Coordination Chemistry Reviews, 37 (1981) 77—89
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

5. NIOBIUM AND TANTALUM

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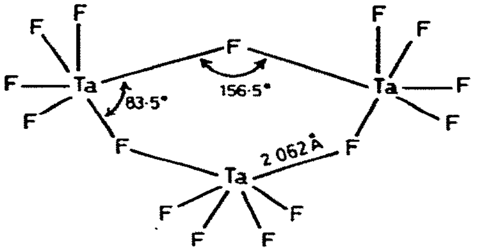
CONTENTS

5.1 NIOBIUM(V) AND TANTALUM(V)

5.1.1 Complexes with Group VII elements

A number of fundamental studies on the pentavalent halides of niobium and tantalum have appeared this year. A re-investigation of the enthalpy of formation of $TaF_5(g)$ (298 K) has been carried out and ΔH_f (298 K) is given as —1776.5 (±12.5) kJ mol^{-1}, a value some 54.4 kJ mol^{-1} lower than that previously reported [1]. From solution calorimetric measurements, ΔH_f^θ (298 K) for the formation of crystalline $TaBr_5$ was found to be —597.9 (±1.7) kJ mol^{-1}, and, by measuring heat capacities, values for the formation of the liquid [—552.3 (±1.7) kJ mol^{-1}] and gaseous species [—485.3 (±2.5) kJ mol^{-1}] were calculated [2].

Further structural evidence on the pentahalides has been obtained. The molecular structure of gaseous tantalum(V) fluoride has been determined by electron diffraction [3]. The data obtained at 45°C are consistent with the species existing as a trimer [$(TaF_5)_3$] having D_{3h} symmetry (1). The



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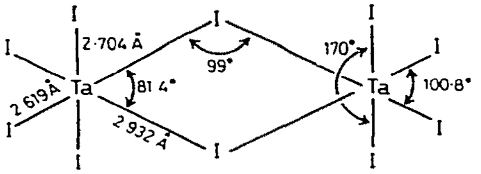
reported trimeric structure is in contrast to the tetrameric structure observed in the solid state. Similar electron diffraction studies at 170°C on tantalum(V) bromide provided evidence for a monomeric trigonal bipyramidal molecule having axial bonds (2.473(8) Å) longer than the equatorial ones by 0.61(10) Å [4]. The barrier to pseudorotation was estimated as 5.4 (±2.5) kJ mol^{-1}. X-ray diffraction patterns of tantalum(V) iodide show sharp and diffuse reflections. These are deduced as evidence for one-dimensional disorder. Structural details were obtained for tantalum(V) iodide which can be considered to consist of halogen bridged dimers $[(TaI_5)_2]$ (2) [5]. Raman spectroscopic measurements at 220°C on molten tantalum(V) chloride provided evidence for the presence of the chlorine bridged dimer $[(TaCl_5)_2]$ [6]. On raising the temperature to 350°C, the Raman spectrum changed and resembled that of gaseous tantalum(V) chloride, which exists as monomeric D_{3h} molecules.



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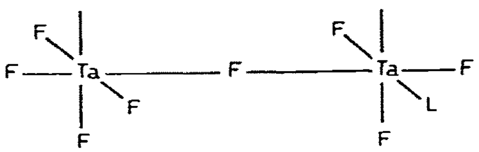
Similar Raman studies on mixed halide melts indicate that molten $KCl/TaCl_5$ contains $[TaCl_6]^-$, while the dimers $[(AlCl_3)_2]$ and $[(TaCl_5)_2]$ are present in melts formed from $AlCl_3/TaCl_5$ [6]. Reduction of niobium(V) chloride is reported to occur when $NbCl_5/TiCl_4/TiCl_3$ mixtures are heated. The nature of the niobium product varies with the temperature of the melt and the niobium(V) to titanium(III) ratio. Both niobium(IV) and niobium(III) compounds were claimed [7].

