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5. NIOBIUM AND TANTALUM

D.A. RICE

CONTENTS

INTRODUCTION

The pattern adopted for this review of the literature published in 1980 is essentially the same as that used for the review of the 1979 material. Thus the material is divided into sections according to the oxidation state of the metal. Within a section the material is further sub-divided according to the groups to which the elements bound to the metal belong.

There have been exciting developments in the organometallic chemistry of niobium and tantalum this year, especially relating to carbon to metal multiply bonded species (alkylidenes), but this material is not included as it is reviewed elsewhere. Similarly papers devoted mainly to solid-state matters or, catalysis or kinetics are not included.

5.1 NIOBIUM(V) AND TANTALUM(V)

5.1.1 Halogen-containing species

A new triclinic form of niobium(V) iodide has been prepared by treating niobium with a 3 to 4 bar pressure of iodine in a temperature gradient of 400 to 230 °C. Within the crystal are Nb_2I_{10} molecules in which the bridging NbI distances are 2.933 and 2.939 Å, while the terminal Nb-I distances span the range 2.639 to 2.720 Å. The structure is isotypic with the β-form of uranium(V)

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chloride. Four Nb-I stretches were observed in the infrared spectrum at 148, 202, 214 and 242 cm^{-1} [1]. The Raman spectra of $NbCl_5/AlCl_3$ melts has been examined, and the results obtained at 210 °C have been said to indicate the presence of $NbCl_5$, Nb_2Cl_{10} and Al_2Cl_6. In the ternary $NbCl_5/AlCl_3/MCl$ (M = Na or K) melts, the nature of the species present was shown to be dependent upon the acidity of the melt and its temperature. Thus $[NbCl_6]^-$ is present only in very basic melts, while Nb_2Cl_{10} is stable only in acid melts [2]. Phase equilibria studies on $NbCl_5/WOCl_4$ mixtures have been reported [3].

Attack of water vapour on solid niobium(V) chloride was studied at 5.32 to 19.25 kPa partial pressure of water vapour over the temperature range 50 to 150 °C. The reaction mechanism is complex but the energy of activation was found to be 63 kJ mol^{-1} and the order unity (with respect to P_{H_2O}) for the initial stage [4]. In a further kinetic study, the fluorination of niobium and tantalum by $[NH_4][HF_2]$ over the temperature range 135 to 208 °C has been studied. The rate of reaction at a given temperature is higher for tantalum than niobium, and estimated values for the enthalpies of formation of $[NH_4]_2[MF_7]$ {M = Nb; ΔH_f = -301 kJ $gatom^{-1}$: M = Ta; ΔH_f = -176 kJ $gatom^{-1}$} were obtained [5].

A collection of X-ray data for complex fluorides of titanium, zirconium, hafnium, niobium and tantalum containing divalent cations has been published [6], as have coefficients for the diffusion of niobium(IV) and niobium(V) in chloride and chloride/fluoride melts [7].

The ^{19}F NMR spectra of TaF_5 solutions (in CH_2Cl_2) containing R_3AsO (R = Ph or Bu) or Ph_3AsS have been measured: evidence for the existence of $[TaF_5(SAsPh_3)]$, $[TaF_5(OAsR_3)]$ and $[TaF_4(OAsR_3)_2]^+$ (both *cis* and *trans*) in solution was obtained. From a consideration of the chemical shift data, the donor strength towards TaF_5 is $R_3AsO>R_3PO>R_3AsS>R_3PS$ [8]. The same group of workers have studied the complexes formed by TaF_5 with $Ph_2P(O)SH$. The results of ^{19}F NMR studies are interpreted as indicating *cis*-$[TaF_4(OPPh_2SH)_2]^+$ and $[TaF_5(OPPh_2SH)]$ being present in solution [9]. The phosphine sulphide ligand $(4\text{-}MeC_6H_4)_3PS$ (L), when reacted with $TaF_5/TaCl_5$ mixtures in CH_2Cl_2, forms a range of complexes namely $[TaF_4Cl(L)]$ (*cis* and *trans*), $[TaF_3Cl_2(L)]$ (*trans* Cl), $[TaF_2Cl_3(L)]$ (*fac* Cl) and $[TaF_2Cl_3(L)]$ (*trans* F and *mer* Cl). The ligand, L, can be replaced from its complexes by MeCN, the products being a mixture consisting of $[TaF_5(NCMe)]$, *trans*-$[TaF_4(NCMe)_2]^+$, $[TaF_3Cl_2(NCMe)]$ and $[TaF_4Cl(NCMe)]$ [10]. Partial hydrolysis of TaF_5 (H_2O: TaF_5 = 0.2:1) in a MeCN solution containing Et_3N leads to the formation of $[TaOF_5]^{2-}$. At relative concentrations Et_3N: H_2O: TaF_5 = 2:0.2:1, $[Ta_2F_{10}O]^{2-}$ is formed, which is converted to the monomeric anion $[TaOF_5]^{2-}$ by addition of further water. The monomeric anion can be precipitated by the addition of Et_2NH and in the resulting salt, $[Et_2NH_2]_2[TaOF_5]$, there is thought to be hydrogen bonding between the cation and the oxygen atom. The interaction of $Ta(OEt)_5$ and $[TaOF_5]^{2-}$ gave $[Ta(OEt)F_5]^-$ [11].

The structure of the fluoro-oxo-niobium(V) species $Na_2[NbF_5(O_2)].H_2O$ (Fig. 1) has been determined by single crystal X-ray studies. The coordination sphere around the niobium atom is approximately pentagonal bipyramidal (C_{2v}) with the axial positions being filled by two fluorine atoms that are bent away from the oxygen atoms, which are situated in the pentagonal plane {O(1)-$\hat{Nb}$-F(1) = 95.0(2)°; O(1)-$\hat{Nb}$-F(3) = 98.5(2)°} [12].

