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7. NIOBIUM AND TANTALUM

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CONTENTS

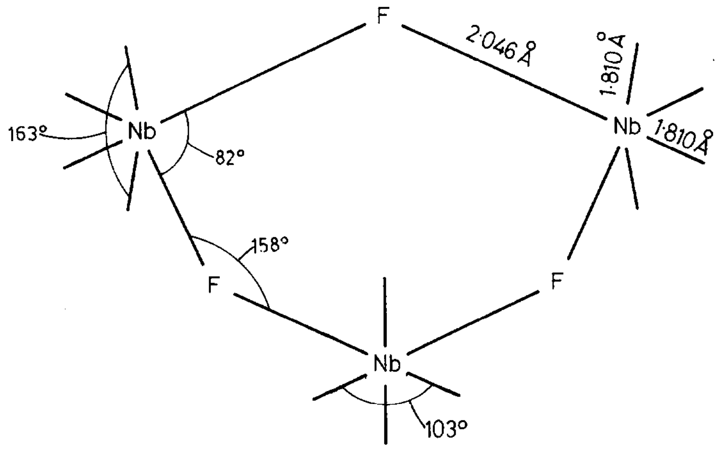
INTRODUCTION

The material covered by this review is mainly to be found in Chemical Abstracts, Volumes 93 (no. 19) to 95 (no. 18). In addition, the major English language journals have been covered for the calendar year 1981. The review is mainly concerned with publications of interest to co-ordination chemists. Work of essentially an organometallic nature has not been included unless it is of more general interest. Likewise, most papers concerned with intercalation have not been included.

7.1 NIOBIUM(V) AND TANTALUM(V)

7.1.1 Halides and oxohalides

Two determinations of the molecular structure of niobium(V) fluoride in the gas phase have been made. The predominant species is a trimer of D_{3h} symmetry, with each metal atom in a six coordinate environment and with symmetrical fluorine bridges (*1*) [1,2].



(1)

Some thermochemical data on the gaseous fluorides and oxofluorides of tantalum have been reported as part of a larger programme of thermochemical measurements. These provide a clear explanation for the observed resistance of tantalum to attack by F_2 at high temperature and low pressure [3]. Thermodynamic properties of the gaseous tantalum chlorides have also been reviewed and evaluated [4].

7.1.2 Halide, oxohalide, and azidohalide complexes

Several studies of ternary fluorides have appeared this year. The equilibria in M_2TaF_7-MF (M = Na, K, Rb) and $CsTaF_6$-CsF melts have been studied by IR spectroscopy. The position of the equilibrium (1), and the vibrational

$$[TaF_7]^{2-} \rightleftharpoons [TaF_6]^- + F^- \qquad (1)$$

frequencies of the anions, were found to be cation dependent [5]. DTA measurements on $MgTaF_7$ and $Ca[TaF_6]_2$ indicated that the former dissociates directly to give MgF_2 and TaF_5 whereas the latter decomposes in three steps through $CaTaF_7$ and $Ca_3[TaF_8]_2$; equilibrium constants and enthalpies of reaction were given for each process [6]. TGA was used to investigate the thermal properties of K_3NbF_8 and K_3NbClF_7 [7].

Other studies of binary and ternary halide melts have been concerned with the electrodeposition of niobium. Thus the electrochemical reduction of $K_2[NbF_7]$ in KF-KCl melts has been shown to proceed in two steps *via* niobium(IV) [8,9], whereas an examination of the NaCl-KCl-$NbCl_5$ system implicated niobium(III) and niobium(II) as solution species [10]. The latter authors have also studied the chemical reduction of $NbCl_5$ by niobium metal at temperatures between 200 and 800 °C. Below 400 °C, $NbCl_4$ and $NbCl_3$ were identified in the products, whereas at 800 °C Nb_3Cl_8 is formed [11].

Three publications this year have been concerned with ternary chloride systems in which complex formation was indicated. $NbCl_5.GaCl_3$ is formed when equimolar mixtures of $NbCl_5$ and $GaCl_3$ are fused together. On the basis of Raman measurements a structure was assigned consisting of {$NbCl_6$} octahedra and {$GaCl_4$} tetrahedra with one shared edge [12], although other workers preferred the less likely formulation $[MCl_4][GaCl_4]$ (M = Nb or Ta) [13]. ECl_4 (E = Se or Te) reacts with MCl_5 (M = Nb or Ta) to give $[ECl_3][MCl_6]$ [13]. The sulphur analogues, $[SCl_3][MCl_6]$, have been isolated from the reaction between M_2O_5, SCl_2, and Cl_2 at 120-200 °C, and characterised by ^{35}Cl NQR and IR spectroscopy [14].

Oxohalide complexes have received scant attention this year. The peroxo complex $K_2[Nb(O_2)F_5].H_2O$ has been prepared and the kinetics of its isothermal decomposition, to give $K_2[NbOF_5]$, examined over the temperature range 463-523 K [15]. $[PMe_3Ph]_2[Cl_5TaOTaCl_5]$ contains a centrosymmetric anion of approximately D_{4h} symmetry. The Ta-Cl bond *trans* to O is significantly longer than those *cis* {$r(\text{Ta-Cl}_t)$ = 2.381 Å; $\bar{r}(\text{Ta-Cl}_c)$ = 2.336 Å; r(Ta-O) = 1.880 Å}. The structural parameters were discussed in terms of the bonding in this and other related complexes [16].

Treatment of MX_5 (M = Nb or Ta; X = Cl or Br) with $[EPh_4]X$ or $[EPh_4][N_3]$ (E = P or As) in CH_2Cl_2 leads to the isolation of complexes containing $[MX_6]^-$ or $[X_5M(N_3)]^-$, respectively. The latter reacts with PPh_3 to give $[X_5MN{=}PPh_3]^-$, although in the case of tantalum this requires photochemical activation. The IR spectra of the hexahalometallate(V) anions suggested departure from O_h symmetry, which was confirmed for $[PPh_4][NbCl_6]$ and $[PPh_4][NbBr_6]$ by X-ray methods, which showed the anion symmetry to be C_{4v} and C_i respectively {$r(\text{Nb-Cl}_{ax})$ = 2.33 and 2.27 Å; $r(\text{Nb-Cl}_{eq})$ = 2.35 Å; r(Nb-Br) = 2.492, 2.507, and 2.508 Å} [17,18]. $[PPh_4][Cl_5Nb(N_3)]$ was found to contain a disordered anion, with the niobium atom on an inversion centre. Additional disorder of the $(N_3)^-$ moiety means that it is statistically distributed about four different positions. Figure 1 shows a view of the anion without the disorder due to the inversion centre {mean angles: $(Nb\text{-}\hat{N}\text{-}N) = 138°$, $(N\text{-}\hat{N}\text{-}N) = 173°$} [17].

