a salt by complexation with the added phosphonium chloride and pyridine (Py).

$$Nb(O)Cl_3 + {}^tBuNH_2 + [Ph_3PCH_2Ph]Cl + Py \longrightarrow [Ph_3PCH_2Ph][Nb(=N^tBu)Cl_4(Py)] \quad (16)$$

The crystal structure of $[Ph_3PCH_2Ph][Nb(=N^tBu)Cl_4(Py)]$ has been determined and shown to be monoclinic (space group $P2_1/c$) in which the niobate anion exists as a distorted octahedon with the imido and pyridine ligands mutually *trans* as shown in structure (8).



Crystal structure of the complex anion present in $[Ph_3PCH_2Ph][Nb(N^tBu)Cl_4(Py)]$ (8).
Reproduced with permission from ref. 39.

The (Nb-Cl) distances in the anion in (8) range from 2.425 (2) Å to 2.446 (2) Å. The $(Nb\text{-}N)_{Py}$ separation is 2.479 (4) Å and the $(Nb\text{-}N)_{imido}$ separation is 1.731 (3) Å. The very short distance of the metal imido linkage coupled with the near linearity of this group (Nb-N-C = 176.4 (4)°) suggests that the imido ligand is acting as a neutral four-electron donor ligand in this complex thus allowing the metal centre a valence-electron count of sixteen [39].

7.2 *LOWER OXIDATION STATES OF NIOBIUM*

7.2.1 *Complexes with group 17 ligands*

As mentioned in the introduction, most chemistry dealing with niobium in lower oxidation states falls within the realm of organometallic chemistry and consequently outside the remit of this article. However, some studies have been reported on coordination compounds.

The vibration frequencies of $[NbX_6]^{2-}$ (X = F, Cl, Br, I) have been calculated and compared to experimentally determined values with which agreement is good [3].

The M(V)/M(IV) reduction potentials ($E_{1/2}$) for the mixed chloro-acetonitrile complexes $[NbCl_{6-n}(CH_3CN)_n]^m$ have been studied as mentioned in Section 1.1 [4].

Lower oxidation state coordination compounds have found use as precursors to organometallic complexes. Thus, $NbCl_4(thf)_2$ can be converted smoothly to complexes such as $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ and $[Nb(\eta^7\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ [40].

The complexes $M_2[NbF_6]$ (M = Rb, Cs) have been prepared as illustrated in equation 17. Both are isostructural, hexagonal space group *P*3*m*1 and isotypic with K_2GeF_6. Both compounds are reported to be paramagnetic as expected for Nb(IV) d^1 species [41].

$$2\,MF + NbF_4 \longrightarrow M_2[NbF_6] \qquad (17)$$

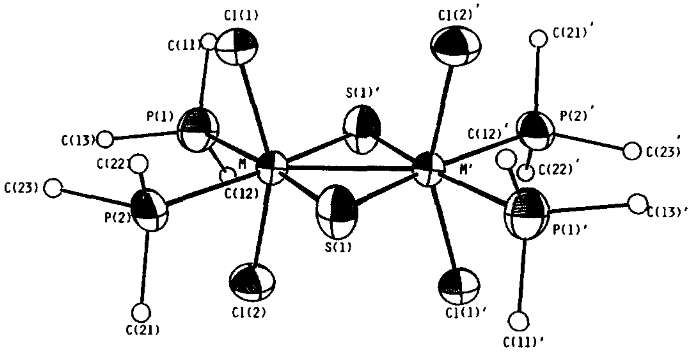
$$[M = Rb\ (650°C),\ Cs\ (600\,°C)]$$

7.2.2 *Complexes with group 16 ligands*

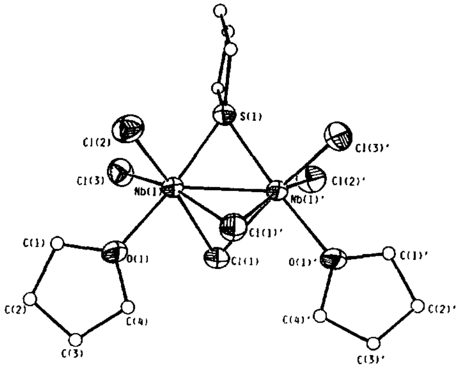
Four complex of niobium(IV) containing sulfur have been reported and their crystal structure determined [42]. $Nb_2(\mu\text{-}S)_2Cl_4(PMe_3)_4$ was isolated from the reaction between $NbCl_4(thf)_2$ and Li_2S in the presence of PMe_3 and shown to possess the structure (9).