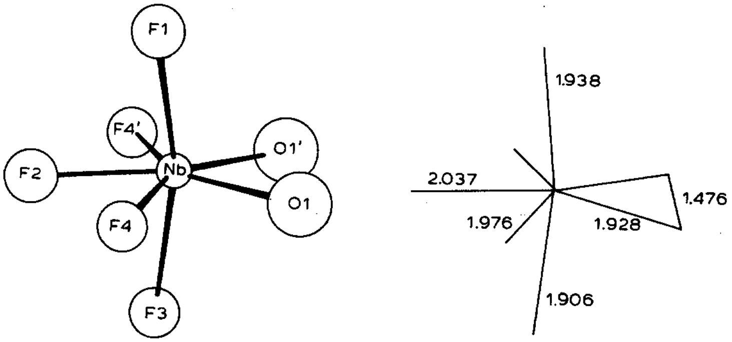

Fig. 1: The $[NbF_5(O_2)]^{2-}$ ion, reproduced with permission from [12], R. Stromberg, *Acta Chem. Scand. Ser. A*, 34 (1980) 193.

The salt $[AsPh_4]_2[NbOCl_5]$ is formed when $NbOCl_3$ and $[AsPh_4]Cl$ are mixed in CH_2Cl_2 solution. The anion $[NbOCl_5]^{2-}$ has the infrared and Raman spectra to be expected for a C_{4v} species. The Nb-Cl distances cover the range 2.555(4) to 2.345(4) Å with the longest distance *trans* to Nb-O {at 1.967(6) Å} [13].

Strähle and co-workers have continued their studies on species containing niobium- or tantalum-nitrogen multiple bonds. From the reaction of the azide $NbCl_4N_3$ with PPh_3 in 1,2-dichloroethane solution, the yellow species $Nb(NPPh_3)Cl_4$ was isolated. Dimeric units exist within the crystal (see Figure 2), and thus the niobium atom attains six coordination *via* halogen bridges. The Nb-$\hat{N}$-P angle is 171° with distances of 1.776(8) (Nb-N) and 1.637(9) Å (N-P) and these facts lead the authors to suggest that both bonds contain some multiple character [14].

By heating $[NH_4]Br$ and $TaBr_5$ at 400 °C in a sealed glass ampoule, the salt $[NH_4]_3[Ta_2NBr_{10}]$ was isolated. Crystallographic investigations have shown that the $[Ta_2NBr_{10}]^{3-}$ anion has D_{4h} symmetry with a Ta-N distance of 1.849(2) Å. Thus a Ta=N=Ta moiety exists in the anion, and noticeably the Ta-Br bond which is *trans* to Ta-N is much longer than the Ta-Br bond which is *cis* to Ta-N {2.738(6) Å compared to 2.514(3) Å} (see Fig. 3) [15].

Tantalum-nitrogen multiple bonding is also said to be indicated by the length of the Ta-N bonds in $[TaCl_3\{N(SiMe_3)_2\}_2]$ {1.928(7) and 1.933(7) Å}. The compound has a *pseudo*-trigonal bipyramidal structure with two chlorine atoms filling the axial positions. The angle subtended at the metal by these axial atoms is 168°

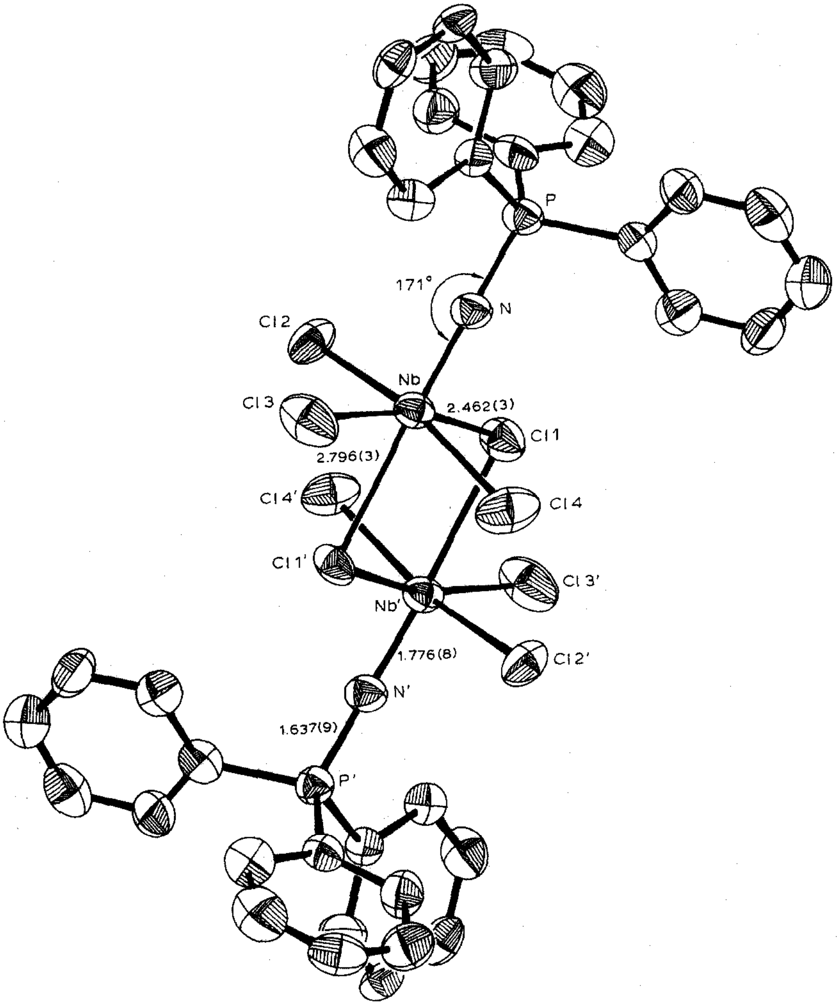

Fig. 2: The dimeric $[Nb_2(NPPh_3)_2Cl_8]$ unit, reproduced with permission from [14], H. Bezler, J. Strähle and J. Weidleim, *Z. Naturforsch, Teil B: Anorg. Chem. Org. Chem.*, 34 (1979) 1199.

and this is said to be caused by steric constraints [16]. The reaction of $[TaCl_3\{N(SiMe_3)_2\}_2]$ with Me_3SiN_3 yields $[Ta(N_3)_3\{N(SiMe_3)_2\}_2]$ $\{\nu(N_3) = 2105\ cm^{-1}\}$ [17].