The major area of interest concerning the pentahalides is their adducts. The two fluorides $MgNbF_7$ and $CaNbF_7$ both exist in more than one crystallographic form. The face-centered cubic forms of both are isostructural with $Na[NbF_6]$ and the rhombohedral forms isostructural with $Li[NbF_6]$. Thus $MgNbF_7$ and $CaNbF_7$ contain $[NbF_6]^-$ moieties with interstitial fluoride ions [8]. Buslaev and co-workers have made extensive use of ^{19}F NMR spectroscopy in studying the adducts of niobium(V) and tantalum(V) fluorides. In solution, equimolar amounts of TaF_5 and $OPPh_2(SEt)$ (L) were shown to give rise to *cis* and *trans* $[TaF_4L_2]^+$ (ratio *cis* to *trans* 8 : 1), $[Ta_2F_{11}]^-$ as well as $[TaF_5(L)]$. On increasing the relative concentration of TaF_5, evidence for $[Ta_2F_{10}(L)]$ was obtained, in which the ligand is thought to be *cis* to the fluorine bridge (3) [9]. The ^{19}F NMR spectra of solutions containing TaF_5



(3)

and either R_3PS or R_3PSe consist of two signals with the intensity ratio 4 : 1; thus the presence of a simple $[TaF_5(L)]$ adduct is indicated [10]. The nature of the products in solution obtained by allowing TaF_5 and Et_2NH to react is dependent upon the molar ratio of the reactants. The reactions were shown to be complex, and simple adducts (such as $[TaF_5(HNEt_2)]$, ions (for example $[TaF_4(HNEt_2)_2]^+$), and a whole range of products derived from the elimination of HF and the formation of Ta—NR_2 fragments were observed [11]. Niobium NMR spectroscopic measurements (^{93}Nb) on NbX_5 (X = Cl or Br) dissolved in MeCN/HF solution have been utilised to study the halogen exchange reactions [12].

Ligand exchange reactions of the type given in eqn. (1) with niobium(V) and tantalum(V) chlorides or bromides and a range of ligands, have been studied at high pressure using Fourier Transform ^1H NMR spectroscopy. From these studies, the volume of activation has been shown to be negative when the ligand (L) is Me_2S, Me_2Se or Me_2Te. Thus the exchange is deduced to be associative. In contrast, when the ligand is Me_2O, MeCN, Me_3CCN, $(MeO)Cl_2PO$ or $(Me_2N)_3PS$, the reaction is thought to be dissociative as the volume of activation is positive [13]. Similar exchange reactions between $[TaX_5(Et_2O)]$

$$[MX_5(L)] + L' \rightleftharpoons [MX_5(L')] + L \qquad (1)$$

M = Nb or Ta
X = Cl or Br
L = L′

(X = Cl or Br) and azomethines (for example *N*-salicylidene aniline) gave either 1 : 1 or 1 : 2 nitrogen bonded complexes. The stoicheiometry of the product appears to be dependent upon the bulk of the ligand [14].

Research into solvent extraction of niobium(V) and tantalum(V) continues, presumably in the hope of more efficiently separating the two elements from their naturally occurring mixtures. The kinetics of the extraction of $NbCl_5$ from an aqueous HCl solution into a benzene solution containing bis(3,5,5-trimethylhexyl)ammonium chloride have been investigated with special attention being given to the concentration of the reacting species at the interface [15,16].

Oxohalospecies of niobium(V) and tantalum(V) have been studied in a number of contexts. Two oxofluorides whose structures have been reported are $K_2Ta_4F_4O_9$ [17] and $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$ [18]. The former contains $[Ta_{12}X_{54}]$ (X = O or F) units similar to those found in some hexagonal tungsten bronzes; the potassium atoms are situated in the tunnels formed by linking of the $[Ta_{12}X_{54}]$ units. In contrast, the latter can be rationalised as consisting of two interpenetrating sublattices, namely $(Ta_5X_{17})_{3n}$ and $(Ta_{0.5}X_3)_n$, that give rise to a three dimensional structure; the $(Ta_5X_{17})_{3n}$ sublattice consists entirely of $\{TaX_6\}$ octahedra, while the other sublattice $(Ta_{0.5}X_3)_n$ is an infinite chain of trigonal prisms. A similar $(Ta_{0.5}X_3)_n$ chain was detected in $K_6Ta_{6.5}F_{9.5}O_{14.5}$, as was a three dimensional skeleton of octa-

