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PROGRESS IN NIOBIUM AND TANTALUM COORDINATION CHEMISTRY

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CONTENTS

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1. INTRODUCTION

The material covered by this review was mainly found in Chemical Abstracts, Volumes 102-107, i. e. the years 1985, 1986 and 1987. Thus, the majority of the papers mentioned has been published in previous years, i.e. approximately between 1984 and mid-1987. A few newer references are included. The review can be considered as a continuation of previous reviews in this series [1-3] and of other reviews on niobium, tantalum and in some cases vanadium coordination chemistry [4-9].

The papers are referred in the following sections mainly according to the formal oxidation state of the metal, ranging from (V) to below (0). In some cases it is not trivial to divide after the oxidation state. Within a section, the material is further sub-divided according to the kind of ligands bound to the metal. The basic order of sections is such: halogens, halogens mixed with non-halogens, no halogens.

Short modern reviews on basic niobium and tantalum chemistry can be found in many textbooks on inorganic chemistry, *e.g.* [7, 10-11]. Niobium and tantalum compounds are of importance in several areas of scientific interest, but some of these areas are of less importance from the point of view of a coordination chemist. Hence, papers dealing with subjects such as the structural chemistry of hydrides of Nb and Ta metals, *or* the catalytic activity of *e.g.* Nb_2O_5 or NbO_2 supported catalysts [12], are not referenced. Likewise, papers dealing with *e.g.* sputtering for the preparation of thin-film optical devices, *or* the characterization of nonlinear optical crystals of doped compounds (typically $LiNbO_3$ and $KTaO_3$), *or* the preparation of ceramics (*e.g.* NbC-NbO-NbN sintered phases), alloys, superconductors or magnetic materials, and the properties of such materials, are generally not referenced. The new research-field on charge density waves in *e.g.* niobium and tantalum sulphides is covered by referring to some of the most important new papers. Extraction chemistry on niobium and tantalum is shortly included (the extraction of niobium from ore or scrap to ferroniobium, niobium complexes and finally high-purity niobium metal has recently been reviewed [13-15].

Traditionally, coordination chemistry has been concerned with molecular species, but in recent years it has become increasingly linked with solid state chemistry. Structural results are now often described in terms of polyhedra, see Table 1, instead of sometimes rather mysterious close-packed arrays, as discussed in a recent account on the relation between coordination chemistry and the solid state [16]. Thus, the dramatic increase in the reseach for new materials with interesting properties is reflected in the large number of solid state structural results referred in this review.

Table 1. Oxidation states and common stereochemistry of Niobium and Tantalum compounds [7], [10-11].*

Oxidation state	Electronic state	Coordination number	Polyhedron	Examples
M(V)	d^0	4	Tetrahedron	$[\mathrm{NbO_4}]^{3-}$, $[\mathrm{NbO}\{\mathrm{N(SiMe_3)_2}\}_3]$
		5	Trigonal bipyramid	$[\mathrm{MCl_5}]$(vapour), $[\mathrm{TaMe_5}]$,
			Distorted square pyramid	$[\mathrm{M}\{\mathrm{NMe_2}\}_5]$, $[\mathrm{NbOCl_4}]^-$, $[\mathrm{NbSCl_3(Ph_3PS)}]$
		6	Octahedron	$[\mathrm{TaF_6}]^-$, $[\mathrm{Nb_2Cl_{10}}]$, $[\mathrm{TaOCl_3}]$, $[\mathrm{NbAlCl_8}]$, $[\mathrm{Nb(SO_4)_6}]^{7-}$, $[\mathrm{NbCl_5{\cdot}OPCl_3}]$, $[\mathrm{Nb(OMe)_5}]_2$, $[\mathrm{MCl_3(OR)_2}]_2$, $[\mathrm{TaCl_5{\cdot}S(CH_3)_2}]$, $\mathrm{NaNbO_3}$ (perovskite)
			Trigonal prism	$[\mathrm{Nb(S_2C_6H_4)_3}]^-$
		7	Distorted pentagonal bipyramid	$[\mathrm{NbOF_6}]^{3-}$, $[\mathrm{Nb(O_2)F_5}]^{2-}$, $[\mathrm{NbO(C_2O_4)3}]^{3-}$, $[\mathrm{NbO(S_2CNEt_2)_3}]$, $[\mathrm{Ta{=}S(S_2CNEt_2)_3}]$, $[\mathrm{Ta(NMe_2)(S_2CNMe_2)_3}]$, $[\mathrm{Ta(Me)_3(S_2CNR_2)_2}]$
			Capped trigonal prism	$[\mathrm{TaF_7}]^{2-}$
		8	Bicapped trigonal prism or square antiprism	$[\mathrm{TaF_8}]^{3-}$, $[\mathrm{Ta(PS_4)S_2}]$
			Dodecahedron	$[\mathrm{M(O_2)_4}]^{3-}$, $[\mathrm{Ta(S_2CNMe_2)_4}]^+$, $[\mathrm{Nb(O_2)_2(C_2O_4)_2}]^{3-}$
		9	?	$[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{TaH_3}]$, $[\{\mathrm{NbCl_2}(\eta^5\text{-}\mathrm{C_5H_5})_2\}_2\mathrm{O}]$
		10	?	$[\mathrm{NbCl_5(O_2CCOOH)_5}]$
M(IV)	d^1	4	D_{2d} Tetrahedron	$[\mathrm{Nb(NEt_2)_4}]$
		5	Trigonal bipyramid	$[\mathrm{NbH_2(OSiBu^t{}_3)_2}]_2$
		6	Octahedron	$[\mathrm{NbCl_6}]^{2-}$, $[\mathrm{TaCl_4(py)_2}]$
		7	Distorted pentagonal bipyramid	$[\mathrm{NbF_7}]^{3-}$
			Capped octahedron	$[\mathrm{NbCl_4(PMe_3)_3}]$
		8	Dodecahedron	$[\mathrm{Nb(CN)_8}]^{4-}$
			Square antiprism	$[\mathrm{Nb_2Cl_8(PMe_3)_4}]$
		high	?	$[(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{NbMe_2}]$
M(III)	d^2	6	Octahedron	$[\mathrm{Nb_2Cl_9}]^{3-}$, $[\mathrm{NbCl_3(py)_3}]$, $[\mathrm{Ta_2Cl_4(\mu\text{-}Cl_2)(SMe_2)_4}]$
			Trigonal Prism	$\mathrm{LiNbO_2}$
		7	Complex	$[\mathrm{TaCl_3(CO)(PMe_2Ph)_3}]$, $[\mathrm{TaH(PPh_3)_2(dmpe)_2}]$
		8	Dodecahedron	$[\mathrm{Nb(CN)_8}]^{5-}$
M(II)	d^3	4	Square	NbO
		6	Octahedron	$[\mathrm{NbCl_2(PMe_3)_4}]$
			Trigonal prism	NbS
		8	Dodecahedron	$[\mathrm{TaH_2Cl_2(PMe_3)_4}]$
			Square antiprism	$[\mathrm{TaH_2Cl_2(dmpe)_2}]$
M(I)	d^4	5	Pentagonal bipyramid	$[\mathrm{TaL_2R(C_2H_4)_2}]$
		6	?	$[\mathrm{Nb}(\eta^4\text{-}\mathrm{C_4H_6})_2(\eta^3\text{-Meallyl})]$
		7	Capped octahedron	$[\mathrm{TaH(CO)_2(dmpe)_2}]$, $[\mathrm{Ta(CO)_3(PMe_3)_4}]^+$
			Capped trigonal prism	$[\mathrm{TaX(CO)_2(dmpe)_2}]$, $[\mathrm{NbCl(CO)_3(PMe_3)_3}]$
			'4-legged pianostool'	$[\mathrm{Nb(CO)_4(C_5H_5)}]$
M(0)	d^5	6	Octahedron	$[\mathrm{Nb(dmpe)_3}]$
M(-I)	d^6	6	Octahedron	$[\mathrm{Nb(CO)_6}]^-$
M(-III)	d^8	5	Trigonal bipyramid	$[\mathrm{Ta(CO)_5}]^{3-}$
		6	?	$[\mathrm{M(CO)_3(C_5H_5)}]^{2-}$

* For meaning of ligand names, see list of abbreviations.

2. Nb(V) and Ta(V) compounds (d^0)

2.1 Nb(V) and Ta(V) complexes containing only halides

The NbF_5 and TaF_5 *mono*meric molecules have been studied in the gas phase by means of electron diffraction [17]. A D_{3h} symmetry is preferable to describe the structure of the molecules. In the solid state MF_5 (M = Nb, Ta) exists as tetrameric molecules, M_4F_{20} [18, 19]. Solid Ta_4F_{20} was studied by ^{181}Ta NQR spectroscopy at low temperature, and evidence was found for the presence of hexadecapole interactions obtained (I = 7/2 for ^{181}Ta). The Ta_4F_{20} entity is rhombohedrally distorted [19].

Thermodynamic data for gaseous tantalum fluorides, TaF_5, Ta_2F_{10}, and Ta_4F_{20} were reviewed and data were given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20]. The molecular constants and thermodynamical characteristics of the NbF_6^- and TaF_6^- ions were determined in vapours over the oxyfluorides between 730 and 960 K [21]. The electronic structure of the TaF_6^- anion was calculated by the discrete-variation $X\alpha$ method in an expanded basis of numerical Hartree-Fock functions [22]. Graphite can accomodate trigonal-*bi*pyramidal NbF_5 molecules and octahedral NbF_6^- ions, forming intercalation compounds [23].