Solvolysis reactions involving niobium or tantalum halides and phenols or alcohols have been studied by a number of groups this year. A range of phenoxy/salicylaldehyde (L) complexes of niobium and tantalum (of general formula $MCl_n(OPh)_{4-n}(L)$ (n = 0 to 3; M = Nb or Ta) have been characterised by spectroscopic studies [18] and the $[M(OPh)_4]^+$ cation (M = Nb or Ta) has been isolated

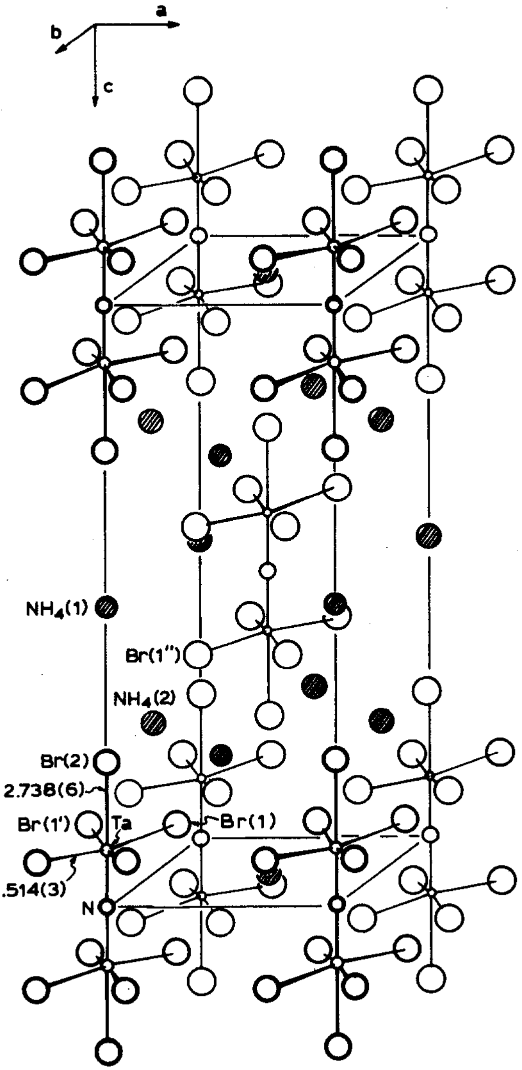

Fig. 3: The packing of $[NH_4]_3[Ta_2NBr_{10}]$, reproduced with permission from [15], K.P. Frank and J. Strähle, *Z. Naturforsch, Teil B: Anorg. Chem. Org. Chem.*, 35 (1980) 300.

by treating $[M(OPh)_4]Cl$ with $SbCl_5$ [19]. The related phenoxy iodides have been prepared from $TaI_5/Ta(OPh)_5$ mixtures in CH_3CN solution and in particular $[Ta(OPh)I_4(NCMe)]$ was characterised. The reaction of $Ta(OPh)_5$ with MeCOI in CCl_4 solution yields $Ta(OPh)_4I$, while from $TaI_5/Ta(OEt)_5$ in MeCN solution $TaOI_3(NCMe)$ was obtained [20]. The solvolysis of $NbOCl_3$ by a range of alcohols in the presence of dry ammonia has led to the isolation of $NbO(OCH_2CF)_3(NCMe)$,

$\{NbO(OCH_2CF_3)_2(OCH{=}CF_2)\}_2(CF_3CH_2OH)$, and $NbO(OCH_2CH_3)_3$, while from a solution of $NbOCl_3$ in C_6H_6, $NbCl_2O(OMe)(CH_3OH)$ was obtained by the addition of MeOH. The nature of these products was determined by molecular weight and NMR measurements, and evidence was obtained that suggested both μ-OR and μ-oxo isomers exist in solution in dynamic equilibrium [21]. The complexes $NbCl_2(OR)_3(L)$ [R = Me, Et, Pr or Bu; L = phen] have been isolated [22].

5.1.2 Species containing (at least formally) oxo-, oxofluoro- or sulphido-anions

In many complex fluoride oxides of niobium and tantalum there is disorder between the oxygen and fluorine atoms: hence these oxofluoro compounds are best discussed with the oxo-compounds.

Two new oxofluoroniobates(V) have been isolated that are isotypic with the previously detected tantalum phases. The new compounds $K_6Nb_{6.5}F_{9.5}O_{14.5}$ and $K_{12}Nb_{15.5}F_{18.5}O_{35.5}$ have hexagonal symmetry [23]. The full X-ray structural determination on one of the tantalum analogues $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$ has been executed and it consists of a three-dimensional framework formed by the interpenetration of two distinct sublattices of formulation $\{Ta_5X_{17}\}_n$ and $\{Ta_{0.5}X_3\}_n$ (X = O or F) [24]. The same group of workers, continuing their study of species with either layer or tunnel structures that are suitable for fast ion transport, have reported a study of the structure of $K_3Ta_4F_7O_8$. The structure has an assembly of two-dimensional $\{Ta_4X_{15}\}$ infinite blocks that are held together by bridging K^+ ions [25].

The compound $KF.4KNbO_3$ contains double columns of $\{NbO_6\}$ octahedra joined along edges [26]. A mixed oxofluoro copper niobate was obtained by the fluorination of $CuNb_2O_6$. It has the formula $CuNb_2F_{0.7}O_{5.3}$; X-ray measurements indicate it is orthorhombic and electronic activation energy measurements indicate there is some electron delocalisation [27]. Another oxofluoro copper niobate $CuNbFO_3$, has been shown to be triclinic and to contain strings of edge-sharing $\{Nb(O,F)_6\}$ octahedra which are linked *via* the copper(II) ions [28]. A different space group has been assigned to $(Ce,Ta)Ta_6O_{19}$ using convergent-beam electron diffraction than was initially assigned using X-ray techniques. However the structure determined by X-ray methods is said to be essentially correct [29]. A monoclinic form of $Ca_2Nb_2O_7$ has been isolated and shown (like the orthorhombic form) to consist of stacked slabs with a perovskite-type structure. The difference between the two forms is in the method of stacking the slabs [30]. The titanoniobate $CsTi_2NbO_7$ which is formed by heating $CsNO_3/TiO_2/Nb_2O_5$ mixtures has puckered layers formed by edge sharing octahedra [31], while the niobium and tantalum compounds ATi_3MO_9 and $(A_2Ti_6O_{13})_n.A(Ti_3MO_9)$ (A = K, Rb, Tl or Cs; M = Nb or Ta) have tunnel structures [32]. The double oxide $Rb_4Nb_6O_{17}.3H_2O$ has a mica-like appearance and the crystals cleave easily; thus, it is not surprising that X-ray studies have shown the compound to consist of sheets. Each sheet is made up of two layers of $\{NbO_6\}$ octahedra linked by half the rubidium atoms. The remaining rubidium atoms and the water molecules hold the sheets together [33].