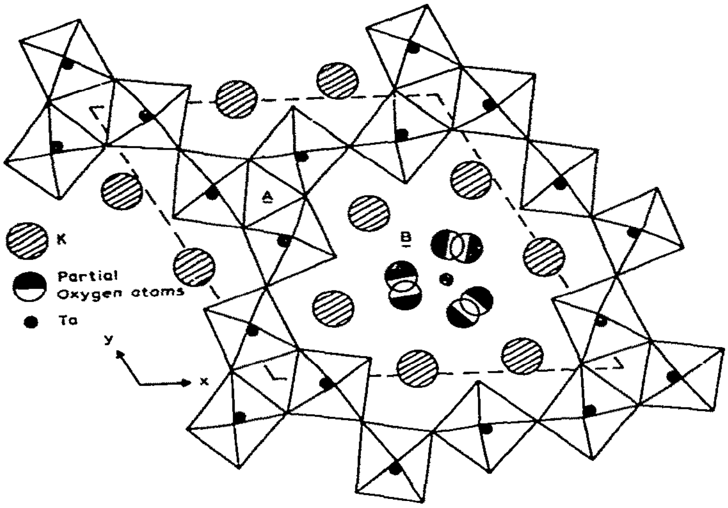
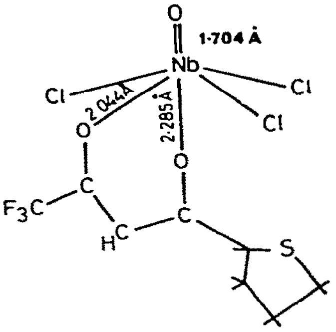


Fig. 1. The structure of $K_6Ta_{6.5}F_{9.5}O_{14.5}$ [19].

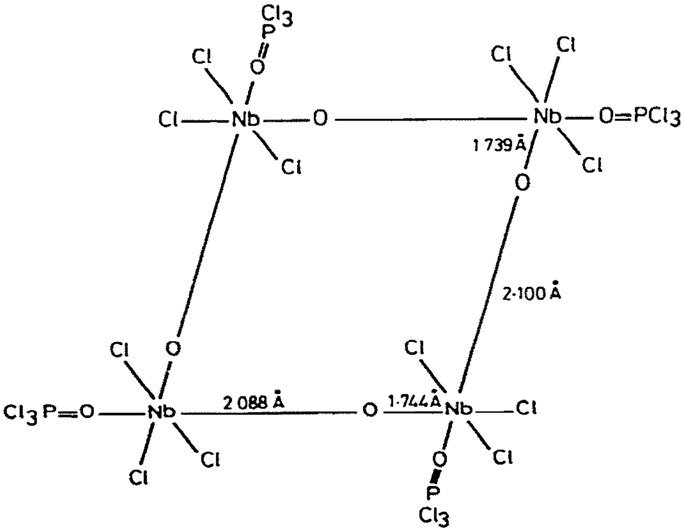
hedra formed of $[Ta_6X_{21}]_n$ (Fig. 1). In these oxofluorides, it is difficult to distinguish by X-ray crystallography between the fluorine and oxygen atoms. Thus, although the structure of $K_2Ta_4F_9O_4$ has been determined by X-ray crystallography, the use of ^{19}F NMR spectroscopy was needed to pinpoint the actual positions of the fluorine atoms, which were at the corners of the octahedra forming an infinite chain along the *c* axis [20]. The non-stoicheiometric phase $Tl_xNbO_{2+x}F_{1-x}$ $(0.5 \leqslant x \leqslant 1)$ has a cubic pyrochlore structure; the conductivity was shown to increase with *x* and the properties of the motion of the Tl^+ ions were related to the high polarisability of the Tl^+ ion and the presence of a large number of suitable cation sites within the $NbO_{2+x}F_{1-x}$ network [21].

The oxohalide $NbCl_3O$ has been the subject of a number of recent studies. From β-diketone/$NbCl_3O$ mixtures, anions of the type $[(\beta\text{-diketone})NbCl_3O]^-$ have been isolated. The ^1H NMR spectra of the anion formed with $CH_3COCH_2COCH_3$ indicates that at 17°C there is only one methyl resonance, while at −40°C there are two [22]. This fluxional behaviour is, however, lost when the multiply bonded Nb=O group is replaced by the peroxo-species Nb—(O—O). Structural work on tetraethylammonium trichlorooxo(1,1,1-trifluoro-4-thenoylbutane-2,4-dionato)niobate(V) has shown that the oxygen atom of the CF_3CO fragment is in the same plane as the three chlorine atoms while the oxygen atom adjacent to the 4-thenoyl group is *trans* to the niobium—oxygen multiple bond (4) [23]. Oxohalo-species have been isolated by the reaction of niobium(V) and tantalum(V) chlorides with Cl_2O in PCl_3O solutions; with tantalum only one compound was isolated, $[TaCl_2O(O_2PCl_2)]$, whilst with niobium $[NbCl_3O(OPCl_3)]$, $[NbCl_2O(O_2PCl_2)(OPCl_3)]$, and [NbClO-