Thermodynamic data for gaseous tantalum halides, $TaCl_5$, $TaBr_5$ and TaI_5 were reviewed and data were given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20]. Enthalpy contents and molar heat capacities of $NbCl_5$ and $TaCl_5$ were measured as function of temperatures [24]. The stability of $NbCl_5$ gas in contact with metallic niobium was studied by DTA and TG methods in order to find the optimum conditions for the synthesis of lower chlorides [25]. The reduction to $NbCl_4$ starts at *ca.* 205 °C. $NbCl_5$ does not exhibit fluorinating behaviour towards *poly*fluorinated *cyclo*alkenes at 150 °C [26]. Experimental hints for the preparation of solid $NbCl_5$ was described [27]. The heat capacity of niobium *penta*chloride was measured from 8 to 315 K and thermodymanic data evaluated [28].

The IR spectra of Ar and N_2 matrices trapping vapours coming from solid NbX_5 (X = Cl and Br) have been investigated [29]. The vapours contain *mono*meric NbX_5, *di*meric Nb_2X_{10} and also *poly*meric species. Assignments of the spectra were given.

$NbCl_5$ and $NbBr_5$ molecules of D_{3h} symmetry have been subjected to vibrational normal coordinate analyses using Wilson's GF method. Assignments of observed vibrational frequencies and calculated potential energy distribution values for each vibration are given [36].

Solid $NbCl_5$ and $TaCl_5$ compounds have been reexamined by X-ray diffraction and IR spectroscopy [37]. $NbCl_5$ was studied by ^{93}Nb and ^{35}Cl nuclear quadrupole resonance spectroscopy in the temperature range 4.2 - 440 K [38]. Catalytic properties of $NbCl_5$ and $TaCl_5$ on the preparation of triphenylbenzene was reported [39,40]. The sublimation pressure of solid $NbBr_5$, NbI_5 and TaI_5 has been determined by a spectrophotometric method, as function of temperature [41]. The melting point of NbI_5 was 673 ± 1 K, and the vapour pressure of the melt was given versus temperature [41]. The photoelectron spectrum ($AlK\alpha$, HeI) of NbI_5 was studied in an attempt to find the relation between the energy of the niobium core levels and the oxidation number [42].

Both NbF_5 and TaF_5 have been intercalated into graphite in the presence of chlorine, and it has been thought to happen via the formation of complex chloride-fluoride ions NbF_5Cl^- and TaF_5Cl^-. This idea has found support by the characterization (by X-ray diffraction and mass spectroscopy) of intercalates formed via reaction between HgF_2 and NbF_5 or TaF_5. The NbF_6^- and TaF_6^- ions were identified by Raman spectroscopy [43].

Not just TaF_6^- but a mixture of the ions TaF_6^-, TaF_7^{2-}, TaF_8^{3-} in mutual exchange of F^- seems to exist in a saturated solution of K_2TaF_7 dissolved in 48 % HF, according to ^{181}Ta NMR data [44]. Also, the ^{181}Ta NMR spectrum of the $[TaCl_6]^-$ ion in solution was obtained and interpreted in terms of a perfect octahedral symmertry: Tantalum has a large quadrupolar moment and, without the cubic environment, the NMR band would be much broader than found [44]. The TaF_6^- anion has been identified in dry methylene chloride solution by means of ^{19}F NMR spectroscopy [18].

Vibrational spectra were studied of niobium and tantalum complexes in hydrofluoric acid [45]. For high concentrations of HF and metal, TaF_6^-, TaF_7^{2-}, NbF_6^- and $NbOF_5^{2-}$ ions exist in the solutions. According to the interpretation of the spectra, dilution leads to a relative increase in TaF_7^{2-} and $NbOF_5^{2-}$ concentrations [45]. Raman spectra of K_2NbF_7, K_2TaF_7 and $CsTaF_6$ have been published in connection with extraction experiments [46].

Alkali metal hexafluorotantalates, $A[TaF_6]$ with A = Li, Na, K, Rb, or Cs, were prepared and characterized by IR and X-ray diffraction. Crystal symmetries and lattice constants were determined [47]. Based on coordination geometry, a classification of fluorides and oxyfluorides of niobium or tantalum, i.e. the compounds $AMF_{6-2x}O_x$ with A = Li, Na, K, Rb, Cs and M = Nb or Ta, has been attempted [48]. Low-temperature phase transitions in $KNbF_6$ and $KTaF_6$ were determined by the ^{19}F NMR relaxation method and related to rotation of the MF_6^- octahedral anions [49].

The lightly blue silver(II) hexafluoro niobate and tantalate Jahn-Teller-compounds, $Ag[MTaF_6]_2$ with M = Nb or Ta (Ta is paramagnetic), were prepared from oxides in an autoclave at *ca.* 380 °C and under a F_2-pressure of *ca.* 3 kbar. Single crystal needles were characterized by X-ray diffraction (layer structure with cumulated AgF_6 and MF_6 octahedra) [50].

Methods of preparing shiny crystals of the new compounds $Hg_3[MF_6]$ and $Hg_{3-x}[MF_6]$, M = Nb and Ta, and x small, have been described [51]. These compounds are exceptional in containing electrically conducting either layers or linear chains of mercury atoms in between layers of $[NbF_6]^-$ and $[TaF_6]^-$ octahedra. A transformation between the two kinds of structures takes place in contact with liquid SO_2 or liquid AsF_3 at temperatures from room temperature to 120 °C [51].

The compounds $K[NbCl_6]$ and $K[TaCl_6]$ have been studied [52] to elucidate the mechanism of their superionic conduction. Methods applied involved ac-conductivity, differential scanning calorimetry, and powder neutron diffraction. Crystal symmetries and phase relations versus temperature were reported [52]. The electrical conductivity of $NbCl_5$-NaCl, $NbCl_5$-KCl, $TaCl_5$-NaCl and $TaCl_5$-KCl binary melt systems were measured to determine the phase diagrams [53]. Enthalpy contents and molar heat capacities of $RbNbCl_6$, $CsNbCl_6$, $RbTaCl_6$ and $CsTaCl_6$ were measured as function of temperatures, and all these compounds undergo allotropic solid-solid transformations as well as fusion, and enthalpies and entropies associated with these transformations have been evaluated [24].

New pyridinium salts, $(py\text{-}H...py)^+[MCl_6]^-$ and $(py\text{-}H...py)^+[MX_5Y]^-$, with M = Nb, Ta; X = F, Cl; Y = Cl, Br, and py = C_5H_5N (pyridine), have been characterized [54]. Also, new acidic hydrogen-bound etherate salts, $(Et_2O\text{-}H...OEt_2)^+[MCl_6]^-$ and $(Et_2O\text{-}H...OEt_2)^+[MX_5Y]^-$, with M = Nb, Ta; X = F, Cl; Y = Cl, Br and Et_2O = *di*ethylether, have been prepared [54]. Furthermore, acidic ethylenediamine salts, $H[MCl_6]\cdot n(en)$ and $H[MX_5Y]\cdot n(en)$, with M = Nb, Ta; X = F, Cl; Y = Cl, Br; n = 2, 3 or 4 and en = $H_2NCH_2CH_2NH_2$ (ethylenediamine), were obtained [54]. The compounds were characterized by chemical analysis and IR spectra.

Electron-transfer-induced ligand-exchange reactions have been discovered by electrochemical methods (cyclic voltammetry and constant potential electrolysis) applied on niobium chlorides $(Et_4N)[NbCl_6]$, $(Et_4N)_2[NbCl_6]$, $[NbCl_5]$, and $[NbCl_4(NCMe)_2]$, in "superdry" acetonitrile (NCMe). Two one-electron reduction waves were observed, corresponding to consecutive reductions to Nb(IV) and Nb(III) compounds [55].

Cyclic voltammograms have been obtained on $NbCl_5$ dissolved in a room temperature molten salt liquid consisting of 49.0:51.0 mol % $AlCl_3$-(1-methyl-3-ethylimidazolium chloride), proving that the *di*meric niobium oxide chloride species (formed by reaction with the usually present oxide impurities) can be converted to the "oxide-free" $[NbCl_6]^-$ species by a treatment of the melt with $COCl_2$ [56].

Crystalline $NbAlCl_8$ was prepared directly from Al_2Cl_6 and Nb_2Cl_{10}: The crystal structure consists of an $AlCl_4$ tetrahedron sharing an edge with an $NbCl_6$ octahedron [57], see Figure 1.

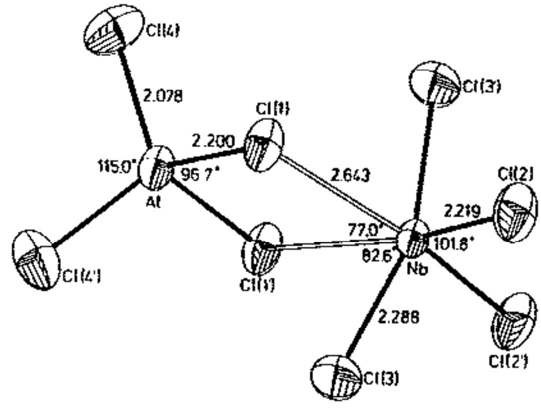


Figure 1. Structure of the [$NbAlCl_8$] molecule. Reproduced with permission from [57], B. Krebs, H. Janssen, N. J. Bjerrum, R. W. Berg and G. N. Papatheodorou, *Inorg. Chem.* **23** (1984) 164.