The phosphate $NbO(PO_4)$ is the ultimate product obtained by heating the complex species $NbO(OH)(HPO_4).(2.25H_2O)$ to 900 °C. Three stages occur in the decomposition: at 300 °C $NbO(H_2O)PO_4$ is formed, while between 300 and 700 °C the mixture $\{NbO(H_2O)PO_4\}\{NbO(PO_4)\}_n$ exists [34]. The pyrophosphate $KNbO(P_2O_7)$ consists of K^+, NbO^+ and $[P_2O_7]^{4-}$ ions with the niobium atom being in a six coordinate all-oxygen environment, five of the oxygen atoms being from five different $[P_2O_7]^{4-}$ anions [35]. A $\{NbO_8\}$ dodecahedron has been detected in crystals of $K_3[Nb(SO_4)_4]$. The structure consists of discrete K^+ and $[Nb(SO_4)_4]^{3-}$ ions [36].

Related to the above oxo-compounds is the tantalum disulphide thiophosphate. The compound has the unusual stoicheiometry $TaPS_6$, which can be understood when it is realised two-thirds of the sulphur atoms are present as S^{2-} (in $\{PS_4\}$ tetrahedra) and the remainder as $[S_2]^{2-}$. The structure (Fig. 4) consists of

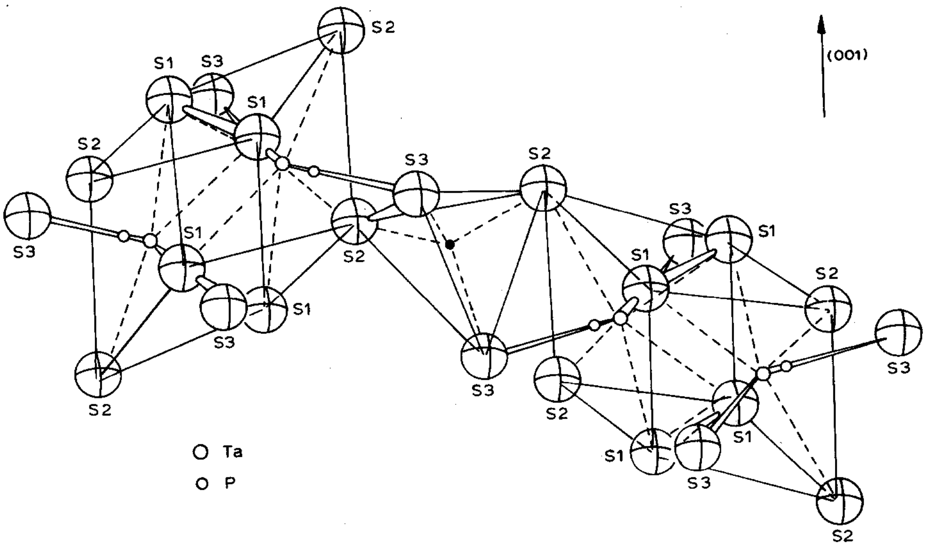

Fig. 4: The basic building blocks of $TaPS_6$: $\{Ta_2S_{12}\}$ units connected *via* $\{PS_4\}$ tetrahedra. Dashed lines indicate Ta-S bonds within the double prism of S atoms and P-S bonds within the tetrahedron. Bonds between Ta and S(3) (capping the prism faces) are drawn in perspective. $[S-S]^{2-}$ pairs formed by S(1) atoms are indicated by thick lines. Reproduced with permission from [37], S. Fiechter, W.F. Kuhs and R. Nitsche, *Acta Crystallogr. Sect. B*, 36 (1980) 2217.

$\{Ta_2S_{12}\}$ units linked by $\{PS_4\}$ tetrahedra, with the coordination sphere around each metal atom being that of a capped trigonal prism [37].

5.2 NIOBIUM(IV) AND TANTALUM(IV)

5.2.1 Halogen-containing species

Various aspects of the coordination chemistry of niobium(IV) and tantalum(IV) chlorides have been reported in the last year. A thermochemical study of tantalum(IV) bromide is discussed in section 5.3. Interestingly, some reduction of the niobium(V) and tantalum(V) chlorides was observed when they were allowed to react with crown ethers {di-benzo-18-crown-6(L^1), 18-crown-6(L^2) and 15-crown-5(L^3)}. Thus besides the niobium(V) and tantalum(V) compounds $2NbCl_5(L)$ ($L = L^1$, L^2 or L^3), $NbCl_5L$ ($L = L^1$ or L^2) $2TaCl_5(L^1)$ and $TaCl_5(L^3)$, the species $2NbCl_4(L^2)$, $3NbCl_4(L)_2$ ($L = L^2$ or L^3) and $TaCl_4(L^1)$ were isolated [38]. The EPR spectra of $[NbCl_4(PEt_3)_2]$ and $[TaCl_4(PEt_3)_2]$ have been examined over a temperature range. The frozen solution spectra (-130 °C in toluene) display parallel and perpendicular components indicative of an axially symmetric species being present (that is *trans*-$[MCl_4(PEt_3)_2]$), while the room temperature spectra show hyperfine splitting due to the interaction of the unpaired electron with the metal nuclei. From the measurements it was deduced that the unpaired electron is in the b_{2g} (d_{xy}) orbital [39]. The EPR spectrum of the tantalum(IV) ion in silver chloride crystals has been obtained; the reduction was induced by γ-irradiation of the tantalum(V) ion in silver chloride crystals at 77 K [40].