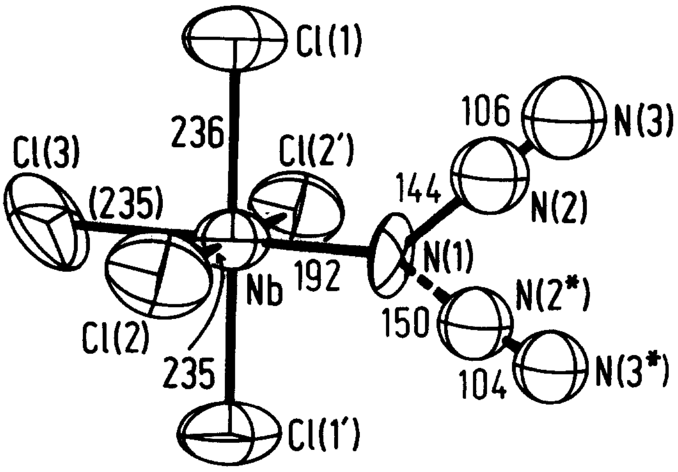
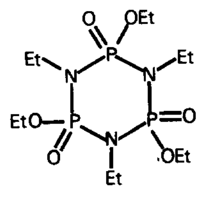


Figure 1: A view of $[Cl_5NbN_3]^-$. Reproduced with permission from [17].

7.1.3 Pentahalide complexes with O-, S-, and N-donor ligands

There have been three reports this year of pentahalide complexes containing other than Group VII ligands. ^{19}F NMR studies of the reaction between MF_5 (M = Nb or Ta) and (*2*) showed the formation of adducts of general type



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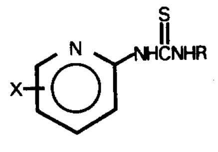


(3)

$nMF_5.L$ {L = (*2*); n = 1 to 3}. Co-ordination through the phosphoryl oxygen atoms was suggested [19]. The reaction between $NbCl_5$ and (*3*) gave a series of complexes $[NbCl_4L]Cl$ {L = (*3*); R = Ph, 2- or 4-MeC_6H_4; X = H, 4-Me or 6-Me}. On the basis of conductivity and IR measurements, the compounds were formulated as ionic with the ligand chelating through the *S* and ring-*N* atoms [20]. A range of compounds $TaCl_5.2L$ ($L = 4\text{-}Me_2NC_6H_4CH{=}NC_6H_4R$; R = H, 2- or 4-Me, 4-OMe, 3- or 4-Br, 4-NO_2 or 4-Cl) has also been reported, and on the basis of IR data it was suggested that L was monodentate and co-ordinated through the azomethine *N* atom [21].

7.1.4 *Complexes containing oxygen and sulphur acido ligands*

The reaction between MCl_5 (M = Nb or Ta) and $Me_2C{=}NOH$ (HL) in $CHCl_3$ leads to complexes of the type $MCl_4L.HL$, $MCl_3L_2.HL$, and $NbCl_2L_3.HL$, in which partial halogen substitution has taken place [22]. A ^{19}F NMR study has shown that TaF_5, PhOH, and NEt_2H react in MeCN to form a range of six coordinate anionic species $[TaF_{6-x}(OPh)_x]^-$ (x = 1, 2, 3 or 4), in addition to $[TaF_4(OPh)(NEt_2H)]$ and $[TaF_2(OPh)_3(NEt_2H)]$. Reactions involving the formation of a Ta–N covalent bond with concomitant production of HF were not reported [23]. The phenolates $M(OPh)_xCl_{5-x}$ (M = Nb or Ta; x = 1, 2, 3, 4 or 5) have all been assigned dimeric oxygen-bridged structures on the basis of IR studies [24]. The preparation of the complexes $M(OPh)_5L$ (L = py, pyNO, Ph_3AsO, acetophenone or benzophenone), $MCl_4(OPh)L$ (L = py, 2-Mepy, acetophenone or benzophenone), and $A[M(OPh)_6]$ (A = Li, Na or K) was also reported [24,25].

$[NbO(OMe)_2(OC_6H_4\text{-}2\text{-}CHO)]$, $[NbO(OMe)_2(HBPz_3)]$, $[NbOCl(OCH_2CCl_3)_2(dmso)_2]$, and $[TaOCl_2(OMe)(dmso)_2]$ have been synthesised. All were found to be monomeric in solution and showed IR bands in the solid state which could be assigned to M=O. The structures in solution were investigated using ^1H NMR spectroscopy [26].

$Nb(OCHMe_2)_5$ has been allowed to react with a number of facultative ligands. The semicarbazones and thiosemicarbazones, $RR'C{=}NNHC(E)NH_2$ (E = O or S), and the azines $RR'{=}NN{=}CR'R$ (H_2L, R = C_6H_4OH, R' = H or Me; R = $C_{10}H_6OH$, R' = H) all gave complexes of the types $Nb(OCHMe_2)_3L$, $Nb(OCHMe_2)L_2$, $NbL_2(HL)$, and Nb_2L_5 [27,28]. Compounds having the same general stoicheiometries have also been reported with a range of Schiff's bases [29]. The monomeric complexes $[M(OR)_4L]$ {M = Nb or Ta; R = Me, Et, $CHMe_2$ or CMe_3; HL = $R'CSCH_2COR''$ (R' = R'' = Me or Ph; R' = Ph, R'' = Me; R' = Me, R'' = Ph)} have been prepared from $M(OR)_5$ and HL in dry benzene, these were characterised by IR and ^1H NMR spectroscopy [30]. $[NbO(dtc)_3]$ (dtc = *N*-cyclopentyl- or *N*-cycloheptyl-dithiocarbamate) has been prepared, and characterised by IR and electronic spectroscopy [31].

7.1.5 *Oxides, niobates(V), tantalates(V) and related sulphur systems*

The reduction and polymorphic transformation of *B*-Nb_2O_5 has been studied. The transformation *B*-Nb_2O_5 → *H*-Nb_2O_5 was discussed in terms of alternative reaction paths [32]. Metastable Nb_2O_5 modifications, produced by oxidation of non-stoicheiometric NbO_x ($2.4<x<2.5$) phases, have been found to show a "memory of structure" when reduced with H_2O/H_2 mixtures, giving in all cases the original NbO_x phases [33]. $Ta_3O_7(OH)$ has been prepared by heating amorphous tantalic acid with 3*M* H_2SO_4 in a sealed vessel at 300 °C; it is isomorphous with Nb_3O_7F and $Nb_3O_7(OH)$ [34].