Two salts, [PCl_4][$NbCl_6$] and [PCl_4][$NbCl_6$]·$SOCl_2$, of the tetrachlorophosphonium and hexachloroniobate ions have been prepared from PCl_5 and $NbCl_5$ in thionyl chloride solution [58]. Their structures were studied by vibrational spectroscopy.

The *penta*chlorides MCl_5 (M = Nb, Ta) were found to be reactive with an excess of *tri*thiazyl chloride, $(NSCl)_3$ in CCl_4 suspension to give the ionic compounds, [S_4N_4Cl][MCl_6]. Furthermore, with SCl_2, the ionic species [$N(SCl)_2$][MCl_6] can be obtained. The products were characterized by chemical analysis and IR-spectra [59].

The electrochemical behaviour of Ta(V) was studied at 400-550 °C in mixed melts containing LiCl-KCl-$TaCl_5$ [60]. By reduction, the anionic $[TaCl_6]^-$ complex most probably forms a stable and soluble Ta(III) complex, which in a second step can be further reduced to the metal. By titration of such melts with solid KF it was shown that in mixed chloride-fluoride melts, primarily $[TaF_7]^{2-}$ complexes are present, but also small amounts of $[TaF_6]^-$ and $[TaClF_6]^{2-}$ coexisted with them [60].

The crystal structure of K_2TaF_7 has been determined by using single crystal X-ray diffraction data [61]. The $TaF_7{}^{2-}$ *poly*hedra may be described as *mono*capped trigonal prisms (distorted from true *mm* or C_{2v} symmetry) with the capping atom located on one of the rectangular faces, see Figure 2. The Ta-F bond lengths varied from 1.918 to 1.975 Å. Raman spectra showed bands at 645 cm^{-1} (Ta-F stretching) and 395 and 280 cm^{-1} (Ta-F bending). The previously unreported luminescense properties of crystals of K_2TaF_7 as well as of K_2NbF_7 have been reported [61-62]. The emission spectrum of crystalline K_2NbF_7 showed a long progression in a Nb-F deformational mode at 290 cm^{-1} [62]. The mechanism of electrochemical reduction of K_2NbF_7 and K_2TaF_7 on a nickel electrode in LiF-NaF molten mixtures was studied, and stable $NbNi_3$ and $TaNi_3$ phases identified [63].

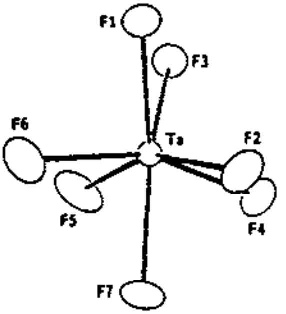


Figure 2. Structure of the $[TaF_7]^{2-}$ ion in the potassium salt. Reproduced with permission from [61], C. C. Torardi, L. H. Brixner, and G. Blasse, *J. Solid State Chem.* **67** (1987) 21.

The reaction of Ta_2O_5 with NH_4HF_2 and alkaline earth fluorides on heating was shown to give $CaTaF_7$, $BaTaF_7$, $SrTaF_7$, $Ba_3(TaF_8)_2$, $Ta_2O_3F_6$, and $Ba(TaF_6)_2$, and the stability of these and analogous compounds was discussed [64].

The hydrazinium heptafluorotantalate monohydrate compound, $(N_2H_6)TaF_7 \cdot H_2O$, decomposes in four steps through the intermediates $(N_2H_6)TaF_7$, $(N_2H_5)TaF_6$ and $(NH_4)TaF_6$, according to results obtained by thermogravimetry, differential thermal analysis, X-ray powder diffraction, chemical analysis and vibrational spectra [65].

An organic molecular charge-transfer salt, $(BEDT\text{-}TTF)_3Ta_2F_{11}$ has been prepared electrochemically (BEDT-TTF is a short name for bis-ethylenedithiolotetrathiafulvalene) [66]. This salt contains the $Ta_2F_{11}^-$ anion with a unique linear fluorine bridge between two tantalum atoms, according to a crystal structure determination [66]. The salt exhibits an optically enhanced magnetic phase transition which was detected by ESR absorption spectroscopy [67]. The $Ta_2F_{11}^-$ anion has also been been identified in dry methylene chloride solution by means of ^{19}F NMR spectroscopy [18] and in the crystal structure solution of $(Hg_4^{2+})(Ta_2F_{11}^-)$ [68].

2.2 Nb(V) and Ta(V) oxyhalide complexes

2.2.1 Oxyfluoride complexes

Molecular compounds $NbOF_3$, $TaOF_3$, NbO_2F and TaO_2F were formed by the reaction between NbF_5 or TaF_5 and silica under various conditions [69]. The compounds were identified by X-ray diffraction and mass spectroscopy [69]. Thermodynamic data for gaseous tantalum oxyhalides, $TaOF_3$ and TaO_2F were reviewed and data are also given for a large number of liquid and solid tantalum halide and oxyhalide compounds [20]. Chemical and structural data were given for $NbOF_3$ and $TaOF_3$ [69]. A powder sample of NbO_2F was investigated by ^{93}Nb NMR two-dimensional spectroscopy [70].

"Non-stoichiometric" niobium oxide fluorides, $Nb_{31}O_{77}F$, $Nb_{34}O_{84}F_2$, $Nb_{59}O_{147}F$, and $Nb_{65}O_{161}F_3$ were prepared by reacting Nb_2O_5 with Nb_3O_7F at 1200 °C [71]. According to high-resolution electron microscopy and computer image simulations, these compounds have block-structures, like *e.g.H*-Nb_2O_5 [71].

The molecular constants and thermodynamical characteristics of the $NbOF_4^-$ ion were determined in vapours over niobiumoxyfluorides between 730 and 960 K [21]. Based on the coordination geometry, development of a classification system has been attempted for the fluorides and oxyfluorides of niobium or tantalum, i.e. the compounds $AMF_{6-2x}O_x$ with A = Li, Na, K, Rb, Cs and M = Nb or Ta, and x = an integer [48].

The crystal structures of sodium *penta*fluoro oxy-niobates(V), $Na_2[NbOF_5]$ and α-$Na_3[NbOF_6]$ were solved [72-72A], see Figure 3. $Na_2[NbOF_5]$ contained discrete $[NbOF_5]^{2-}$ ions of slightly distorted octahedral configuration [72]. The O-Nb-F equatorial angles were larger than 90°, being on the average 97° ± 2°, and the symmetry of the ion was found to be approximately C_{4v}. In $Na_3[NbOF_6]$, the $[NbOF_6]^{3-}$ ion with pentagonal *bi*pyramidal configuration was determined, adding diversity to the earlier found *mono*capped octahedral geometry of the ion [72A].

Unexpectedly, crystal structure solutions of $(Hg_3)[(MF_5)_2SO_4]$ salts, with M = Nb or Ta, have proven that ions $[(MF_5)_2SO_4]^{2-}$ with a MF_5-O-SO_2-O-MF_5 bonding geometry have a significant stability [68].

^{19}F NMR spectroscopy was used to study the oxyfluoride complexes present in acidic aqueous solutions and in acetonitrile [73]. The *trans*-$[NbOF_4(OH_2)]^-$ anion and the $[NbOF_5]^{2-}$ anion were detected.

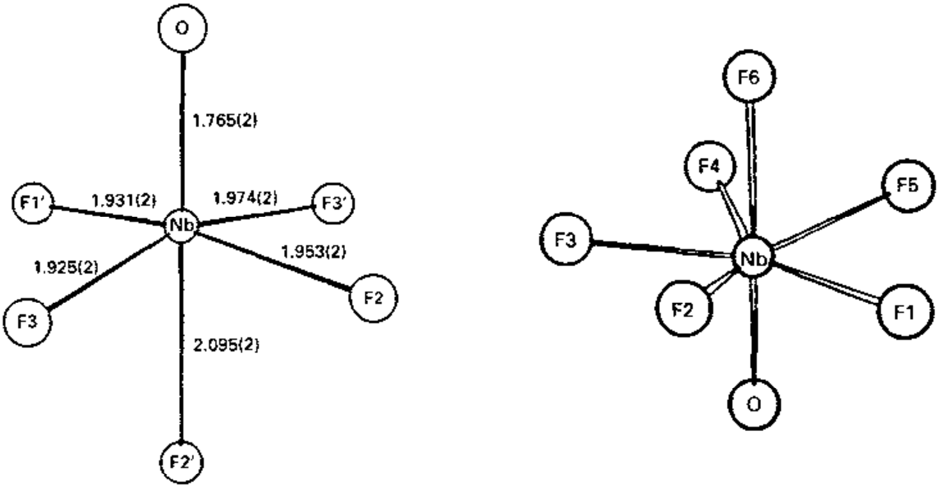


Figure 3. The $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ anions as found in the crystal structures of the sodium salts. Reproduced with permission from [72-72A], R. Stomberg, *Acta Chem. Scand.* **A 38** (1984) 603 and **A 37** (1983) 453.