From single crystals of the sulphido-halides NbX_2S_2 (X = Cl, Br or I), high resolution infrared and visible absorption spectra were obtained over the temperature range 4.2 to 300 K. A detailed interpretation of the optical transitions was evaluated in terms of a molecular orbital diagram of the $Nb-(S_2)-Nb-(S_2)$ moiety [41]. Another compound containing a niobium-sulphur core is the tetrahydrothiophen adduct of $Nb_2Br_4S_3$. The compound $Nb_2Br_4S_3$(tht) contains two niobium atoms that are bridged by formal S^{2-} and $[S_2]^{2-}$ groups. The niobium-niobium distance of 2.837(7) Å is said to be indicative of a single metal-metal bond and the species is diamagnetic [42].

5.2.2 Compounds with sulphur-donor ligands

Single crystal electron paramagnetic resonance studies have been carried out on a range of vanadium(IV) and niobium(IV) dithiobenzoic and dithioethanoic acid complexes. To obtain magnetically dilute samples, the species under investigation were diluted with the diamagnetic molybdenum(IV) analogues. All the compounds are monomeric, eight-coordinate species with geometries between that

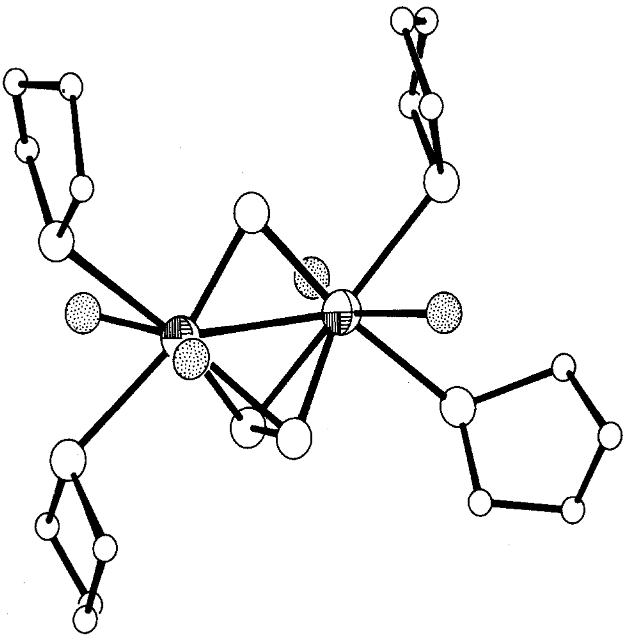

Fig. 5: The molecular structure of the tetra(tetrahydrothiophene) adduct of $Nb_2Br_4S(S_2)$, reporduced with permission from [42], M.G.B. Drew, I.B. Baba, D.A. Rice and D.M. Williams, *Inorg. Chim. Acta*, 44 (1980) L217.

of a triangular dodecahedron and a square antiprism. The molybdenum compound $[Mo(S_2CCH_3)_4]$ has two crystal forms, and the spectra of the analogous vanadium compounds in both forms have been obtained. From an examination of the spectra it was deduced that the ground state is of the type $a|x^2-y^2\rangle - b|z^2\rangle$ and the values of a and b have been obtained from the experimental results and related to the structures of the species under consideration [43]. From a related study the quadrupole coupling tensors of ^{51}V and ^{93}Nb in tetrakis(dithiobenzoato)molybdenum(IV) and tetrakis(diethyldithiocarbamato)titanium(IV) have been obtained [44].

The structure of the monoclinic form of TaS_3 (a tantalum(IV) species) has been investigated and shown to consist of three types of trigonal prism stacked along the *b* axis. The sulphur-sulphur distances between some of the sulphur atoms (2.105(4)-2.068(3) Å) indicate the presence of $[S_2]^{2-}$ groups, and a Peierls-type transition occurs at 210 K and is associated with Ta-Ta pairing [45]. The sulphides and selenides MY_2 (M = Nb or Ta; Y = S or Se) have been investigated in a number of contexts but primarily the work has concerned intercalation studies. Nuclear spin-lattice relaxation times for ^{93}Nb and ^{181}Ta at low temperatures in their 2-*H* polytype MS_2 sulphides have been determined.

Similar studies have been carried out on the intercalates formed by the sulphides with pyridine [46]. With the niobium compound $2(NbS_2)$(pyridine), evidence for a super-lattice was obtained from electron diffraction measurements [47]. A thermodynamic study has been made of the intercalation of sodium into TaS_2. The variation of the chemical potential of Na in Na_xTaS_2 as a function of x was investigated using chemical cells that incorporated propylene-carbonate and β-alumina as electrolytes [48]. The reaction of lithium with TaS_2 or VSe_2 has been compared with the similar reaction undergone by TiS_2 and it has been shown that only the Li/TiS_2 system is highly reversible [49].

5.2.3 Compounds with Group VB or Group IVB donor ligands

The UV photoelectron spectra of $[M(NMe_2)_5]$ (M = Nb or Ta) have been found to be very similar, thus indicating that the compounds are isostructural in the gas-phase which is unlike the situation in the solid state where $Nb(NMe_2)_5$ is approximately square-pyramidal while the tantalum analogue is trigonal bipyramidal [50].

The reaction of the tetrahydrofuran adduct of niobium(IV) chloride with Me_3CNC has been reported to yield $[\{NbCl_3\{C(Cl)NCMe_3\}(CNCMe_3)\}_2]$, which reacts with sodium dithiocarbonate (Na[dtc]) to give $[\{NbCl\{C(Cl)NCMe_3\}(dtc)_2\}_2]$ and with Li[8-quinoline] to yield $[\{NbCl\{C(Cl)NCMe_3\}(8\text{-quinolinyl})_2\}_2]$. These latter two compounds are diamagnetic and the authors postulate a Nb-Nb interaction [51]. The same authors also report that $VCl_3/NCCMe_3$ mixtures yield $[\{VCl_2\{C(Cl)NCMe_3\}(CNCMe_3)_2\}_2]$, a point which has been challenged (see Section 4.3.1) by Lippard and co-workers who, *via* crystallographic measurements, find the species found to be *mer*-$[VCl_3(NCCMe_3)_3]$ [52].