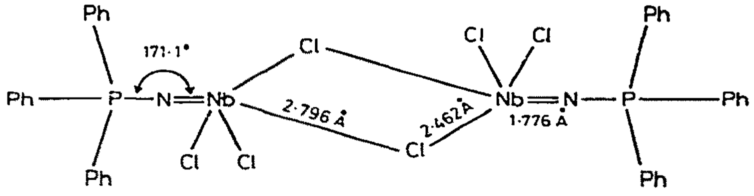
(4)

$(O_2PCl_2)_2]$ were isolated. The structure of $[NbCl_3O(OPCl_3)]$ has been determined; the species exists as a tetramer with bridging oxygen atoms linking the four niobium atoms that form an approximate square [Nb—$\hat{O}$—Nb = 178.0(3)°, 172.1(4)°; O—$\widehat{Nb}$—O = 94.7(2)°, 92.9(2)°]. Besides bonding to the two bridging oxygen atoms, the metal is also bound to three chlorine atoms [r(Nb—Cl) = 2.295(3) to 2.338(3) Å] and an oxygen atom of a PCl_3O molecule [r(Nb—O) = 2.204(6), 2.240(6) Å]. The bridging oxygen atoms form an unsymmetrical bridge, suggesting the existence of a Nb=O → Nb system [$r(NbO)_{short}$ = 1.739(5), 1.744(6) Å; $r(NbO)_{long}$ = 2.088(6), 2.100(6) Å] (5) [24].



(5)

Another compound containing a niobium to main group element multiple bond is $[NbCl_4—N—PPh_3]$, which was obtained by the reaction of $NbCl_4N_3$ with Ph_3P. Structural studies have shown that the molecule is dimeric, with the two niobium atoms being linked via bridging chlorine atoms. The P—N—Nb angle is 171.1(6)° and the Nb—N distance is 1.776(8) Å, suggesting the existence in a formal sense of a $Nb\overset{\rightarrow}{=}N$ grouping (6) [25].



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5.1.2 Complexes with Group VI donor ligands

The majority of compounds discussed in this section concern species in which the niobium or tantalum atoms are, in a formal sense, contained in oxo-anions. Nevertheless, there continues to be an interest in the binary compounds formed by niobium and tantalum with group VI elements, especially the sulphides. However, even the highest oxidation sulphide NbS_3 contains niobium(IV), and the use of such chalcogenides in intercalation studies will be discussed in a later section.

The metatantalates MTa_2O_6 (M = divalent metal ion) have been studied in a number of contexts. A new metastable orthorhombic form of $ZnTa_2O_6$ was obtained by the reaction at 500°C of $LiTaO_6$ and $K_2Zn(SO_4)_2$ [26], while normal coordinate analysis of $CaTa_2O_6$, $BaTa_2O_6$, and the structurally related niobate $SrNb_2O_6$ has been carried out and accurate assignments made for the observed IR and Raman spectra [27]. The trirutile structure has been found for MTa_2O_6 (M = Mg, Ni or Co) and their vibrational spectra were also examined [28].

Crystals of the rare earth compounds $GdTaO_4$, $DyTaO_4$ and $ErTaO_4$ were obtained by allowing M_2O_3 (M = Gd, Dy or Er) and Ta_2O_5 to react in a PbF_2/PbO (8 : 2) flux. The lattice parameters of the prepared compounds, as well as those of Gd_3TaO_7, Y_3TaO_7 and Er_3TaO_7, were determined [29].

The compound $K_{4+5x}Ta_{16-x}O_{42}$, which is formed from K_2O/Ta_2O_5 mixtures, has been subjected to X-ray crystallographic investigation. The structure consists of units of six octahedra which are linked by edge and corner sharing in a complex manner. Three of these units are linked through one octahedron, thereby giving rise to sheets. There are two tantalum sites, one type {Ta(1)} is found in the six octahedra that make up a unit, while the other {Ta(2)} is in the octahedra that link three six-octahedral units together (Fig. 2) [30].

The vibrational spectroscopic investigations of hexagonal perovskites with cationic vacancies continues with studies concerning $Ba_5Ta_4\square O_{15}$ being reported. The $M_2\square O_{12}$ and $M_3\square_2O_{18}$ units of face-sharing octahedra can be identified by means of the symmetrical (O—O) stretching frequencies that are in the 300 cm^{-1} region [31].