$[MOF_5]^{2-}$ anions (M = Nb and Ta) have been identified by IR spectroscopy as corrosion products, formed by the attack of HF-DMF-H_2O_2 solutions on the metal [74]. The Raman spectrum of K_2NbOF_5 has been published in connection with extraction experiments [46]. The preparation of alkali metal *mono*oxofluoroniobates, ANbOF$_4$ and A_2NbOF$_5$ (A = Li, Na, K, Rb and Cs), in molten NH_4HF_2 was described [75]. IR spectra indicate ANbOF$_4$ to have a chain structure and A_2NbOF$_5$ a discrete-ion structure. X-ray data were given for $LiNbOF_4$ and $NaNbOF_4$ [75]. In the KF-Nb_2O_5 system, three intermediate tetragonal-tungsten-bronze phases, KNb_2O_5F, $KNb_4O_{10}F$ and $KNb_6O_{15}F$ were identified [76]. Also, unit cell dimensions of K_2NbOF_5, K_2TaOF_5, $K_3NbO_2F_4$ and $K_3TaO_2F_4$ were determined by X-ray powder diffraction [77]. The compounds were prepared by heating the corresponding fluoro-*per*oxy-metallates [77].

The reaction between Nb_2O_5 and CoO in molten NH_4HF_2 has been studied by DTA, IR spectroscopy and X-ray diffraction [78]. $CoNbOF_5$ was formed. At high temperatues it pyrolysed to $Co_2NbO_3F_3$ giving off NbF_5 and HF vapours [78].

An attempt has been made [79], to make it possible beforehand to distinguish, among niobium and tantalum oxide fluorides, those compounds which will have a coordination type of structure (containing isolated octahedra): The ions present must be of a similar size; otherwise island, chain, layer, or framework type structures seem to be the result [79]. New niobium and tantalum oxyfluoride double salts, Li_4NbO_4F and Li_4TaO_4F, have been prepared and characterized by X-ray powder diffracion and infrared spectroscopy [80-82]. When passing from $LiMF_6$ complex salts to $LiMO_3$ through oxy-fluorides, a transition from compounds of an island-type through chain and laminated ones to framework structures was observed [80]. The reaction between NbO_2F and alkali metal carbonates was studied by DTA, DGA and X-ray analysis; M_4NbO_4F and M_2NbO_3F (M = Li, Na, K, Rb and Cs) were formed [83]. The reaction between TaO_2F and lithium, sodium and potassium carbonates was studied by DTA, DGA and X-ray analysis; Li_4TaO_4F, $Na_{0.95}TaO_{2.95}F_{0.05}$, $Na_2Ta_2O_5F_2$, K_2TaO_3F and $K_6Ta_{6+x}O_{15-x}F_{6+7x}$ (x is small) were the main components formed [84].

By heating Nb_2O_5 and NbO_2F with Cu_2O it was possible to obtain red crystals of $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$, suitable for X-ray structure solution [85]. The structure is of the same type as that of $LiNb_6O_{15}F$, H-$LiTa_3O_8$ and $Cu_{0.8}Ta_3O_8$, containing pentagonal columns with seven-coordinated niobium atoms in NbX_7 pentagonal *bi*pyramids (X = F or O), sharing edges with five NbX_6 octahedra (see Figure 4). These building units are further linked *via* corner-sharing.

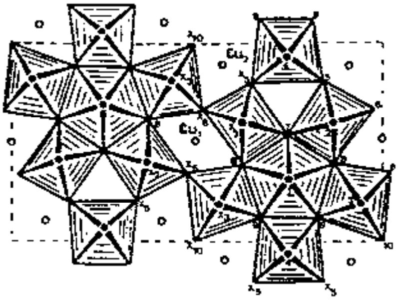


Figure 4. Projected structure of $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$. Niobium is displaced from the center of the (hatched) octahedra. Reproduced with permission from [85], P. N. Wa Llunga, *Acta Chem. Scand.* **A38** (1984) 641.

Within the system PbO-PbF_2-M_2O_5-MO_2F (M = Nb, Ta), several crystal structures have been obtained:

a) $Pb_2Nb_3O_7F_5$ is built of slabs of ReO_3 structure type of net composition $Nb_3O_7F_3{}^{2-}$, separated by layers of $Pb_2F_2{}^{2+}$, and related to the $Bi_4Ta_3O_{12}$ structure [86].

b) The $Pb_3Nb_4O_{12}F_2$ and $Pb_3Ta_4O_{12}F_2$ structures contain corner-sharing $M(O,F)_6$ octahedra, related to the pyrochlore, fluorite and β-$Na_2Ta_2O_5F_2$ structures [87].

c) The $Pb_3Ta_5O_9F_{13}$ structure can be described as made up from slabs of ReO_3 structure type and bands of red PbO_2 structure type [88].

d) The $Pb_{12}Ta_9O_{20}F_{29}$ structure contains columns of ReO_3 structure type, 3 times 3 octahedra wide, separated by layers of $Pb_2F_2^{2+}$, and related to the layered $Bi_2O_2^{2+}$ perovskites (Aurivillius phases) [89].

e) The $Pb_xM(O,F)_{3+x/2}$ (x = *ca.* 0.25, M = Nb, Ta) structures which are disordered superstructures of the hexagonal tungsten bronze type [90], see Figure 5.

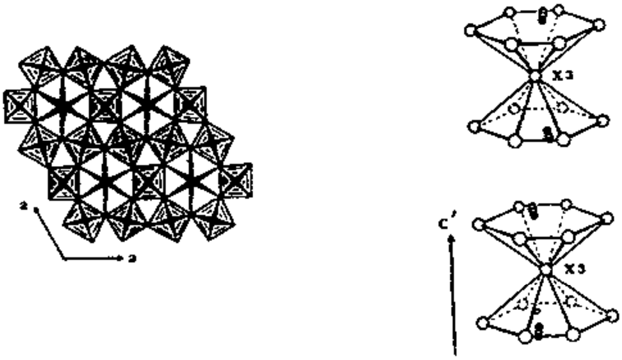


Figure 5. Structure of $Pb_xM(O,F)_{3+x/2}$, with x = *ca.* 0.25 and M = Nb, Ta. The Pb atoms are located in the hexagonal tunnels (left). A view of a suggested Pb-X-Pb arrangement (X is F or O) in the tunnels (right). Reproduced with permission from [90], Ö. Sävborg, *J. Solid State Chem.* 57 (1985) 160.

2.2.2 Other Oxyhalide complexes

Thermodynamic data for gaseous tantalum oxyhalides, $TaOCl_3$, TaO_2Cl, $TaOBr_3$, TaO_2Br, $TaOI_3$ and TaO_2I were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20].

The IR spectra of Ar and N_2 matrices trapping vapours coming from solid $NbOX_3$ and NbX_5/Nb_2O_5 mixtures (X = Cl, Br and I) have been investigated [29]. The vapours contain *mono*meric $NbOX_3$ and also *poly*meric species. Assignments of the spectra were given.

The He I α photoelectron spectrum of gaseous *mono*meric $NbOCl_3$ was assigned using the new semi-empirical molecular-orbital calculation technique SCC-X α [30]. Molecular orbital correlation diagrams are given and bonding modes of $NbOCl_3$ are discussed in comparison with similar molecules like $POCl_3$ and $VOCl_3$ [30]. The sublimation pressure and the standard entropy of $NbOCl_3$ was redetermined [31].

$NbOCl_3$ and $TaOCl_3$ powders have been examined by X-ray diffraction; the two compounds were found to be *iso*-structural and indexed powder diagrams were given [32]. The sublimation pressure of solid $NbOCl_3$ has been determined by the transportation method, as a function of temperature [33]. Thermodynamic functions for solid and gaseous $NbOCl_3$ were given [33]. Compounds like NbO_2Cl Nb_3O_7Cl, $Nb_5O_{11}Cl_3$, NbO_2Br, $TaOCl_3$, TaO_2Cl, Ta_3O_7Cl, TaO_2Br (some of which are new) have been made and studied [34]. The structure of $NbOBr_3$ was investigated by electron diffraction [35].

Niobium *penta*chloride reacts with *tri*chloromethane, forming $NO^+[NbOCl_4]^-$ and CCl_4 [91]. The $[M_2OCl_{10}]^{2-}$ anions, M = Nb or Ta, were found in crystal structures [92-93], in the case of Nb for the first time. Both of the ions consist of two $MOCl_5$ octahedra sharing the oxygen apex and with linear M-O-M bonding arrangements and inversion symmetries.

Lightly red $NH_4[NbOBr_4]$ is formed when a mixture of $NbOBr_3$ and NH_4Br is heated in a sealed ampoule at 400 °C. X-ray data and vibrational spectra of $NH_4[NbOBr_4]$ have been reported [94, 94a].

Potentiometric investigations of niobium(V) and tantalum(V) oxychloro complex formation were done in $NaCl$-$AlCl_3$ melts at 175 °C [95]. Results were explained by a two-equilibria model:

$$\begin{array}{lcl} MOCl_4^- & \longleftarrow\ \longrightarrow & MOCl_3 + Cl^- \\ MOCl_3 & \longleftarrow\ \longrightarrow & MOCl_2^+ + Cl^- \end{array}$$

with pK values of 2.2 and 3.95 for M = Nb, and 2.74 and 4.52 for M = Ta, respectively.