5.3 NIOBIUM(III), NIOBIUM(II), TANTALUM(III) AND TANTALUM(II)

The standard enthalpy of formation of tantalum(IV) bromide at 298 K has been determined by solution calorimetry as -525.5±2.1 kJ mol^{-1} and the standard enthalpies of formation of $TaBr_{3.16}$ (-480±13 kJ mol^{-1}) $TaBr_{2.83}$ (-431±17 kJ mol^{-1}), $TaBr_3$ (-456±17 kJ mol^{-1}) and $TaBr_{2.5}$ (-397±17 kJ mol^{-1}) were estimated [53].

The reflectivity of Nb_3I_8 has been measured and the spectrum has four peaks at 7500, 11800, 20000 and 28600 cm^{-1} [54]. The reaction of the same cluster halide, or Nb_6I_{11}, with niobium and caesium iodide in a sealed niobium tube at 910 °C yields $CsNb_6I_{11}$. The structure consists of face capped Nb_6I_8 octahedra, which are linked to other octahedra *via* bridging iodine atoms (see Figure 6). The Nb-Nb distances span the range 2.771(2) to 2.940(2) Å, the average (2.825 Å) being shorter than the distance observed in Nb_6I_{11}. Reaction of $CsNb_6I_{11}$ with dihydrogen at 400 °C yields $CsNb_6I_{11}H$ [55].

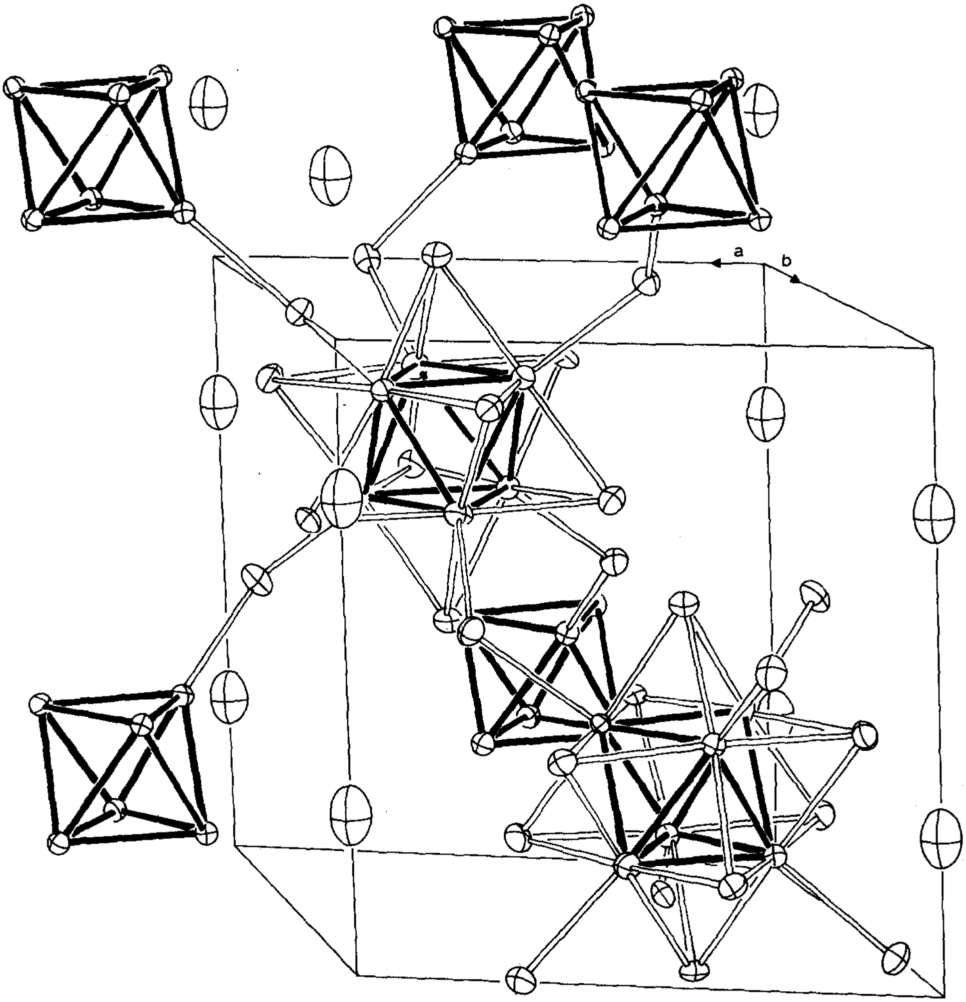

Fig. 6: The $[(Nb_6I_8)I_{6^2}]$ anion and the manner in which it is bridged to six other adjacent anions. Reproduced with permission from [55], H. Imoto and J.D. Corbett, *Inorg. Chem.*, 19 (1980) 1241.

There continues to be interesting developments in the chemistry of compounds that can formally be considered to be derived from niobium(III) and tantalum(III) halides. The initial impetus for the work was provided by Templeton and McCarley, who reported a study on $[Ta_2Cl_3(tht)_3]$ in which the two metal atoms are bridged by one tht molecule and two chlorine atoms [56]. Last year the reactions of this compound with PhC≡CPh and a range of cyanoalkanes were briefly reported [57], and this year full structural details of pyridinium tetrachloro(pyridine)(PhC≡CPh)-

tantalate have been given. In particular it was noted that the tantalum-carbon bond distances are shorter than expected for either the presence of a μ-PhC≡CPh molecule, or the formation of two single Ta-C bonds (C atoms of C≡C moiety). It is suggested that two Ta-C single bonds (C atoms of C≡C moiety) do exist but there is also some π-donation from the double bond which is formed by the tantalum atom adding across the alkyne [58]. A further alkyne, $Me_3CC≡CCMe_3$, has been allowed to react with $[Ta_2Cl_6(tht)_3]$ and following recrystallisation from tetrahydrofuran, $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}Me_3CC≡CCMe_3)(thf)_2]$ was obtained. Crystallographic studies have revealed a very short Ta-Ta distance 2.6177(1) Å which is said to be consistent with a tantalum-tantalum double bond. The structure is shown in Figure 7. The alkyne acts as a two π-electron donor to each metal atom and the whole molecule has C_2 symmetry, with the alkyne slightly asymmetrically bound to the metal atoms as shown by the Ta-C distances [r{Ta(1)-C(20)} = 2.214(11) Å; r{Ta(1)-C(20')} = 2.416(11) Å] [59]. A further binuclear tantalum(III) compound, $[Ta_2Cl_6(PMe_3)_4]$ has been obtained by the sodium amalgam reduction of tantalum(V) chloride in the presence of PMe_3. Interestingly, the two tantalum atoms are bridged only by two chlorine atoms,