The structure is based on an edge-shared bioctahedron with mutually eclipsed pairs of phosphine ligands occupying the equatorial plane. The (Nb-Nb) separation, at 2.869 (1) Å, is consistent with a single bond [42]. Three complexes were found to be isostructural, $[Nb_2(\mu\text{-}$

Cl)$_2$Cl$_4$(tht)(PMe$_3$)$_2$], [Nb$_2$(μ-Cl)$_2$Cl$_4$(tht)(PEt$_3$)$_2$] and [Nb$_2$(μ-Cl)$_2$Cl$_4$(tht)(thf)$_2$] **(10)** [43]. In each case the tetrahydrothiophene ligand bridges the two niobium centres.



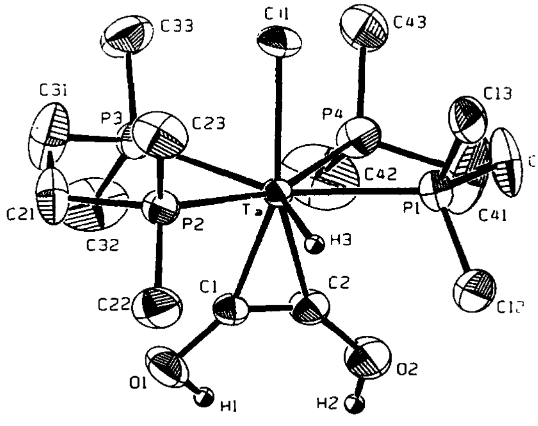
Crystal structure of [Nb$_2$(μ-S)$_2$Cl$_4$(PMe$_3$)$_4$] (9).
Reproduced with permission from ref. 42.



Crystal structure of [Nb$_2$(μ-Cl)$_2$Cl$_4$(tht)(thf)$_2$] (**10**).
Reproduced with permission from ref. 43.

7.2.3 Complexes with group 15 ligands

Apart from the complex Nb$_2$(μ-S)$_2$Cl$_4$(PMe$_3$)$_4$ described above which contains tertiary phosphine ligands, all other lower oxidation state complexes of niobium are organometallic in nature and are not discussed here. However, one interesting example worthy of mention is the complex [Nb(H)(HOCCOH)(dmpe)$_2$Cl]Cl formed by treatment of Nb(Me$_3$SiCCSiMe$_3$)(dmpe)$_2$Cl with HCl$_{aq}$ [44]. This species is formally a complex of niobium(III) and contains the unusual combination of hydride and dihydroxyalkyne ligands. The tantalum analogue has also been synthesised and its crystal structure determined (11). Presumably the niobium analogue has a similar structure. Thus this system illustrates how a combination of control over metal oxidation state and ligand field can stabilise unusual coordination environments.



Crystal structure of [Ta(H)(HOCCOH)(dmpe)$_2$Cl]Cl (11).
Reproduced with permission from ref. 44.

Nitrogen-based ligands can also stabilise lower oxidation states of niobium, especially if they are constrained within chelate rings. Thus, the complex Tp'NbCl$_2$(PhC≡CMe) is synthesised as shown in equation 18 [45]. (Tp' is the 3,5-dimethyl trispyrazolylborato ligand).

$$NbCl_3(dme)(PhCCMe) + KTp' \longrightarrow Tp'NbCl_2(PhCCMe) + KCl \quad (18)$$

X-ray diffraction and NMR spectroscopic studies show that the alkyne ligand is orientated in the molecular mirror plane with a relatively high barrier to ligand rotation on the NMR timescale [45].

REFERENCES

1. R.W. Berg, *Coord. Chem. Rev.*, 113 (1992) 1.
2. M. Chakravorti, G.V.B. Subrahmanyam and D. Bandyopadhyay, *Polyhedron*, 10 (1991) 2605.
3. E. Hahn and R. Hebisch, *Spectrochim. Acta.*, 47A (1991) 1097.
4. C.M. Duff and G.A. Heath, *Inorg. Chem.*, 30 (1991) 2528.
5. B. Siewert, G. Koellner, K. Ruhlandt-Senge, F. Schmock and U. Mueller, *Z. Anorg. Allg. Chem.*, 593 (1991) 160.
6. A.M Ellern, M.Y. Antipin, A.V. Sharababarin and Y.T. Struchkov, *Zh. Neorg. Khim.*, 36 (1991) 2266. *Chem. Abst.*, 115 (1991) 267316f.