The X-ray structure of prepared Bi_4NbO_8Cl single crystals was solved and consists of $[NbO_4]$ layers composed of much distorted octahedra which are canted with respect to one another. From powder data it was concluded that Bi_4TaO_8Cl and Bi_4NbO_8Br crystallize with the same structure [96].

Luminescence properties of $La_3TaO_4Cl_6$ crystals have been reported [97]. The structure is similar to that of $Pr_3NbO_4Cl_6$ [98] and contains infinite linear chains of corner-sharing TaO_5 trigonal *bi*pyramids with the equatorial oxygens corner-sharing the oxygens of the $LaCl_7O_2$ *poly*hedra. Crystals in which lanthanum(III) was partly replaced with indium or other rare earth ions (Sm, Eu, Tb, Dy and Tm) have been prepared and their peculiar luminescence properties examined [99].

Iso-structural $Ln_3MO_5XCl_3$ crystals have been prepared and their crystal data reported, with Ln = La, Ce, Pr, Nd, Th; M = Nb, Ta; X = O, OH, F [100]. The single crystal structures of $La_2ThTaO_6Cl_3$ and $Ce_3TaO_6Cl_3$ [100], as well as of $La_3TaO_5(OH)Cl_3$ [101] were solved. The structures consist of TaO_6 *poly*hedra with unusual trigonally prismatic environments for Ta, see Figure 6.

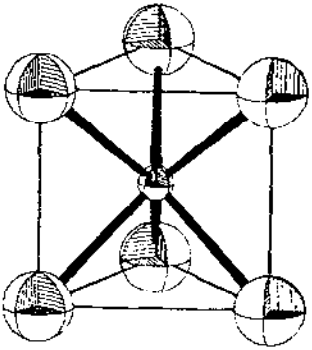
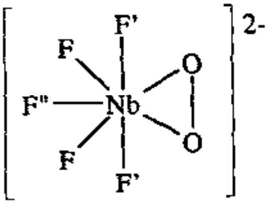


Figure 6. The unusual trigonally prismatic coordination *poly*hedron of TaO_6 in the structure of $La_2ThTaO_6Cl_3$. Ta-O bond length = 1.984 Å. Reproduced with permission from [100], U. Schaffrath and R. Gruehn, *J. Less-Comm. Met.* 137 (1988) 61.

2.3 Nb(V) and Ta(V) *per*oxyhalide and *per*oxy-pseudohalide complexes

The *penta*fluoro-*per*oxy-niobate(V) ion, $[NbF_5O_2]^{2-}$, 1, which is known [102] to be pentagonal *bi*pyramidally seven-coordinate, has been investigated in the sodium and potassium salts



1

by means of Raman and IR spectroscopic techniques [103-105, 106]. For the sodium salt, bands observed at 955, 880 and 900 cm^{-1} were assigned to ν(O-O), ν_s(Nb-O) and ν_{as}(Nb-O), respectively, based on C_{2v} symmetry, but the assignments were questioned because of probable impurities present in the sample. A diagram shows the π-bonding involved in between NbF_5 and the *per*oxide ion. (The work by Nour *et al.* has been published three times in virtually identical forms [103-105]).

*Mono-per*oxy-chloroniobates $A_2[Nb(O_2)Cl_5]$ with A = K, NH_4 or Et_4N were found to react with HF in CH_3CN giving $A_2[Nb(O_2)F_5]\cdot n$HF, with n = 2-5 [107]. In the presence of various acido ligands, $A_2[Nb(O_2)F_3L_2]$ (A = K, Cs, NH_4 or Et_4N; L = NCS, OAc, CF_3CO_2, HCO_2) and $A_3[Nb(O_2)F_2L'_2]$ (L' = SO_4 and C_2O_4) were formed. The complexes were characterized by IR spectroscopy [107].

The *di-per*oxy-compound $K_3[Ta(O_2)_2F_4]$ was shown to undergo UV-photodecomposition [108]. The kinetics of oxygen evolution obey a parabolic rate equation, indicating a *mono*-excitation process for the photolysis [108]. The activation energy was determined and the decomposition given as

$$K_3[Ta(O_2)_2F_4](s) \longrightarrow K_3[TaO_2F_4](s) + O_2(g)$$

according to chemical analyses, IR spectroscopy and thermogravimetry [109].

2.4 Nb(V) and Ta(V) chalcogeno-halide complexes

Niobium sulphide *tri*chloride, $NbSCl_3$, has been obtained by reacting $NbCl_5$ with hexamethyl*di*silthiane, Me_3Si-S-$SiMe_3$, in *di*chlormethane at room temperature [110]. The reaction is fast and gives a precipitate which does not react further. The $NbSCl_3$ product was characterized by IR spectroscopy as a coordination polymer containing Nb-S-Nb bonds, in contrast to other kinds of $NbSCl_3$ which contain Nb=S bonds [110].

In the solid state at 100 °C and under vacuum, Nb_2Cl_{10} reacts with B_2S_3 to form $NbSCl_3$ [111]. In CH_2Cl_2 solution, $NbSCl_3$ and $P(Ph)_4Cl$ form crystals of $[P(Ph)_4][NbSCl_4]$, which contain quadratic-pyramidal $[NbSCl_4]^-$ ions with a 2.09 Å long Nb=S bond, according to the X-ray structure determination [111], see Figure 7. An improved synthetic procedure to obtain $[P(Ph)_4][NbSCl_4]$ has recently been described [112]. IR spectra of the crystals are discussed in reference [111]. By hydrolysis of $[P(Ph)_4][NbSCl_4]$ in the presence of $POCl_3$ in CH_2Cl_2, $[P(Ph)_4]_2[NbOCl_4(O_2PCl_2)]\cdot CH_2Cl_2$ is formed [113].

Presumably, solid NbS_2Cl has been obtained from NbS_2Cl_2 by electrochemical oxidation at 160-200 °C in a cell using a $NaAlCl_4$ molten salt as electrolyte [114]. The structure of $NbSBr_3$ was investigated by electron diffraction [35]. The reactivity of $NbSBr_3$ and $NbSeBr_3$ with respect to the formation of complexes was studied [115].

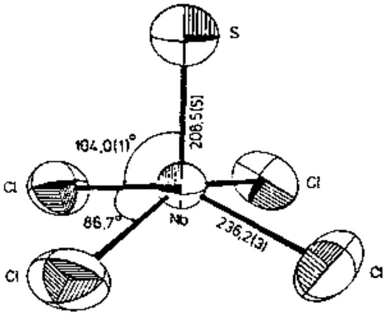


Figure 7. The X-ray structure of the quadratic-pyramidal $[NbSCl_4]^-$ ion in $[P(Ph)_4][NbSCl_4]$. Reproduced with permission from [111], U. Müller and P. Klingelhöfer, *Z. Anorg. Allgem. Chem.* **510** (1984) 109.

The preparation of $NbSCl_3$ and some thiohalogeno compounds containing $[NbSCl_5]^{2-}$, $[TaSCl_5]^{2-}$ and $[NbSBr_5]^{2-}$ will soon be described [115A]. The crystal structures of $(PPh_4)_2[NbSCl_5]\cdot 2(CH_2Cl_2)$ and $NEt_4[NbCl_6]$ were solved [115A].

2.5 Nb(V) and Ta(V) halide complexes with O-donor ligands

2.5.1 Fluoride complexes with O-donor ligands

According to ^{19}F NMR spectral data, tantalum*penta*fluoride TaF_5 reacts with O,O-*di*phenyl-N-benzoylamidophosphate, $(PhO)_2P(O)NHC(O)Ph$, in methylene chloride solution to form essentially a *di*meric complex cation $[F_5Ta\text{-}O\text{-}P^+(OPh)_2\text{-}NH\text{-}C^+(Ph)\text{-}O\text{-}TaF_5]$ and *mono*meric complex cations, $[F_5Ta\text{-}OP^+(OPh)_2NHC(O)(Ph)]$ and $[F_4Ta\{\text{-}OP^+(OPh)_2NHC(O)(Ph)\}_2]$, balanced by TaF_6^- anions [116]. The *mono*dentate *mono*meric cation forms $[F_5Ta\{\text{-}OP(OPh)_2{=}NC(O)(Ph)\}]$ by splitting off one proton from the NH group [116].

2.5.2 Chloride complexes with O-donor ligands

The $[NbOCl_4(THF)]^-$ (THF = tetrahydrofuran) anion has been characterized by spectroscopy and crystallography [117]. It has two oxygens in trans positions and four chlorines in a nearly octahedral configuration.

By hydrolysis of $[P(Ph)_4][NbSCl_4]$ [111] in the presence of $POCl_3$ in CH_2Cl_2 solution, $[P(Ph)_4]_2[NbOCl_4(O_2PCl_2)]\cdot CH_2Cl_2$ was formed [113]. Attempts to prepare the compound directly from Nb_2Cl_{10}, $POCl_3$, $P(Ph)_4Cl$ and H_20 yielded crystals of $[P(Ph)_4][NbOCl_4(OH_2)]$ [113]. Crystal structures of both compounds, determined by means of X-ray diffraction data, show quadratic-pyramidal $[NbOCl_4]^-$ ions, to which a molecule of either H_2O or a $[PO_2Cl_2]^-$ ion is attached in *trans*-position to the O atom, see Figure 8. IR spectra of the crystals are discussed in reference [113].