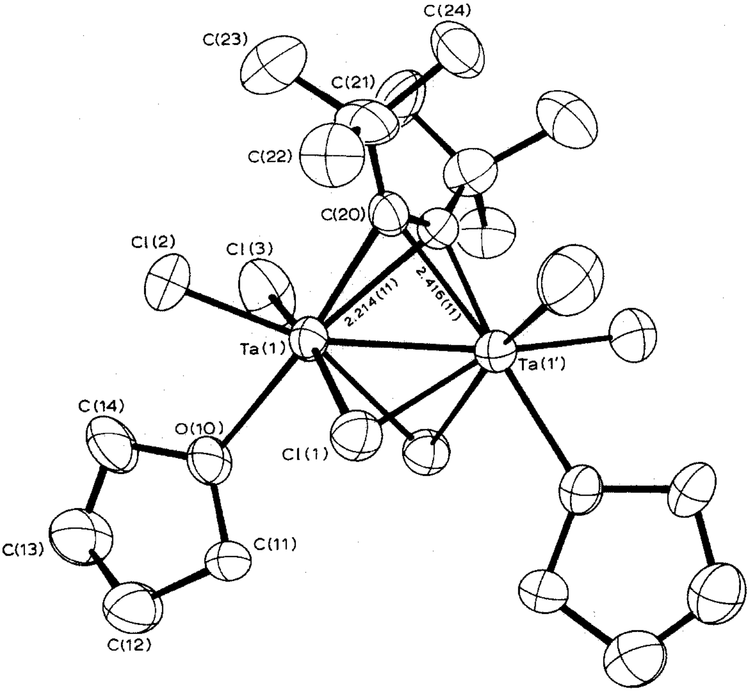

Fig. 7: The molecule $[Ta_2Cl_6Me_3CC≡CCMe_3)(thf)_2]$, reproduced with permission from [59], F.A. Cotton and W.T. Hall, *Inorg. Chem.*, 19 (1980) 2354.

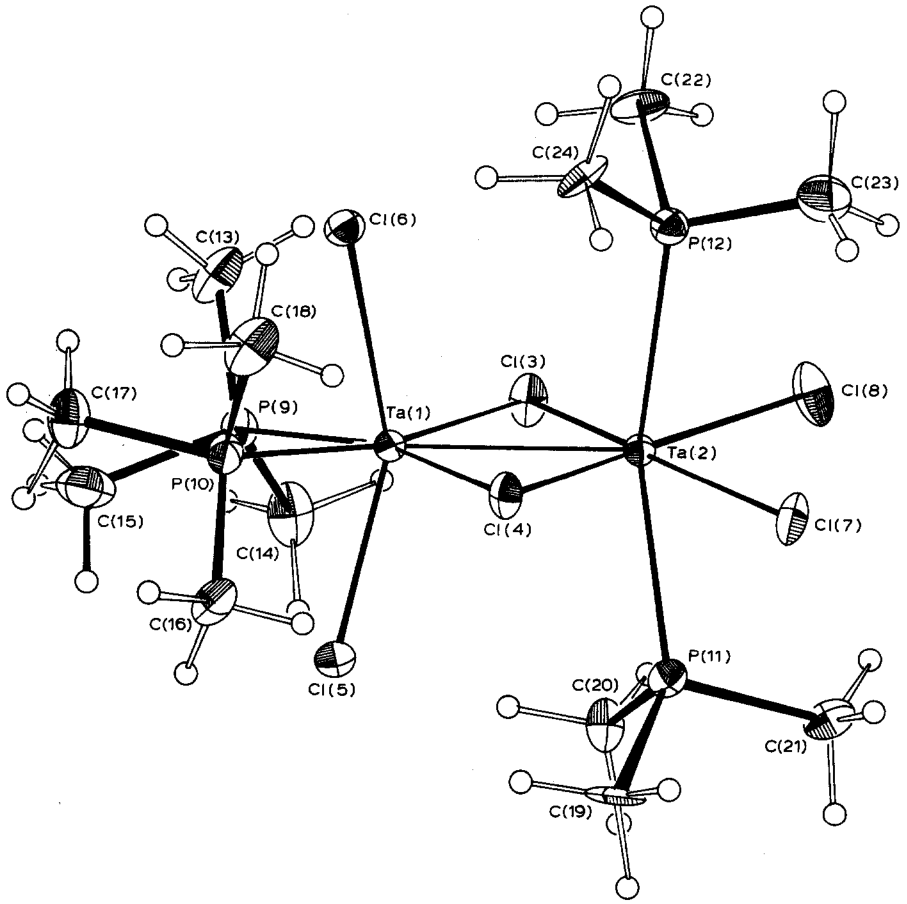

Fig. 8: The molecule $[Ta_2Cl_6(PMe_3)_4]$, reproduced with permission from [60], A.P. Sattelberger, R.B. Wilson (Jr.) and J.C. Huffman, *J. Am. Chem. Soc.*, 102 (1980) 7111.

unlike previous studies where besides the two halogen bridging atoms there is also a neutral ligand in the bridge. The Ta-Ta distance of 2.721(1) Å is noticeably longer than in $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}Me_3CC{\equiv}CCMe_3)(thf)_2]$ (see above). The arrangements of the ligand atoms is different for the two metal atoms (see Figures 8) being *cis* for one and *trans* for the other, and the ^{31}P NMR shows two singlets of equal intensity [60].