The mechanism of lithium tantalate(V) formation reactions has been studied [35] and the solid phase syntheses of strontium and barium niobates(V) have been examined using thermal analysis [36]. $TiTaO_4$ has been shown to be the only compound formed in the Ti_2O_3-Ta_2O_5 system. It has a rutile-like structure with a disordered distribution of cations. Magnetic susceptibility measurements suggest the presence of clusters containing an odd number of magnetic ions [37]. The HfO_2-Ta_2O_5 system, however, forms a series of intermediate phases at high HfO_2 concentrations of composition $nHfO_2.Ta_2O_5$ (n = 5, 6 or 7); cell dimensions were determined from X-ray powder data [38]. The X-ray powder pattern of $V_2Nb_6O_{19}$, prepared by heating mixtures of Nb_2O_5 and VO_2, has been indexed on a tetragonal lattice [39]. IR, NMR, TGA and electron diffraction techniques have been used to examine the formation of $FeNbO_4$ by precipitation from aqueous solution. Lattice parameters were obtained for various crystal modifications formed at elevated temperatures [40]. Single crystals of $CoNbO_4$, prepared by heating Nb_2O_5 and $CoC_2O_4.2H_2O$ in air, have been the subject of an X-ray study. $CoNbO_4$ is isomorphous with $AlNbO_4$ and has an ordered arrangement of cobalt and niobium atoms, each coordinated to six oxygen atoms [41]. In contrast, $CoNb_2O_6$, prepared by heating together stoicheiometric quantities of CoO and Nb_2O_5 in an argon atmosphere, has a rutile-type structure with the cobalt(II) and niobium(V) ions statistically distributed. The differences between $CoNbO_4$ and $CoNb_2O_6$ were discussed [42]. Studies of the RhO_3-M_2O_5 (M = Nb or Ta) systems indicate that only $RhMO_4$ are formed [43]. These decompose before melting to give Rh, O_2 and M_2O_5 [44]. The single crystal structure of $Cu_{0.6}NbO_{2.6}F_{0.4}$ has been interpreted in terms of statistically distributed oxygen and fluorine atoms. Edge and corner sharing $\{Nb(O,F)_6\}$ octahedra form layers, in an arrangement analogous to MoO_3, which are linked by copper(I) atoms *via* linear $\{(O,F)-Cu-(O,F)\}$ bonds [45].

The effect of synthesis conditions on the composition and properties of niobium(V) phosphates has been studied [46]. $TaH(PO_4)_2.2H_2O$ has been reported to be formed when an excess of H_3PO_4 is added to a solution containing tantalum-fluoride complexes. Thermolysis studies indicate that the water molecules are lost in two steps, at 323-370 and 473-512 K, $(TaO_2)_4P_6O_{17}$ is formed at 723-773 K and finally at 1123 K, $TaOPO_4$ is produced [47]. When excess H_3AsO_4 is added to an aqueous HF or HNO_3 solution of niobium, a crystalline product is obtained which was formulated as $NbOAsO_4.4H_2O$. Both this, and the anhydrate, were reported to be tetragonal and cell dimensions were given. Heating $NbOAsO_4$ above 950 °C gives Nb_9AsO_{25} which is isomorphous with Nb_9PO_{25} [48]. A study of the TeO_2-Ta_2O_5 system using X-ray powder methods has revealed four stable mixed-oxide phases. These are $3TeO_2.Ta_2O_5$, $7TeO_2.3Ta_2O_5$, and $2TeO_2.Ta_2O_5$ which exists in a high and low temperature form [49]. A similar examination of the TeO_2-Nb_2O_5 system found only three stable phases, $TeO_2.3Nb_2O_5$, $3TeO_2.Nb_2O_5$, and $4TeO_2.Nb_2O_5$. No isomorphism was observed between the niobium and tantalum systems [50]. However, a subsequent XPES investigation of both systems casts doubt on the existence of the phase $2TeO_2.Ta_2O_5$, suggesting rather the stoicheiometry $TeO_2.2Ta_2O_5$ or $TeO_2.3Ta_2O_5$ [51].

A number of new quaternary oxides have been reported this year. $Li_2B_2Nb_2O_9$ has been identified in a study of the Li_2O-B_2O_3-Nb_2O_5 phase diagram [52], and five new oxides of the type $A_3Ti_5MO_{14}$ (A = K or Rb, M = Nb or Ta; A = Tl, M = Nb) have been synthesised. Their structure was described as similar to that of $Na_2Ti_3O_7$ [53]. Single crystal X-ray structures of KTi_3TaO_9 and $K_3TiTa_7O_{21}$ have been reported. In KTi_3TaO_9, Figure 2, there are two possible environments for

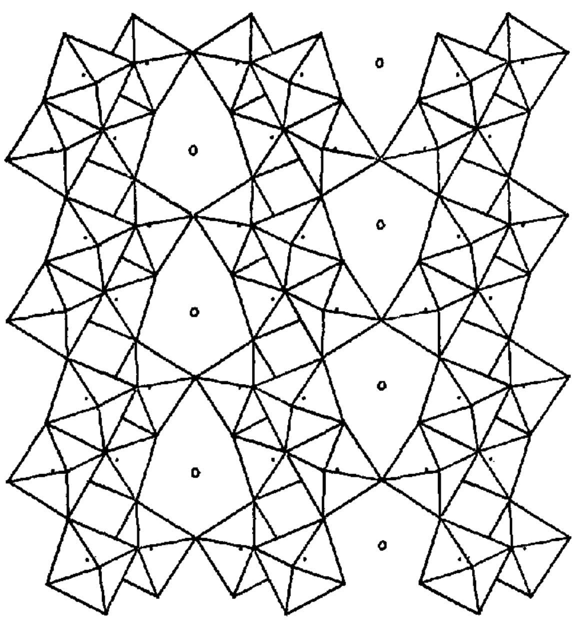


Figure 2: The structure of KTi_3TaO_9. Potassium ions are represented as open circles and the positions of the transition metal ions are indicated by dots. The B1 octahedra are those with one O atom in the mirror plane. Reproduced with permission from [54].