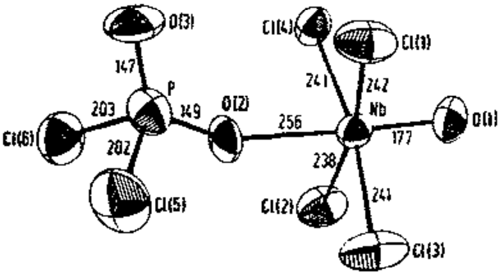


Figure 8. The X-ray structure of the $[NbOCl_4(O_2PCl_2)]^{2-}$ ion in its $[P(Ph)_4]^+$ salt. Distances in pm. Reproduced with permission from [113] P. Klingelhöfer and U. Müller, *Z. Anorg. Allgem. Chem.* **516** (1984) 85.

The *tri*-alkoxy *di*-chloride niobium(V) complexes, $Nb(OR)_3Cl_2$ (where R = CH_3, C_2H_5, i-C_3H_7, and n-C_4H_9) have been prepared as lightly coloured compounds [118-119].

Reactions of $M(OPh)_5$ (M = Nb or Ta) with acetyl or benzoyl chlorides (AcCl or BzCl) in 1:1 or 1:2 molar ratio results in the replacement of phenoxy groups with chloride [120]. On heating, in molar ratio 1 to 3, however, compounds $MCl_3(OPh)_2RCO_2Ph$ and in molar ratio 1 to higher than 4, $MOCl_3RCO_2Ph$ were formed, with R = CH_3 (methyl) or C_6H_5 (phenyl) [120].

Complex formation among $NbCl_5$ and oxygen-containing donors D in organic solvents was studied by titration methods [121]. In the non-solvating solvent benzene, the complexes $NbCl_5D$ and $NbCl_5D_2$ were progressively formed, with $D = (C_4H_9O)_3PO$ and $(iso\text{-}C_5H_{11})_3PO$. In butyl acetate, in which 1:1 solvates with $NbCl_5$ already occur, the addition of oxygen donor molecules D resulted in the progressive formation of $NbCl_5(CH_3COOC_4H_9)D$, $[NbCl_4(CH_3COOC_4H_9)D_2]Cl$ and $[NbCl_4D_3]Cl$ complexes, with $D = (C_4H_9O)_3PO$, $(iso\text{-}C_5H_{11}O)_2(CH3)PO$, $(C_8H_{17})_2SO$, $(C_6H_{13})_2SO$ and $(iso\text{-}C_5H_{11})_3PO$. These D ligands are listed here in the order of increasing oxygen donor power [121].

$NbOCl_3$ reacts with acetamide ($L = H_3CO\text{-}NH_2$) in CH_3CN to give actamidates, 1:1 electrolytes $NbOCl_3L_n$ (n = 2.5,3,4,6,7), in which L is O-bonded [122]. In ethanol the compounds undergo alcoholysis to give $NbOCl_2(OEt)L_4(EtOH)$.

Complexes $[TaCl_nL_{5\text{-}n}]$ with n = 2 and 3 and L = 2,6-*di*-*t*-butylphenoxide have been obtained by letting $TaCl_5$ react with lithium 2,6-*di*-*t*-butylphenoxide in benzene [123]. The compounds were characterized by elemental analysis, IR, and ^1H and ^{13}C NMR spectra. The X-ray crystal structure was determined for the case of $[TaCl_2$(2,6-*di*-*t*-butylphenoxide$)_3]$. This complex is a *mono*mer with a square pyramidal coordination geometry around Ta. The phenyl rings (see Figure 9) are oriented such as to minimise interactions between 2- and 6- substituents. A comparison of the new structure with that of $[TaCl_3$(2,6-*di*-*t*-butylphenoxide$)_2]$ [124], is given in reference [123].

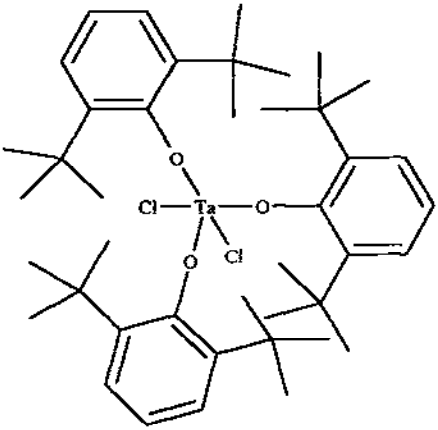


Figure 9. The coordination in square pyramidal $[TaCl_2$(2,6-*di*-t-butylphenoxide$)_3]$, adapted after reference [123].

Lithium 2,6-*di*-*iso*propylphenoxide reacts with $TaCl_5$ to give $[TaCl_2$(*di*ethylether)(2,6-*di*-*iso*propylphenoxide$)_3]$, which on recrystallization in air gives the *bi*nuclear $[Ta_2Cl(\mu\text{-}Cl)_2$(2,6-*di*-*iso*propylphenoxide$)_5(\mu\text{-}O)]$ [123]. The X-ray crystal structure was solved, to give the structure shown in Figure 10. Also, in this structure the phenyl rings are oriented such as to minimise interactions between 2- and 6- substituents.

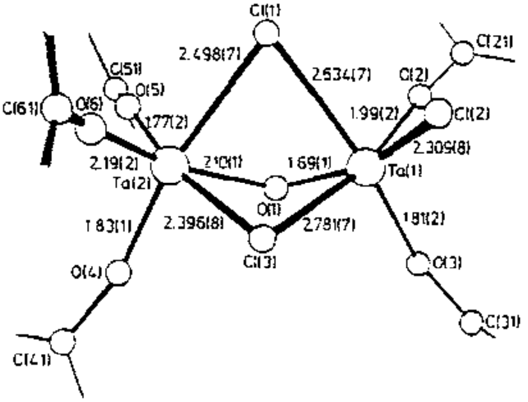


Figure 10. Inner coordination geometry from the crystal structure of *di*nuclear $[Ta_2Cl(\mu\text{-}Cl)_2(2,6\text{-}di\text{-}iso\text{propylphenoxide})_5(\mu\text{-}O)]$. Reproduced by permission from [123],G. R. Clark, A. J. Nielson and C. E. F. Rickard, *Polyhedron* **6** (1987) 1765.

A series of chloro-chlorophenoxy salicylaldehyde complexes, $NbCl_n(OC_6H_4Cl)_{4-n}\cdot(sal)$ with $n = 0$ to 3 can be prepared [125] by refluxing niobium *penta*chloride in the presence of *o*-chlorphenol and salicylaldehyde (salH). The compounds were characterized by several methods, and seem to contain octahedrally coordinated *mono*meric niobium. In one case, for $NbCl_2(OC_6H_4Cl)\cdot 2(sal)$, evidence for a *di*meric structure (see Figure 11), with eight-coordinated Nb was presented [125].

A series of chloro-chlorophenoxy α-hydroxyketone complexes of Nb(V), $[NbCl_n(OC_6H_4Cl)_{4-n}(L)]$ with $n = 0$ to 3 and LH = benzoin (benzH) or 2-hydroxyacetophenone (hapH) was prepared by refluxing niobium *penta*chloride in benzene in the presence of *o*-chlorphenol and H*L* in predetermined molar ratios [126]. Complexes of the type $[NbCl_2(OC_6H_4Cl)(L)_2]$ were likewise obtained. Structures of the complexes were assigned on the basis of elemental analysis, conductance, cryoscopic, magnetic and IR spectral studies. In the case of $[NbCl_n(OC_6H_4Cl)_{4-n}(L)]$ they seem to contain octahedrally coordinated *mono*meric niobium. In the case of $[NbCl_2(OC_6H_4Cl)(L)_2]$, a *di*meric structure (see Figure 11) with eight-coordinated Nb was assumed [126].

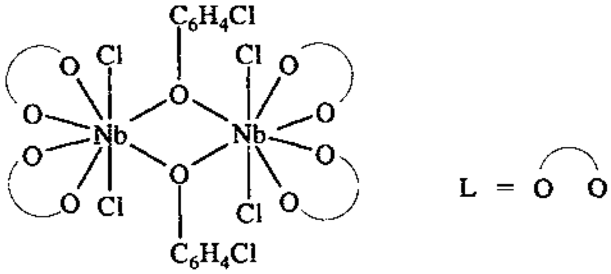


Figure 11. The estimated structure of $NbCl_2(OC_6H_4Cl)(L)_2$ *dimers* with eight-coordinated Nb. Chelate ligands (*L*) are salicylaldehyde [125], benzoin or 2-hydroxyacetophenone [126]. Adapted after [125] and [126], S. C. Chaudhry. J. Gupta and S. Mehta, *Indian J. Chem.* **23 A** (1984) 1036, and **24 A** (1985) 521.

The complexation reaction of 5,5'-methylene-*bis*-salicylaldehyde (MBS) with $TaCl_5$ was studied under various conditions (in DMF solution in dry nitrogen or ambient air or in oxalate solution) [127]. The 1:1 compounds obtained were *dia*magnetic and insoluble in common organic solvents. Probable structures (see Figure 12) were proposed on the basis of elemental analyses, magnetic measurements and infrared spectra [127].