By reaction of $[Ta_2Cl_6(PMe_3)_4]$ with dihydrogen, a dimagnetic species $[Ta_2Cl_6H_2(PMe_3)_4]$ is obtained that ^1H NMR evidence suggest contains two bridging hydrogen atoms. The X-ray crystal study on this compound, while not revealing the hydrogen atoms, does show a very different mode of bonding for the bridging

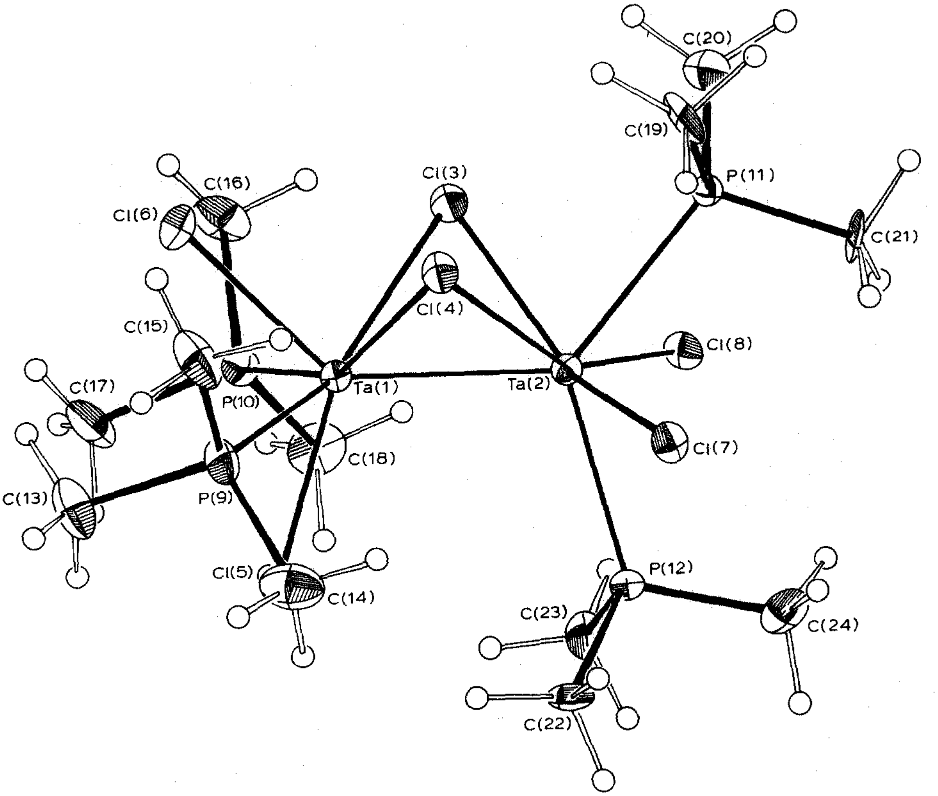

Fig. 9: The molecule $[Ta_2Cl_6(PMe_3)_4H_2]$, reproduced with permission from [60], A.P. Sattelberger, R.B. Wilson (Jr.) and J.C. Huffmann, *J. Am. Chem. Soc.*, 102 (1980) 7111.

chlorine atoms to that seen in $[Ta_2Cl_6(PMe_3)_4]$ (see Fig. 8). Reaction of $[Ta_2Cl_6(PMe_3)_4]$ with ethene was also studied, and shown to lead to the formation of $[TaCl_3(PMe_3)_2(C_2H_4)]$ [60]. Niobium(III) ether and thioether derivatives have been obtained by the reduction of niobium(V) chloride with magnesium turnings in the presence of the ligands, using CH_2Cl_2 as solvent. By this method $[Nb_2Cl_6(1,4\text{-dioxane})_2]$, $[Nb_2Cl_6(SMe_2)_3]$ and $[Nb_2Cl_2(OC_6H_4CHO)(thf)_2]$ were isolated. All the compounds are diamagnetic [61].

The tantalum(II) compound $[TaCl_2(\{Me_2PCH_2\}_2)_2]$ when treated with $K[PPh_2].2$ 1,4-dioxane gives a seven coordinate tantalum(III) hydride $[TaH(PPh_2)_2(\{Me_2PCH_2\}_2)_2]$. The structure consists of a pentagonal bipyramidal arrangement of ligands around the metal atom, with the PPh_2 groups on the axis and with the hydrogen atom and the four ligand phosphorus atoms making the pentagonal plane.

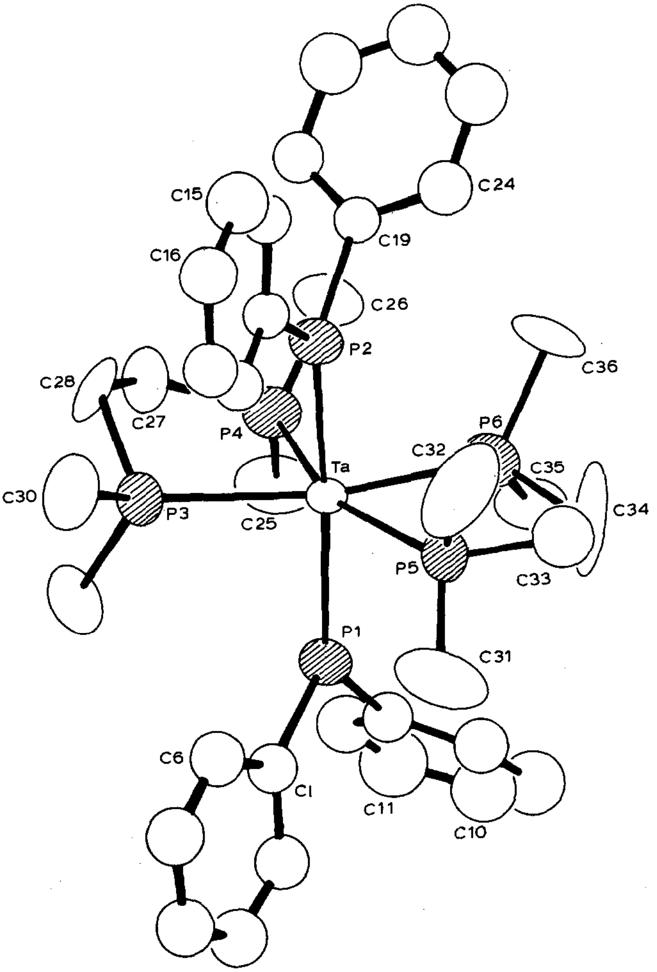

Fig. 10: Molecular structure of [$TaH(PPh_2)(\{Me_2PCH_2\}_2)_2$], reproduced with permission from [62], P.J. Domaille, B.M. Foxman, T.S. McNeese and S.S. Wreford, *J. Am. Chem. Soc.*, 102 (1980) 4114.

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