the transition metal atoms, the "B1 and B2 octahedra". The titanium and tantalum atoms are disordered between these sites but, interestingly, the disorder is not completely random. B1 was found to contain 42% tantalum whereas B2 contains only 8% tantalum compared with a statistical distribution of 25% tantalum in each site. The preference of tantalum for one site was attributed to the close approach of metal atoms brought about by the edge sharing of octahedra. B1 shares three edges and two corners, B2 five edges and one corner. Thus metal-metal repulsion is reduced when tantalum occupies the B1 site. In $K_3TiTa_7O_{21}$, Figure 3, the phenomenon is more marked. Titanium is found in 20% of the B1 sites, two edges and one corner shared; the B2 site shares six corners and is occupied entirely by tantalum [54]. The M_2O_5-$A_2[S_2O_8]$ (M = Nb or Ta, A = Na or K) systems have been studied thermoanalytically. The solid state reactions gave products such as $M_2O_3(SO_4)_2$ and $K_{10}Ta_4O_5(SO_4)_{10}$ [55]. The reaction between RbCl, $TaCl_5$ and H_2SO_4 at 300 °C is said to lead to the formation of rubidium tantalum sulphate, although the analytical data given were a little sparse [56].

The magnetic and electronic properties of the system $Fe_{1-x}Cr_xNbO_4$ have been investigated. Replacement of a few percent of iron(III) with chromium(III) causes a significant reduction of the lowest optical band gap, which results in an increased response to the longer wavelengths of the solar spectrum [57]. A neutron diffraction study of $PbFe_{0.5}Nb_{0.5}O_3$ showed a random distribution of iron(III) and niobium(V) which weakens the magnetic interaction between neighbouring iron(III) ions. The most prevalent magnetic interactions were found between iron(III) ions in adjacent planes [58].

Some compounds of the series $LnTi_2MM'O_{14}$ (Ln = La, Pr or Nd; M = Al, Cr, Fe, Sc or Ga; M' = Nb or Ta) have been reported to have a layered perovskite-type structure [59]. Oxides of general formula $MErM'M''O_7$ (M = Pd, Cd or Mg; M' = Ti, Zr, Hf or Sn; M" = Nb or Ta) were isolated from the reaction of $MM'O_3$ with $ErM''O_4$ at 1200-1300 °C [60].

There have been only two studies of sulphides relevant to this section. The enthalpy and entropy of fusion of Tl_3TaS_4 have been determined [61] and the vibronic properties of Cu_3MS_4 (M = Nb or Ta) have been investigated using IR reflectivity and Raman scattering data over a range of temperatures and pressures [62].

7.1.6 Porphyrin complexes

Thermodynamic and kinetic data on the dissociation in acid media of $[Cl_3Nb(TPP)]$, prepared by heating $TPPH_2$ with an excess of $NbCl_5$ in boiling benzonitrile, have been reported. IR and electronic spectra were also given [63]

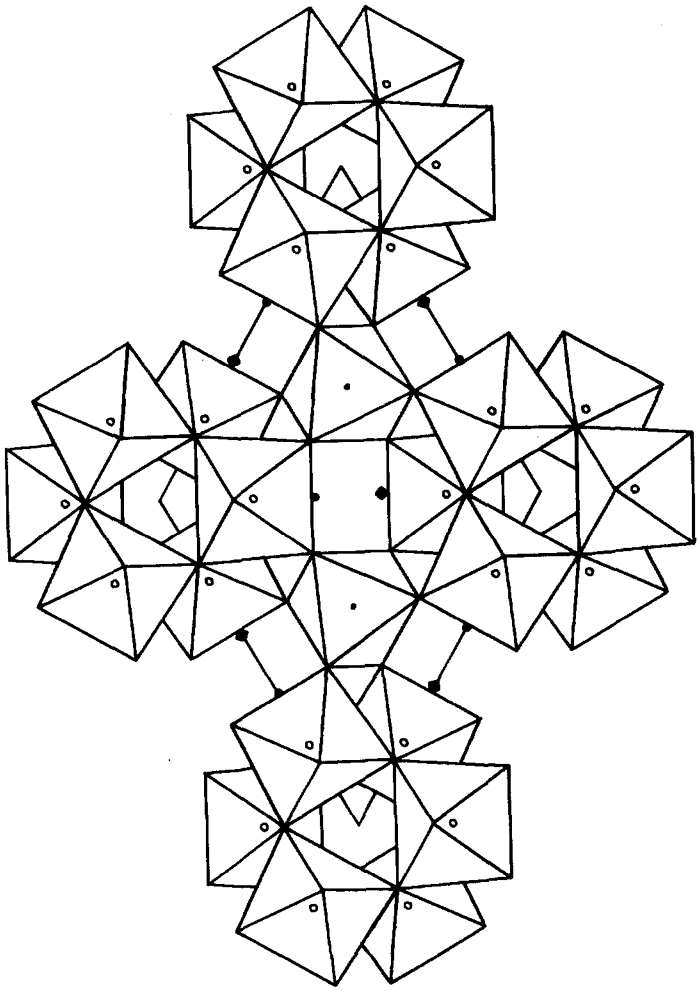
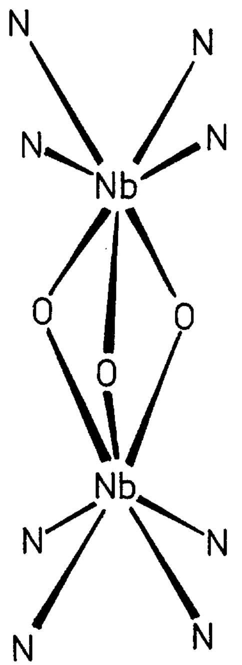


Figure 3: The structure of $K_3TiTa_7O_{21}$. Potassium ions are represented as filled circles and squares and the positions of the transition metal ions are indicated by open circles. The B1 octahedra are those in the edge-shared units of six octahedra. Reproduced with permission from [54].

An explanation has been advanced as to why the two tetraphenylporphine complexes $[\{M(TPP)\}_2O_3]$ (M = Nb or Mo) have such remarkably different structures (*4*, *5*). The structure of the niobium complex was explained in terms of maximum utilisation of vacant d_π orbitals. The linear structure would allow only the d_{xz} and d_{yz}



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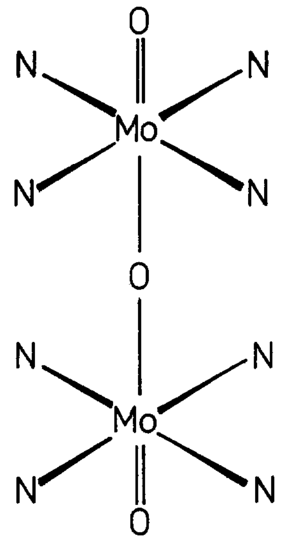


(5)

orbitals to π-bond with donor p_x and p_y orbitals of oxygen, whereas the triply bridged structure allows, in addition, d_{xy} (or $d_{x^2-y^2}$) and d_{z^2} orbitals to contribute to the π interaction. For the molybdenum complex, the energy of the lowest d level (which accepts the last two electrons) is apparently the most important factor [64].