The structure of the tantalum tungstate Ta_2WO_8 has been re-investigated by neutron diffraction and, contrary to previous reports based upon X-ray measurements, Ta_2WO_8 is said to have the same space group as Nb_2WO_8. One

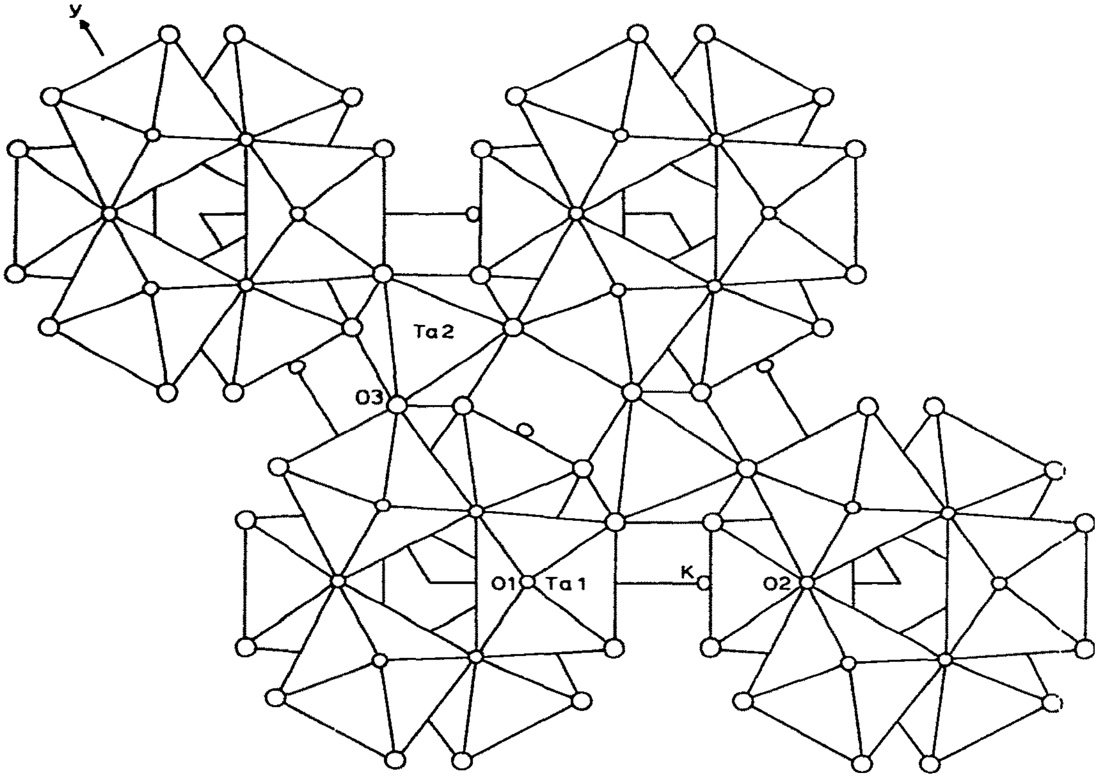
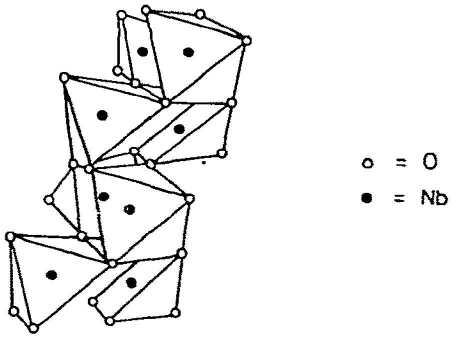


Fig. 2. The structure of $K_{4+5x}Ta_{16-x}O_{42}$ [30].

sixth of the metal atoms are seven coordinate (pentagonal bipyramidal), the remainder being octahedrally coordinated. No attempt was made to determine the Ta/W occupancy ratio at either type of site [32]. A new Gatehouse-tungsten bronze-like thallium niobiate, $TlNb_7O_{18}$, has been obtained from the reaction of $Tl_2[CO_3]$ and Nb_2O_5 in a B_2O_3 flux. The structure is interesting, giving rise to polygons with 3, 4, 5, 6 and 7 sides, formed by the linking of $\{NbO_6\}$ octahedra (Fig. 3). The thallium ions are distributed between the hexagons and heptagons [33]. The reaction between equimolar amounts of $Li_2[CO_3]$ and Nb_2O_5, which ultimately at 900°C leads to the formation of $LiNbO_3$, has been studied. The reaction proceeded in the temperature range 300—700°C with the evolution of CO_2. In the region 600—800°C, $LiNb_3O_8$ and Li_3NbO_4 were detected but above 850°C, $LiNbO_3$ was the only product [34]. The related rubidium compound $RbNbO_3$ contains niobium atoms which are surrounded by five oxygen atoms that form a tetragonal pyramid. The pyramids occur in pairs with the triangular faces facing each other (7) [35].