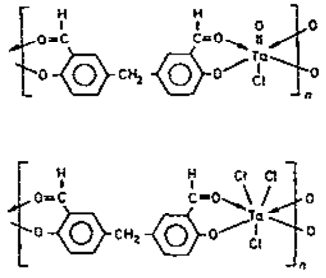
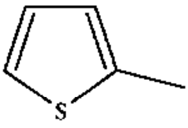
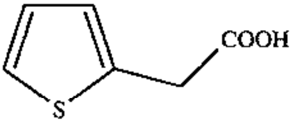


Figure 12. Probable structures of tantalum MBS complexes $[TaCl_3C_{15}H_{10}O_4]$ and $[TaClC_{15}H_{10}O_5]$ with five and seven-coordinated Ta. Reproduced with permission from [127], S. Chomal, A. S. Aazmi and G. C. Shivahare, *Acta Chim. Hung.* **122** (1986) 127.

The preparation of *hetero*cyclic carboxylates of niobium(V) and tantalum(V) in dry benzene has been considered for the acids H*L* = HTCA = 2-thiophenecarboxylic acid and H*L* = HTAA = 2-thiopheneacetic acid:

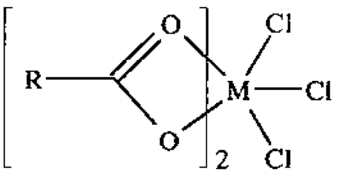


HTCA



HTAA

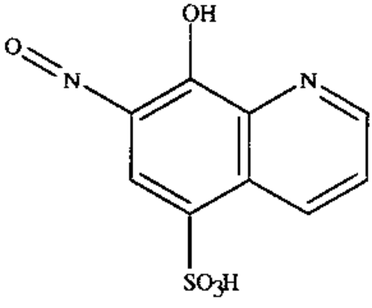
Complexes of the type $M\mathrm{Cl}_{5-n}\mathrm{L}_n$ were obtained, with M = Nb, Ta, n = 1-3 and L = TCA or TAA [128]. The complexes were characterized on basis of chemical analyses as well as IR and ^{1}H NMR data. A tentative seven-coordinated structure was assigned to the $M\mathrm{Cl}_3L_2$ complexes (**2**), with M = Nb or Ta and L = TCA or TAA [128].



2

White crystalline compounds of the general formula $\mathrm{NbCl_4(OOC}R)$ and $\mathrm{TaCl_4(OOC}R)$ can be obtained from the *penta*chlorides and an equimolar amount of the carboxylic acids, RCOOH with R = H, CH_3, C_2H_5, n-C_3H_7, CH_2Cl, $CHCl_2$ and CCl_3. With carboxylic acid anhydrides $(R\mathrm{CO})_2\mathrm{O}$ with R = CH_3 and C_2H_5, brown *poly*meric compounds $\mathrm{NbOCl(OOC}R)_2$ and $\mathrm{TaOCl(OOC}R)_2$ were obtained. The compounds were characterized by chemical analysis and IR spectroscopy [129].

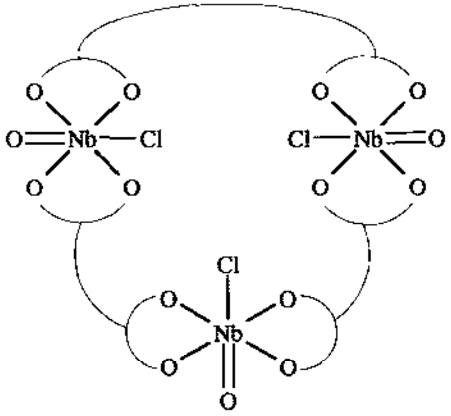
According to results [130] obtained by IR spectrophotometric, conductimetric and potentiometric methods and chemical analysis, the 7-nitroso-8-hydroxyquinoline-5-sulphonic acid, **3**, has an ability to coordinate to Nb(V) forming green chelates such as $[(C_9N_2O_5SH_4)Nb(H_2O)_2(Cl)_2]Cl$ and $Na[(C_9N_2O_5SH_4)_2Nb(H_2O)_2(Cl)_2]$. The ligand is bonded to Nb through the oxygens of nitroso and hydroxy groups. Stability constants are reported [130].



3

Tantalum(V) complexes with citric and *tri*hydroxyglutaric acids have been studied [131].

Niobium(V) complexes with *bis*-ß-*di*ketones (*L*) were studied [132]. When *L* is 2-phenyl-1,1,3,3-*tetra*-acetylpropane (PTAP) or 2-phenyl-1,3-*di*-acetyl-1,3-*di*-benzoylpropane (PDADBP), 1:1 complexes ($NbOCl(C_{17}H_{18}O_4)$ and $NbOCl(C_{27}H_{22}O_4)$) were obtained, according to analytic data and molecular weight determinations, together with IR, UV, ^{1}H-NMR and magnetic measurements. *Tri*meric structures of the type shown below, **4**, were assumed [132].



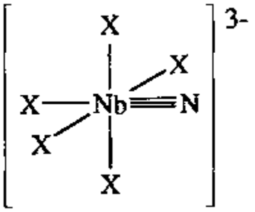
4

2.5.3 Bromide complexes with O-donor ligands

New *tri*bromooxide Nb(V) complexes of the type $NbOBr_3 \cdot 2L$, with L = Ph_3PO, CH_3CN, $(CH_3)_2SO$, $((CH_3)_2N)_2CO$ and C_4H_8S, and $NbOBr_3 \cdot Et_2S$ have been prepared [133].

2.6 Nb(V) and Ta(V) halide complexes with N-donor ligands

Novel compounds with the general formula $A_3[MNX_5]$ (M = Nb, Ta; A = K, Cs, Ph_4P, TEBA = *tri*ethylbenzylammonium; X = F, Cl) have been synthesized by heating dry mixtures of MCl_5, NH_4Cl and ACl in an argon atmosphere [134]. There are no previous report on nitrido-complexes of niobium or tantalum containing a metal-nitrogen tripple bond, **5**.



5

The new compounds were characterized by chemical analysis and by physico-chemical methods; the IR spectra contain a strong narrow band in the range 1000-1050 cm^{-1} due to the *M*-N triple bond streching [134].

Previously, the synthesis of $(NH_4)_3[Ta_2NBr_{10}]$ by ammonolysis of $TaBr_5$ with NH_4Br under HBr formation has been described [135]. This unusual reaction in sealed glass ampoule at *ca.* 400 °C has been used to prepare also the compounds $(NH_4)_3[Nb_2NBr_{10}]$ and $(NH_4)_3[Ta_2NI_{10}]$ [94]. The X-ray crystal structures have been solved [94], showing linear symmetrical Nb=N=Nb bridges (see Figure 13) that also occur in the other compounds. The vibrational spectra of these red μ-nitrido halides were interpreted to contain $\nu_{as}(M_2N)$ at *ca.* 950 cm^{-1} (IR) and $\nu_s(M_2N)$ at *ca.* 215 cm^{-1} (Raman), the frequencies depending on the particular salt [94].

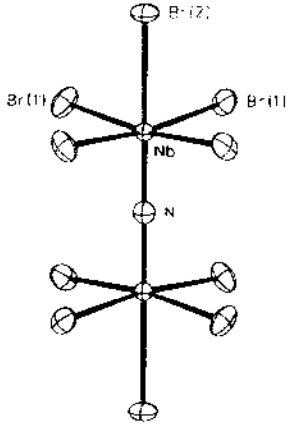


Figure 13. Structure of the $[Nb_2NBr_{10}]^{3-}$ anion. The Nb-N bond distance is 1.845(2) Å. Reproduced with permission from [94], M. Hörner, K.-P. Frank and J. Strähle, *Z. Naturforsch.*, 41 b (1986) 423.

The properties of $Nb_6Br_9N_7$ were studied and reactions leading to $Nb_6Br_4(NH)_{11}(NH_2)_4$ (with ammonia) and to $Na_4Nb_6(C{\equiv}C)_4(N)_8NH$ and $Na_5Nb_6(C{\equiv}C)_5(N)_5(NH)_5$ (with sodium acetylide) were described [136]. Pyrolysis of these compounds gave Nb_4N_3 and NbC products.

Ammonolysis of $NbBr_5$ have been studied in order to obtain precursor compounds (*e.g.* $NbBr(NH_2)_2NH$) that can be thermally converted into advanced ceramic materials such as nitrides or carbonitrides [136]. One reaction was represented by

$$6\ \mathrm{NbBr_5} + 46\ \mathrm{NH_3} \xrightarrow{\text{room temperature}}$$

$$6\ [\mathrm{NbBr_3(NH_2)_2 \cdot 2NH_4Br \cdot 3.66NH_3}] \xrightarrow[\Delta]{220\ ^{\circ}\mathrm{C}}$$

$$\mathrm{Nb_6Br_9N_7} + 21\ \mathrm{NH_4Br} + 18\ \mathrm{NH_3}$$

According to ^{19}F NMR spectra, tantalum *penta*fluoride reacts with *tri*-ethylamin (*L*) in methylene chloride solution to form a *mono*dentate N-donor complex $[TaF_5(L)]$ [116], and with picolinic acid (*L*H) in acetonitrile solution to form *mono*dentate N-donor 1:1 and 1:2 six-coordinated complexes $[TaF_5(LH)]$ and $[TaF_4(LH)_2]$ [137]. The picolinic acid only coordinates *mono*dentately, see Figure 14.