CV and controlled potential electrolysis of [NbO(TPP)(O_2CMe)] shows three one-electron reduction steps. The first two of these were attributed to the reduction of niobium(V) to niobium(III), and the third to the reduction of the porphyrin ring. These deductions were made on the basis of EPR measurements and experiments involving added pyridine. The results were compared and contrasted with those for $[MoO(TPP)(O_2CMe)]^+$ [65].

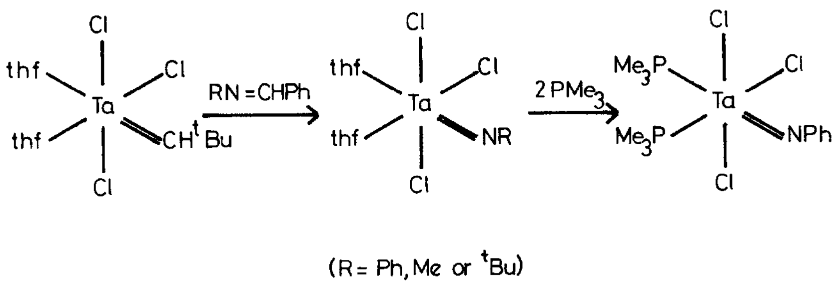
7.1.7 Complexes containing nitrogen acido ligands

When 1,10-phenanthroline or various substituted derivatives are added to H_2SO_4 or HCl solutions of niobium(V) containing $[SCN]^-$, compounds formulated as [phenH][NbO(OH)$(NCS)_3(H_2O)$] or [phenH][NbO$(NCS)_2Cl_2(H_2O)$] are precipitated, whereas with 2,4,6-trimethylpyridine (Me_3py) the isolation of

$[Me_3pyH][NbO(NCS)_4(Me_3py)]$ or $[Me_3pyH][NbO(NCS)_2Cl_2(Me_3py)]$ was reported. Some of these formulations seem questionable in view of the suggested incorporation of the sterically hindered trimethylpyridine ligand in the coordination sphere, but the exclusion of the less hindered phenanthroline [66].

Four six-coordinate chloro(dimethylamido)complexes of tantalum(V) have been prepared and characterised, three by single-crystal structure. Me_3SiCl and $Ta(NMe_2)_5$ react to give $[\{TaCl_2(NMe_2)_3\}_2]$, which is a centrosymmetric chlorine-bridged dimer with the NMe_2 groups in a *facial* arrangement. The reaction between $TaCl_5$ and $NHMe_2$ was found to give three products. $[TaCl_3(NMe_2)_2(NHMe_2)]$, the major product, is monomeric with the NMe_2 moieties *cis*, one *trans* to chlorine and one *trans* to $NHMe_2$. $[TaCl_2(NMe_2)_3(NHMe_2)]$ was assigned a monomeric structure with the NMe_2 groups *facial*, and $[\{TaCl_2(NMe_2)_2(NHMe_2)\}_2O]$, a trace impurity, is a dimer with a near linear oxygen bridge. The ligand arrangement about tantalum is similar to that in $[TaCl_3(NMe_2)_2(NHMe_2)]$, with one of the *trans* chlorine atoms replaced by oxygen. The short Ta-NMe_2 distances (r = 1.968 Å, averaged all structures) and the spatial distribution of the NMe_2 ligands were considered to be indicative of extensive N(p) to Ta(d) π bonding [67].

The preparation of a number of tantalum(V) imido complexes has been reported (equation 2). The structures were assigned on the basis of ^1H, ^{13}C, ^{15}N, and



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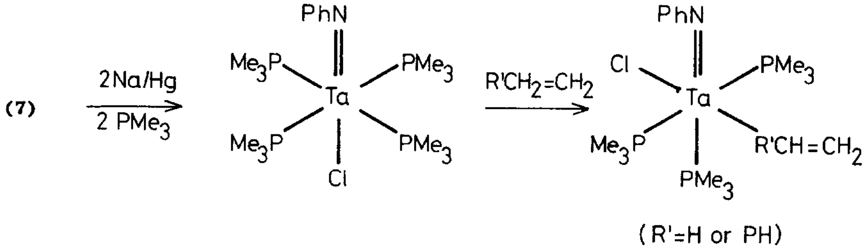
(6) (7)

^{31}P NMR spectroscopy. Reduction of (*7*) leads to the formation of a tantalum(III) imido compound, (*8*), in which one of the PMe_3 ligands may be replaced by an alkene to give (*9*), see equation (3). A band around 1350 cm^{-1} in the IR spectra of all these complexes was assigned to a coupled Ta=N-C stretching mode on the basis of ^{15}N labelling experiments [68]. $[\{Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2\}_2N_2]$ (*10*) represents the first example of a fully characterised dinitrogen complex of a Group VA metal. Its preparation, equation (4), involved the direct reaction with dinitrogen. The structure, (*10*), which is represented schematically, shows each tantalum atom to be in a trigonal bipyramidal environment, with the



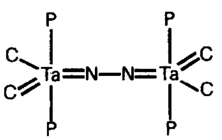
(3)

(8) (9)

$$[Ta(CHCMe_3)Cl_3L_2] \xrightarrow[L,N_2]{2Na/Hg} [\{Ta(CHCMe_3)ClL_2\}_2N_2] \xrightarrow{LiR} [\{Ta(CHCMe_3)RL_2\}_2N_2] \quad (4)$$

(L = PMe_3, R = Me or CH_2CMe_3)

phosphine ligands axial and the two halves of the molecule approximately orthogonal (not shown). The Ta=N bonds are both shorter than the Ta=C bonds



(10)

{r(Ta=N) = 1.837, 1.842 Å; r(Ta=C) = 1.932, 1.937 Å}, the N-N bond is particularly long for this type of bridged complex {r(N-N) = 1.298 Å}, and the {Ta(μ-N_2)Ta} unit is close to linear. On the basis of these observations it was suggested that the μ-N_2 group is "diimido like" (*i.e.* Ta=N-N=Ta, rather than Ta-N≡N-Ta). The preparation and partial characterisation of {$(thf)_2Cl_3Ta$=N-}$_2$, {$(PEt_3)_2Cl_3Ta$=N-}$_2$ and {$(PMe_3)_3(C_2H_4)ClTa$=N-}$_2$, which are related to (*6*), (*7*), and (*9*) respectively, were also reported, although only the last mentioned was produced by direct reaction of N_2. ^{15}N labelling studies indicated that a band around 850 cm^{-1} in the IR spectrum is associated with the {Ta_2N_2} moiety of these compounds [69,70].