(7)

The reaction of the peroxo anions $[M(O_2)_4]^{3-}$ [M = Nb or Ta] with H_4edta has led to the isolation of $[NH_4]_3[M(O_2)_3(edta)] \cdot n\ H_2O$ through the displacement of $[O_2]^{2-}$ ions [36].

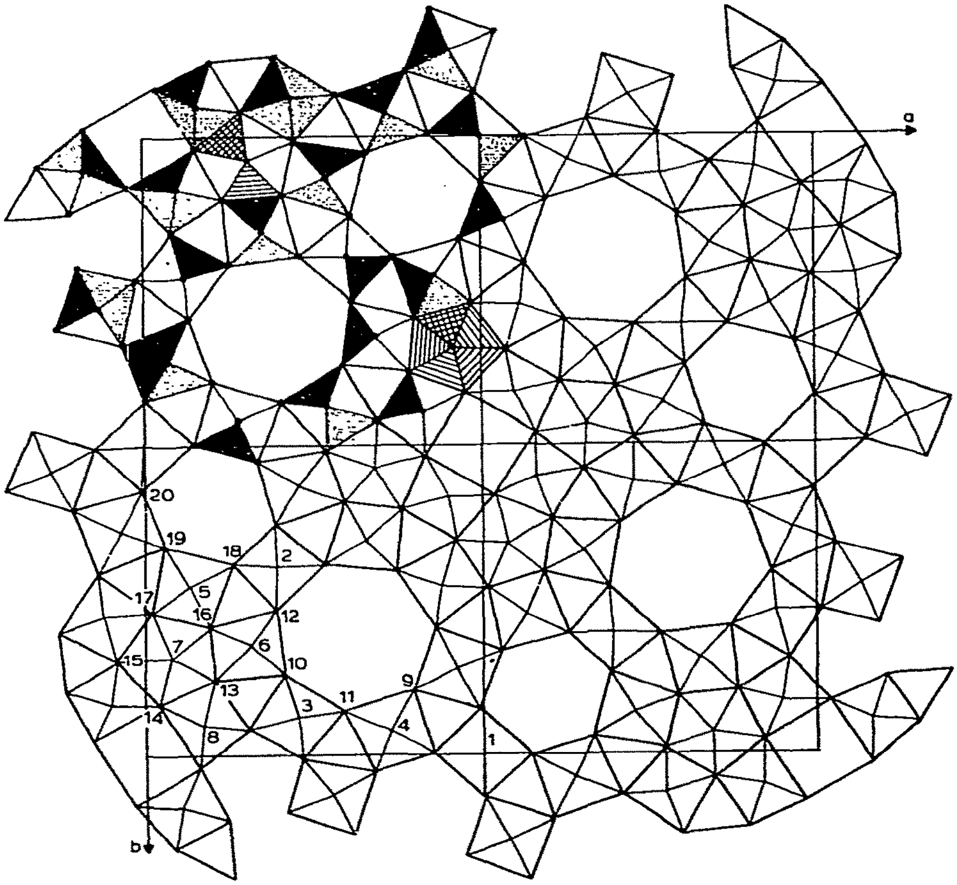
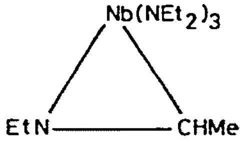


Fig. 3. The structure of $TlNb_7O_{18}$ [33].

5.1.3 Complexes with Group V donor ligands

The enthalpies of formation of a whole range of homoleptic dimethylamido-compounds of Group VA and VIA metals have been determined by solution, combustion and other calorimetric methods. The enthalpy of formation of $[Ta(NMe_2)_5]$ is —326.2 ± 11 kJ mol^{-1} for the solid and —237.2 ± 15 kJ mol^{-1} in the gas phase. The average Ta—N bond enthalpy was evaluated as 328 ± 5 kJ mol^{-1} [37]. Evidence for hydrogen abstraction from the CH_2 group has been provided by the reaction of $Li[NEt_2]$ with $NbCl_5$ or WCl_6. Mixed products were obtained from the reaction, but evidence was established for the formation of a complex containing the EtNCHMe ligand (8) [38].