7. A. Haas, J. Kasprowski, K. Angermund, P. Betz, C. Krueger, Y.H. Tsay and S. Werner, *Chem. Ber.*, 124 (1991) 1895.
8. A.I. Agulyansskii, *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, 27 (1991) 376. *Chem Abst.*, 116 (1991) 142632v.
9. T.P. Kee, *Coord. Chem. Rev.*, following paper.
10. A.M. Srivastava and J.F. Ackerman, *Mater. Res. Bull.*, 26 (1991) 443. *Chem. Abst.*, 115 (1991) 63285k.
11. J.H. Von Barner, E. Christensen, N.J. Bjerrum and B. Gilbert, *Inorg. Chem.*, 30 (1991) 561.
12. J.M. Jehng and I.E. Wachs, *J. Raman Spec.*, 22 (1991) 83. *Chem. Abst.*, 115 (1991) 36563t.
13. U. Calov, M. Schneider and P. Leibnitz, *Z. Anorg. Allg. Chem.*, 604 (1991) 77.
14. H.N. Schaefer, H. Burzlaff, A.M.H. Grimmeiss and R. Weiss, *Acta. Crystallogr. Sect C.*, 47 (1991) 1808.
15. V.K. Ruhlandt-Senge and U. Mueller, *Acta. Crystallogr. Sect. C.*, 47 (1991) 182.
16. R. Geetha, P.S. Rao, V. Babu and S. Subramanian, *Inorg. Chem.*, 30 (1991) 1630.
17. A. Bashall, V.C. Gibson, T.P. Kee, M. McPartlin, O.B. Robinson and A. Shaw, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 980.
18. W-D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, 94 (1972) 1661.
19. A.A. Vashman, A.N. Zozulin and E.G. Ll'in, *Zh. Neorg. Khim.*, 36 (1991) 1790. *Chem. Abst.*, 115 (1991) 196545s.
20. B.N. Wani and U.R.K. Rao, *Thermochim. Acta.*, 176 (1991) 203. *Chem. Abst.*, 115 (1991) 104755j.
21. A. Kashta, N. Brncevic and R.E. McCarley, *Polyhedron*, 10 (1991) 2031.
22. A. Ivsic and T.B. Gojmerac, *Talanta*, 38 (1991) 1403.
23. R. Gupta, A. Singh and R.C. Mehrotra, *Indian J. Chem.*, 30A (1991) 592.
24. R. Gupta, A. Singh and R.C. Mehrotra, *New J. Chem.*, 15 (1991) 665.
25. G. Garg, A. Singh and R.C. Mehrotra, *Indian J. Chem.*, 30A (1991) 866.
26. G. Garg, A. Singh and R.C. Mehrotra, *Indian J. Chem.*, 30A (1991) 688.
27. V.G. Kessler, N.Ya Turova, A.I.Yanovskii, A.I. Belokon and Y.T. Struchkov, *Zh. Neorg. Khim.*, 36 (1991) 1662. *Chem. Abst.*, 115 (1991) 246630p.
28. A.K. Narula, *J. Indian. Chem. Soc.*, 68 (1991) 313.
29. R.G. Lee and J.A. Crayston, *J. Chem. Soc., Dalton Trans.*, (1991) 3073.
30. R.W. Chesnut, G.G. Jacob, J.S. Yu, P.E. Fanwick and I.P. Rothwell, *Organometallics*, 10 (1991) 321.
31. S.G. Bott, M.A. Mazid, M.B. Hursthouse and A.C. Sullivan, *J. Chem. Soc., Dalton Trans.*, (1991) 355.
32. J.H. Meyer and J.D. Corbett, *Inorg. Chem.*, 30 (1991) 963.
33. S.K. Pandey, G. Srivastava and R.C. Mehrotra, *Indian J. Chem.*, 30A (1991) 92.
34. S.J.J. Tsai and S.Yi Lee, *Analyst*, 116 (1991) 615.
35. H.W. Roesky, B. Meller-Rehbein and M. Noltemeyer, *Z. Naturforsch B46*, (1991) 1053.
36. H.W. Roesky, B. Meller-Rehbein and M. Noltemeyer, *ibid*, (1991) 1059.
37. H.W. Roesky, B. Meller-Rehbein and M. Noltemeyer, *ibid*, (1991) 1117.
38. W.A. Herrmann, M. Denk, F. Dyckhoff and I. Behm, *Chem. Ber.*, 124 (1991) 2401.
39. W. Clegg, R.J. Errington, D.C.R. Hockless and C. Redshaw, *Polyhedron*, 10 (1991) 1959.
40. M.L.H. Green, P. Mountford, P. Scott and V.S.B. Mtetwa, *Polyhedron*, 10 (1991) 389.
41. J. Chassaing, M.B. De Bournonville, D. Bizot and M. Quarton, *Eur. J. Solid State Inorg. Chem.*, 28 (1991) 441. *Chem. Abst.*, 115 (1991) 148862w.
42. E. Babaian-Kibala and F.A. Cotton, *Inorg. Chim. Acta.*, 182 (1991) 77.
43. E. Babanian-Kibala, F.A. Cotton and M. Shang, *Acta. Crystallogr., Sect. C*, 47 (1991) 1617.
44. R.N. Vrtis, S.G. Bott, R.L. Rardin and S.J. Lippard, *Organometallics*, 10 (1991) 1364.
45. M. Etienne, P.S. White and J.L Templeton, *Organometallics*, 10 (1991) 3801.