7.1.8 Hydrides

$[NbH_5(PMe_3)_4]$ has been prepared by allowing $[NbMe_5(PMe_3)_2]$ to react with dihydrogen in the presence of an excess of PMe_3; the pure tantalum analogue could not be isolated [71].

7.1.9 *Solvent extraction*

Three solvent extraction studies have been reported this year. The interaction of tantalum(V) with 2-nitrophenylfluorone and 4,4'-diantipyrylmethane has been studied spectrophotometrically and the ratio of the components in the complex established [72]. The extraction of niobium and tantalum from aqueous HF using 4,4'-diantipyrylmethane in the organic phase has been examined. Data on the selectivity of the extraction process were given [73]. A radiotracer study of the extraction of niobium and tantalum from aqueous H_2SO_4 solutions using tributylphosphate has also been reported [74].

7.2 NIOBIUM(IV) AND TANTALUM(IV)

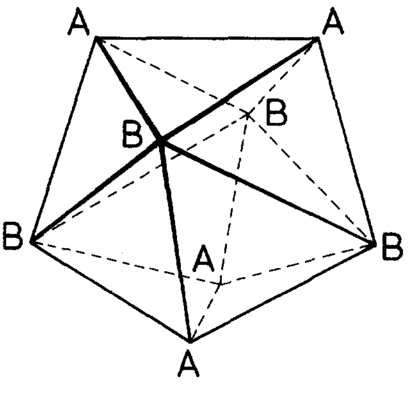
7.2.1 *Halides and halide complexes*

NbF_4 has been prepared by the reduction of NbF_5 with niobium metal followed by sublimation of the excess of NbF_5. The electronic spectrum of the product had maxima at 515 and 565 nm, and various possible assignments were discussed. The magnetic susceptibility showed a weak field dependence, and the magnetic moment fell from 0.8 μ_B at room temperature to 0.2 μ_B at 4 K. These results were interpreted in terms of a $^2T_{2g}$ ground state perturbed by spin-orbit coupling and an axial field component, but in order to obtain good agreement between calculated and experimental values, an abnormally large value for the spin-orbit coupling constant was required [75].

The series of compounds $LnNbF_7$ (Ln = all lanthanides except La) have been prepared and their cell dimensions determined. They are isotypic with the $LnZrF_7$ series [76].

7.2.2 *Halide, sulphido- and selenidohalide complexes with Group VB donors*

The crystal structure of $[NbCl_4(diars)_2]$ shows the coordination about niobium to be dodecahedral with r(Nb-As) = 2.733 Å and r(Nb-Cl) = 2.515 Å. The arsenic atoms occupy the A sites and the chlorine atoms the B sites of the dodecahedron (*11*). Comparison of the bond lengths with those found for $[NbCl_4(diars)]^+$ showed that r\{Nb(IV)-As\} $\nless$ r\{Nb(V)-As\} whereas r\{Nb(IV)-Cl\} > r\{Nb(V)-Cl\}. This was attributed to the single d electron in the d_{xy} orbital of the niobium(IV) complex repelling the four chlorine atoms which lie almost in the same plane [77]. *cis*-$[NbCl_4(NCMe)_2]$.MeCN is obtained when $NbCl_4$ is allowed to react with MeCN.

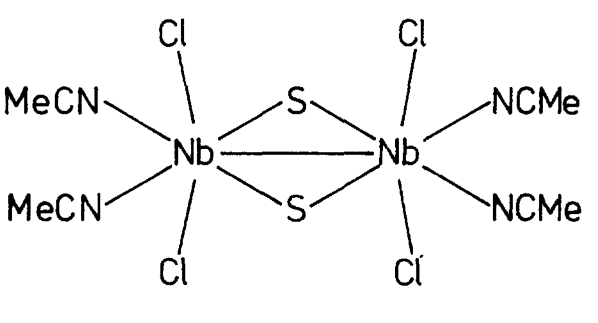


(11)

The molecule has a crystallographically imposed mirror plane which passes through the niobium and two chlorine atoms {r(Nb-Cl) = 2.328-2.349 Å, r(Nb-N) = 2.220 Å}. If this adduct is allowed to react with Sb_2S_3, equation (5), a green precipitate

$$3[NbCl_4(NCMe)_2] + Sb_2S_3 \xrightarrow[50\ ^\circ C,\ 2d]{MeCN} 3[NbSCl_2(NCMe)_2] + 2SbCl_3 \qquad (5)$$

is obtained which, when recrystallised from MeCN, gave two types of crystals. These were shown to be $[\{NbSCl_2(NCMe)_2\}_2].x$MeCN ($x$ = 1 or 2), both containing the same basic unit (*12*) of approximately D_{2h} symmetry {r(Nb-Nb) = 2.862-2.872 Å, r(Nb-Cl) = 2.383-2.403 Å, r(Nb-S) = 2.338-2.349 Å, r(Nb-N) = 2.286-2.334 Å}.

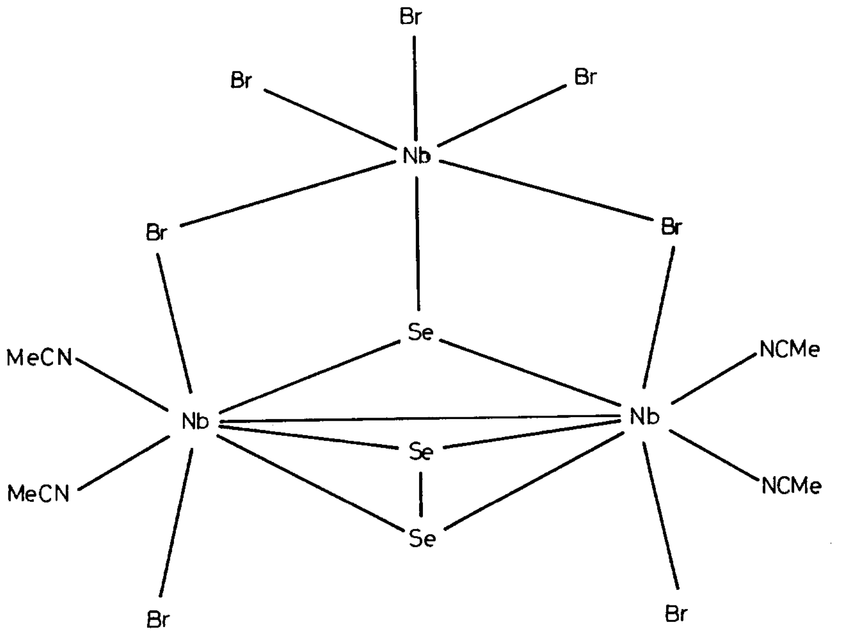


(12)