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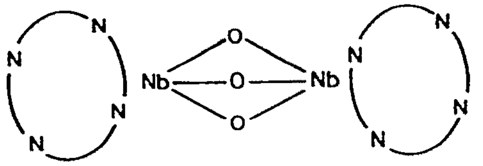
The reactions of niobium(V) chloride with porphyrins have been further studied. By taking the product obtained by allowing $NbCl_5$ to react with 5, 10, 15, 20-tetraphenylporphyrin ($TPPH_2$) and treating the product with water, $[\{Nb(TPP)\}_2O_3]$ (9) was obtained. On recrystallisation of $[\{Nb(TPP)\}_2O_3]$ from ethanoic acid, $[\{Nb(TPP)\}(O)(O_2CMe)] \cdot CH_3COOH$ (10) was isolated. The crystal structures of both species have been determined. In the former, (9), a triple oxygen atom bridge links the two niobium atoms, while in the latter, (10), there is a chelating $[MeCO_2]^-$ ion on one side of the TPP ring, and on the other side there is a terminally bonded oxygen atom [39].



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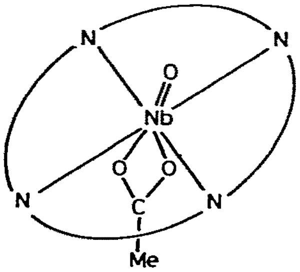


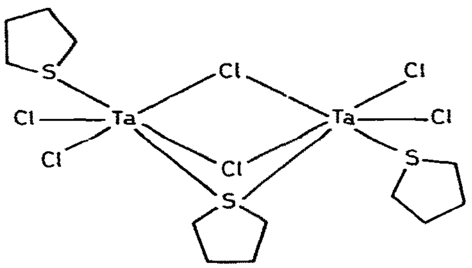
(10)

5.2 COMPOUNDS CONTAINING NIOBIUM AND TANTALUM IN AN OXIDATION STATE $\leqslant$ IV

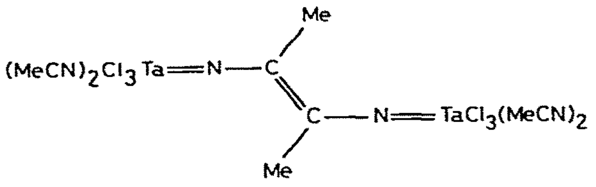
The.majority of the material concerning the oxidation states (IV) to (0) of niobium and tantalum involve organometallic compounds and are thus outside the scope of the present review.

The vibrational and EPR spectra of the $[Nb(CN)_8]^{4-}$ anion are consistent with the anion being an Archimedean antiprism in solution and dodecahedral in the solid state. An X-ray crystallographic investigation has confirmed that the anion is dodecahedral, with a mean Nb—C distance of 2.255 Å which is significantly longer than that observed in $[Mo(CN)_8]^{4-}$ [40].

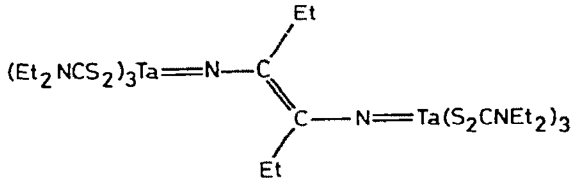
A convenient source of tantalum(III) is reported to be $[Ta_2Cl_6(SC_4H_8)_3]$ (**11**), which has the structure as shown. With ethanenitrile, a tantalum(V)—nitrene species is formed via reductive coupling of ethanenitrile (**12**); these nitrenes react further with diethyldithiocarbamates to give complexes such as (**13**). (**11**) catalyses the polymerisation of 3-hexyne to give hexaethylbenzene, while with PhC≡CPh an adduct is formed that has been isolated as $[pyH][TaCl_4(py)(PhC{\equiv}CPh)]$ (**14**); the Ta—C distances [2.066(8) Å] are only slightly longer than known Ta=C double bonds [41].