An analogous bromide was also reported, and a comparison of the IR spectra of the chloride and bromide allowed the assignment of bands around 470 and 320 cm^{-1} to vibrations of the {Nb-S-Nb-S} unit [78]. By contrast, in the reaction between $[NbBr_4(NCMe)_2]$ and Sb_2Se_3 the redox reaction, (6), apparently occurs. The

$$2Se^{2-} + 2Nb(IV) \longrightarrow [Se_2]^{2-} + 2Nb(III) \quad (6)$$

structure of the product, $[Nb_4(MeCN)_4Br_{10}Se_3]$, shows a $\{(MeCN)_2Br_2Nb\text{-}\mu\text{-}Se\text{-}\mu\text{-}(Se_2)\text{-}NbBr_2(NCMe)_2\}$ fragment weakly linked to two $\{NbBr_3\}$ units (*13*), one of which has been omitted for clarity; this is bonded in an



(13)

identical fashion to that shown on the other side of the Nb-(Se_2)-Nb-Se moiety. A mirror plane passes through the three selenium atoms, the niobium and one bromine atom of both $\{NbBr_3\}$ units. The single selenium atom is bound to all four niobium atoms $\{r(Nb\text{-}Se) = 2.469 \times 2, 3.086$ and 3.095 Å$\}$ and the Br_3Nb-Br bridging bonds are long at 3.125 and 3.195 Å compared to the Nb-Br terminal bonds $\{r(Nb\text{-}Br) = 2.504\text{-}2.545$ Å$\}$. The Nb(IV)-Nb(IV) distance is indicative of a single bond $\{r(Nb\text{-}Nb) = 2.886$ Å$\}$. The compound was found to be diamagnetic and EPR inactive, and possible reasons for this were discussed [79].

7.2.3 Oxides, niobates(IV), and tantalates(IV)

The harmonic equilibrium structure, vibrational frequencies and harmonic force constants of gaseous NbO_2 have been determined from high temperature electron diffraction data [80]. A single crystal EPR study of niobium(IV) doped $ZrSiO_4$ has been conducted. The spectrum showed the expected ten-line signal which was analysed to obtain *g* values and hyperfine coupling constants [81]. The cation distributions in $(Fe_{0.5}Ta_{0.5})O_2$ and $(Fe_{0.45}Nb_{0.53})O_2$ have been redetermined by the combined use of neutron and X-ray powder diffraction. Both compounds have the rutile structure with the metal atoms statistically distributed. The magnetic ordering was also studied [82].

7.2.4 *Sulphides and selenides*

The single crystal structure of 3-*R* $Nb_{1.06}S_2$ shows the majority of the niobium atoms to be in trigonal prismatic sites between pairs of close-packed sulphur-atom layers $\{\bar{r}(Nb-S) = 2.473$ Å$\}$. A fraction of the niobium atoms were found in trigonally distorted octahedral sites within the van der Waals' gaps of successive S-Nb-S layers $\{r(Nb-S) = 2.577, 2.234$ Å$\}$. The distortion prevents a close approach of trigonal and octahedral niobium atoms [83].

The chemical transport of both TaS_2, and Ta_2O_5, by sulphur has been studied. In each case the results were interpreted in terms of transport *via* the previously unknown TaS_5 molecule [84,85]. XPES measurements have been made on NbS_3 and TaS_3 and information obtained on the valence band structure [86]. EXAFS spectra of $TaSe_3$ and the polytypes of TaS_2 and $TaSe_2$ have been measured and used to determine the amount of p character in the conduction band. Intercalation with N_2H_4 was found to modify the p character of this band [87].

7.2.5 *Complexes containing sulphur acido ligands*

EPR spectra of $[Nb(\eta^5-C_5H_5)_2\{S_2P(OR)_2\}]^+$ (R = Et or $CHMe_2$) have been reported. The solution spectra show two superimposed ten-line signals due to hyperfine and superhyperfine coupling of the electron spin with the ^{93}Nb and ^{31}P nuclear spins. A detailed analysis of the spin Hamiltonian parameters was given [88].

7.2.6 *Carbides*

Gaseous NbC and NbC_2 molecules have been identified in a mass spectrometric study, and the Nb-C bond energies were evaluated [89].

7.3 NIOBIUM CLUSTERS WITH OXIDATION STATE > (III)

A preliminary report has appeared of the structure of $K_4[H_5O_2][Nb_3O_2(SO_4)_6(H_2O)_3].5H_2O$, which represents the first fully characterised non-niobium(V) species obtained from aqueous solution. The anion has approximately D_{3h} symmetry, with a triangle of niobium atoms {$\bar{r}$(Nb-Nb) = 2.886 Å} capped on each side by an oxygen atom {$\bar{r}$(Nb-μ_3-O) = 2.052 Å}, and each edge bridged by two bidentate sulphate ions {$\bar{r}$(Nb-OSO_3) = 2.136 Å}. Nine-coordination about each niobium (including the Nb-Nb bonds) is completed by three water molecules at the vertices of the triangle {$\bar{r}$(Nb-OH_2) = 2.241 Å}. The niobium atoms have an average oxidation state of 3.667 and the Nb-Nb bond order was given as 0.667 [90]. [$Nb_4(MeCN)_4Br_{10}Se_3$] was discussed in Section 7.2.2.

7.4 TANTALUM(III)

7.4.1 Halide complexes with sulphur ligands

The crystal structures of [$Ta_2Cl_6(tht)_3$] and [$Ta_2Cl_6(SMe_2)_3$] have been reported. Both are very similar to [$Ta_2Br_6(tht)_3$], with a Ta=Ta bond {*r*(Ta=Ta) = 2.681 and 2.691 Å}, and three bridging atoms, two chlorines and one ligand sulphur. The only difference of note between these complexes and their bromide analogue was found to be the Ta=Ta distance {*r*(Ta=Ta) = 2.710 Å in the bromide complex}, which was attributed to the relative size of the bridging atoms [91].