(**11**)

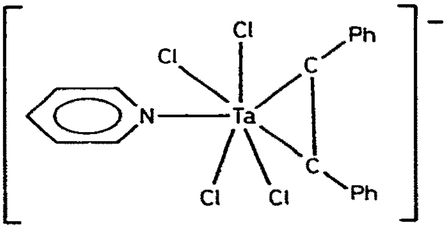


(**12**)



(**13**)

Complexes formed by the niobium and tantalum clusters of the form $[M_6Cl_{12}]^{n+}$ have been examined by X-ray photoelectron spectroscopy. Three types of compound were studied; $[\{M_6Cl_{12}\}Br_6]^{2-}$, $[\{M_6Cl_{12}\}Cl_2 \cdot 4\ L]$ and



(14)

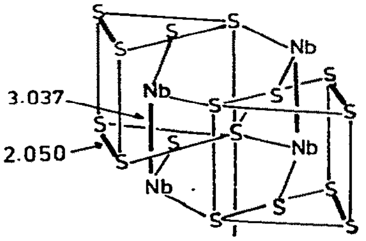
$[\{M_6Cl_{12}\}Cl_6]^{2-}$. The Cl 2*p* spectra obtained for these compounds were subject to deconvolution techniques and this enabled, where appropriate, the Cl (bridging) to Cl (terminal) ratio to be determined. The ratios obtained from spectra coincided with those known from the structure. The binding energies of Cl 2*p* were shown to be Cl (bridging) > Cl (terminal), the difference being between 1.4 and 2.1 eV [42].

The dimer $Nb_2(g)$ has been detected by mass spectrometry using a modified Knudson cell. From these observations, the heat of formation at 298 K of $Nb_2(g)$ was evaluated as 916 ± 12 kJ mol^{-1} and the bond dissociation enthalpy as 511 ± 10 kJ mol^{-1} [43].

5.3 SULPHIDES AND SELENIDES

Recently there has been an upsurge of interest in the sulphides and selenides of niobium and tantalum. Much of this interest has been stimulated by the proposed use of disulphides as cathodes in batteries.

The crystal structure of NbS_3 has been determined. It contains $[S_2]^{2-}$ groups and niobium—niobium bonds (3.04 Å), and thus NbS_3 is best formulated as $\{Nb^{4+}(S_2)^{2-}(S^{2-})\}$. The compound exists as a trigonal prismatic chain with the sulphur atoms forming an approximate isosceles triangle with one short (2.05 Å) and two long (3.32—3.78 Å) sulphur—sulphur distances (15)



(15)

[44]. A new form of tantalum trisulphide with a monoclinic unit cell has also been reported [45].

Many studies of the disulphides have appeared this year. Full details of the preparation of the 2*H* form of TaS_2 have been given, as have details for the preparation of the intercalated species which TaS_2 forms with pyridine, tin and ammonia [46]. The kinetics of lithium intercalation into TaS_2 have been studied by tantalum hyperfine spectroscopy [47]. The efficiency of transition metal chalcogenides as battery materials has, in a wide ranging paper, been shown to be dependent on structure, morphology, electrical conductivity, and stoicheiometry of the chalcogenide [48]. Three recent studies on $TaS_2 \cdot 0.5$ (pyridine) have appeared. It has been shown that the pyridine molecules enter between the adjacent sulphur atom layers, and the molecules lie with the rings perpendicular to the TaS_2 layers, with the long C—N axis parallel to these layers [49]. The intercalation of C_5D_5N into $2H$-TaS_2 has been monitored by neutron diffraction and evidence for two different pyridine fractions with different mobilities was found. From the data, it was not possible to ascertain if two differently bound pyridine fractions were present [50]. The superconducting properties of $TaS_2 \cdot 0.5$ (py) has been investigated [51]. The superconducting transition temperature (T_c) for $M_{0.33}TaS_2$ and $M_{0.5}NbS_2$ varies as M is changed along the series Li, Na, K, Rb and Cs; the variation in T_c does not follow any recognisable group trend for $M_{0.33}TaS_2$ while, with $M_{0.5}NbS_2$, T_c rises on descending Group IA [52].

Cathodic reductions of Nb_3S_4 and Nb_3Se_4 in electrolytes containing small ions (M^{n+}) has led to the formation of ternary species of the type $(M^{n+})_{x/n}$-$(Nb_3X_4)^{x-}$. Unlike intercalation into the layered compounds NbS_2 and TaS_2, where the ions enter into the space between layers of adjacent sulphur atoms, in the reduction of Nb_3X_4 the ions go into the empty channels that exist in the rigid three dimensional chalcogenide structure [53].

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