7.4.2 Alkyne complexes

Tantalum complexes containing alkynes have generated much interest in recent years because of the short Ta-C distances which have been found. These are typically 2.07 Å, indicative of a double bond. The bonding models (*14*) and (*15*) do not account for these short bonds and hence a four-electron donor model, (*16*), was proposed. A recent publication revokes this and suggests instead, by analogy

(14) (15) (16) (17)

with cyclopropene, that a simple metallocene model for transition-metal-alkyne complexes should be described as containing bent bonds, (*17*). A simple method for predicting M-C and C-C distances was proposed and applied to [pyH][$TaCl_4$(PhC≡CPh)(py)]. The results are very convincing, but clearly further tests on other compounds are necessary before this model becomes accepted [92].

The opportunity for such calculations has already arisen in that the structures of two more tantalum-alkyne complexes have been published and described in terms of the four-electron donor model. [Ta(cp)(PhC≡CPh)Cl_2] is monomeric with r(Ta-C) = 2.067 and 2.075 Å for the alkyne carbons and r(C≡C) = 1.337 Å [93]. [{$TaCl_2$(tht)(Me_3C≡CMe)}$_2$(μ-Cl)$_2$] is a centrosymmetric chlorine bridged dimer. The tantalum atoms are seven coordinate if the alkyne carbon atoms are counted separately, with r(Ta-C) = 2.029 and 2.033 Å, r(C≡C) = 1.32 Å and a Ta-Ta distance of 4.144 Å. This precludes a Ta-Ta bond, the absence of which was attributed to the d electrons being localised in bonding with the alkyne group. The chlorine bridges are asymmetric, with the bond *trans* to the alkyne group (2.736 Å) longer than the bond *trans* to the terminal chlorine atom (2.496 Å). This was taken as evidence of significant π-donation from the alkyne to tantalum, so if the bent bond model is to gain acceptance, an explanation must be found for this asymmetry [94].

7.5 NIOBIUM AND TANTALUM CLUSTERS, OXIDATION STATE < (III)

Heterogeneous, reversible redox reactions of $Ta_6Cl_{14}.8H_2O$ have been reported when it is made an electrode of a suitable cell with a 1*M* HCl/1*M* NaCl electrolyte. The anodic oxidation/cathodic reduction reactions proceed as in equation (7),

$$[Ta_6Cl_{14}(H_2O)_4].4H_2O \rightleftharpoons [Ta_6Cl_{14}(OH)_x(H_2O)_{4-x}].4H_2O + xe^- + xH^+ \qquad (7)$$

with $0 \leqslant x \leqslant 1.5$. $Nb_6Cl_{14}.8H_2O$ may be oxidised similarly but cathodic reduction is reported to be kinetically hindered [95]. The complexes [(M_6Cl_{12})Cl_2(PR_2R')] (M = Nb; R = R' = Pr, Et; R = Et, R' = Ph; M = Ta; R = R' = Pr) have been prepared and studied using CV and controlled potential electrolysis. They undergo two reversible one-electron oxidations, and chemical oxidation with [NO][PF_6] was used to produce both tantalum cationic species, although only the mono-cation of niobium could be obtained. The niobium complexes were also found to undergo a one-electron reduction, to give (presumably) $[(Nb_6Cl_{12})Cl_2(PR_3)_4]^-$, but this could not be isolated. XPES measurements on the neutral and cationic species, together with EPR spectra of the mono-cations, were taken in conjunction with the CV results to indicate that the HOMO of the $\{M_6Cl_{12}\}^{n+}$ core is almost exclusively metal based [96]. The X-ray powder patterns of $[M_6X_{12}]Y_2.nH_2O$ (M = Nb or Ta; X = Cl or Br; Y = Cl, Br, I or OH) have been reported and classified into five groups [97]. Nb_6I_{11} and HNb_6I_{11} undergo a phase transition which was found to be accompanied by a crossing of electronic levels, which led to a reduction of the spin degeneracy [98-100].

7.6 TANTALUM(II)

Matrix-isolated TaO has been studied using absorption and MCD spectroscopy. The results were compared with those obtained in the gas phase [101].

7.7 NIOBIUM(0) AND TANTALUM(0)

The complexes $[M(Me_2PCH_2CH_2PMe_2)_3]$ (M = Nb or Ta) have been isolated from the reaction between the metal vapour and the phosphine. This appears to be the first report of a zero-valent tantalum complex [102].

7.8 NIOBIUM NMR SPECTROSCOPY

^{93}Nb studies have been made of complexes purported to contain Nb(V)=S and Nb(V)=Se moieties [103]. These results [103] should be treated with some caution because the stoicheiometries employed in the preparation of the starting materials $NbYX_3.2MeCN$ (Y = S or Se, X = Cl or Br) could easily lead to the formation of complexes containing the Nb–S–Nb–(S_2) unit, which contains Nb(IV) and a metal-metal bond [104]. Furthermore, $NbSCl_3.2MeCN$ is described [103] as a green solid with an Nb=S stretch at 552 cm^{-1} in its IR spectrum, whereas in the hands of the author this compound is orange with ν(Nb=S) at 530 cm^{-1} [105].

An examination of MeCN solutions containing niobium(V), chloride ions and thiocyanate ions has revealed sixteen magnetically non-equivalent niobium environments which, by use of the pairwise additivity model, were assigned to sixteen of the possible fifty-six configurations for the system $[Nb(NCS)_n(SCN)_mCl_{6-(n+m)}]^-$. $[Nb(SCN)_6]^-$ was identified for the first time, and its formation, together with that of mixed thiocyanate/isothiocyanate complexes, was discussed with reference to the hard-soft acid-base model [106].

The multinuclear NMR spectra of $[Nb(PF_3)_6]^-$ and its vanadium analogue have been reported. The ^{93}Nb spectrum showed a well resolved septet ($^1J_{NbP}$ = 1050 Hz) with associated fine structure ($^2J_{NbF}$ = 55 Hz). The ^{31}P spectrum showed ten equidistant, superimposed 1:3:3:1 quartets ($^1J_{PF}$ = 1250 Hz) and the ^{19}F spectrum consisted of a doublet broadened by unresolved fine structure. All of the coupling constants in the vanadium analogue were smaller, and this was interpreted in terms of greater valence s-electron density at the nucleus and enhanced σ-bonding in the niobium complex [107].

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