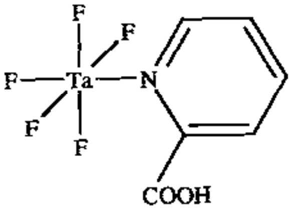
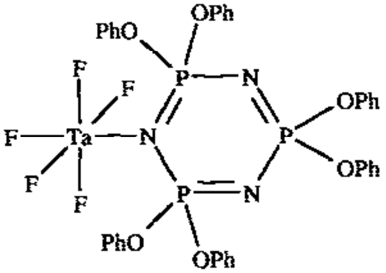


Figure 14. Structure of $[TaF_5(LH)]$ for *L*H = picolinic acid [137].

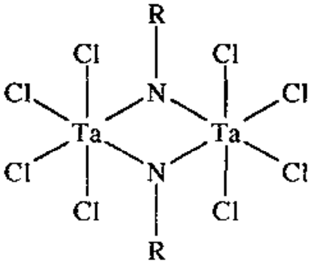
Further molecular complexes of the general formula $[TaF_5L]$, where *L* is a N-donor ligand have been synthesized and characterized. For *L* = hexaphenoxy*cyclo*phosphazene ($N_3P_3(OPh)_6$), the coordination takes place between Ta and one of the N-atoms of the N_3P_3 *hetero*cyclic ring, according to NMR and IR spectroscopic results [18]. The complex is shown below, **6**.



6

The *penta*chlorides MCl_5 (M = Nb, Ta) were found to be reactive with *tri*thiazyl chloride, $(NSCl)_3$ in CCl_4 suspension to give the donor-acceptor complexes $MCl_5 \cdot NSCl$ and $(MCl_5)_2 \cdot N_2S_2$. The products were characterized by chemical analysis and IR-spectra [59].

Tantalum *penta*chloride reacts with *bis*(*tri*methylsilyl)carbo*di*imide $(CH_3)_3SiNCNSi(CH_3)_3$ to give $Si(CH_3)_3Cl$ and $[Cl_4TaNCNSi(CH_3)_3]_2$ [138]. IR and Raman spectra of the white compound, 7, were interpreted [138] to give a planar Ta_2N_2 structure (R = $CNSi(CH_3)_3$):



7

The *penta*chlorides of niobium and tantalum react with N(*tri*methylsilyl)-*t*-butylamine to give $[M(NCMe_3)Cl_3(NH_2CMe_3)]$ and with primary amines to form $[M(NR)(NHR)Cl_2(NH_2R)]$ which contain imido, amido and amine ligands coordinated to the same metal centre (M = Nb, Ta) [139-140].

In benzene, $[Nb(NCMe_3)Cl_3(NH_2CMe_3)]_2$ reacts with 4-picoline (pic) to give $[Nb(NCMe_3)Cl_3(pic)_2]$, with 2,2'-*bi*pyridyl(bipy) to give $[Nb(NCMe_3)Cl_3(bipy)]\cdot 1/12\ C_6H_6$ and with N,N,N',N'-*tetra*methylethylenediamine (tmed) to give $[Nb(NCMe_3)Cl_3(tmed)]$. The tantalum complexes $[Ta(NCMe_3)\text{-}Cl_3(bipy)_2]\cdot 1/3\ C_6H_6$, $[Ta(NCMe_3)Cl_3(tmed)]\cdot 1/6\ C_6H_6$, $[Ta(NCMe_3)(NHCMe_3)Cl_2(bipy)]\cdot 1/2\ C_6H_6$, $[Ta(NEt)Cl_3(NH_2Et)]_2$ and $[Ta(NCHMe_2)(NHCHMe_2)Cl_2(bipy)]$ were also prepared. The complexes were characterized by melting points, chemical analyses and IR and NMR spectra, and suggestions of their geometry given [141]. The crystal structure of $[TaCl(\mu\text{-}Cl)(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$, a Ta(V) complex containing terminal imido, amido and amino ligands, was determined [139] (Bu^t is *tert*-butylamine), see Figure 15.

A methoxynitrene complex of tantalum(V), $[Cl_3(bpy)Ta \equiv NOMe]$, has been prepared and characterized [142]. In the presence of 2,2'-*bi*pyridine (bpy), $TaCl_5$ reacted with O-methylhydroxylamine to form a red *mono*mer complex, exhibiting an X-ray crystal structure with a distorted octahedrally coordinated tantalum atom [142], see Figure 16. The tantalum-nitrogen bond has a distance of 1.744 Å, and it gives an IR absorption band at $950\ cm^{-1}$.

It was shown that $TaCl_5\cdot(CH_3CN)$ and $TaCl_3[O_2S(N{:}C(CH_3)Cl)_2]$ formed when SO_2 was passed through a solution of $TaCl_5$ in CH_3CN; and also isomerization and hydrolyzation reactions were observed, giving $[TaOCl\{N{:}C(CH_3)Cl\}\{OS(O)NHC(O)(CH_3)\}]$ [143].

The preparation of organo-imido complexes of Nb and Ta from reactions of the *penta*halides with amines were studied [140] to obtain simpler and better synthetic procedures. Previously, *mono*alkylamido complexes $Ta(NHR)_2Cl_2(NH_2R)$ with R = Me, Et, Pr^n and Bu^n [144] and

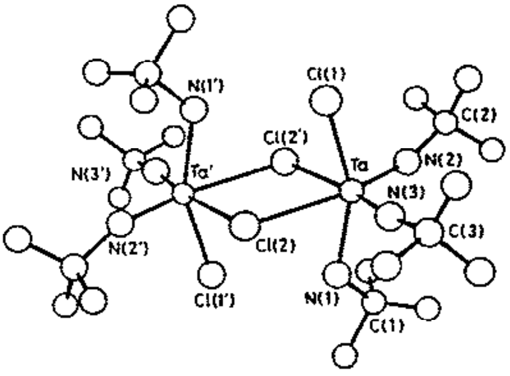


Figure 15. Crystal structure of the *bi*nuclear [TaCl(μ-Cl)(NBu^t)(NHBu^t)(NH$_2$Bu^t)]$_2$ complex. Reproduced with permission from [139], T. C. Jones, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc. Chem. Comm.* **1984** (1984) 205.

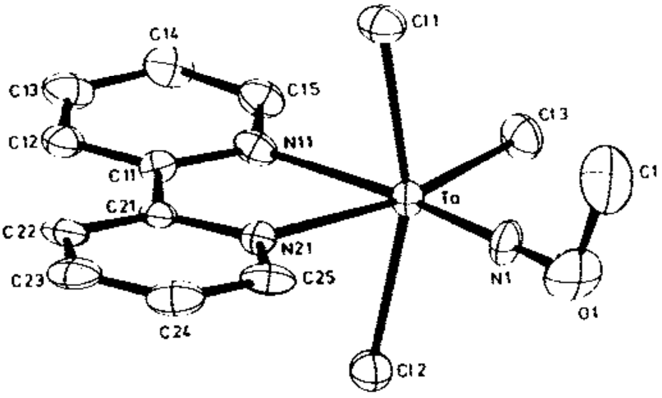


Figure 16. Structure of the [Cl$_3$(bpy)Ta ≡ NOMe] complex. The Nb-N triple bond distance is 1.744 Å and the Ta-N-O angle 174° (nearly linear). Reproduced with permission from [142], K. Haug., W. Hiller and J. Strähle, *Z. Anorg. Allg. Chem.* **533** (1986) 49.

Nb(NHR)$_3$Cl$_2$ with R = Me [145] have been claimed on basis of analytical data. Me$_3$SiNHCMe$_3$ and MCl$_5$ (M = Nb, Ta) react in dry benzene solution to form the imido complexes M(NCMe$_3$)Cl$_3$(NH$_2$CMe$_3$) and these and other compounds were characterized by IR-, ^{1}H and ^{13}C NMR-spectroscopy [140]. The compounds are expected to have octahedral coordination, like what was the case for the one structure which has been solved, see Figure 17. Note the linearity of the $\mathrm{Ta} \equiv \mathrm{N} - \mathrm{C}$ bonding system. Ta-$\mathrm{N_{imido}}$ and Ta-$\mathrm{N_{amido}}$ bond lengths were 1.70 and 2.28 Å, respectively.

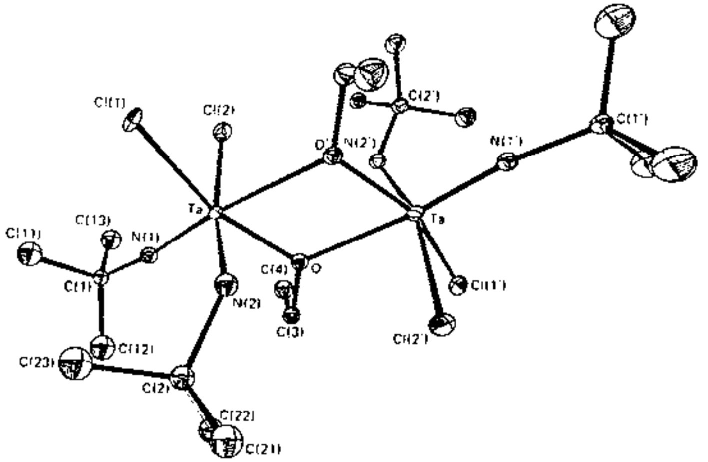


Figure 17. The molecular structure of white $[\mathrm{Ta(NCMe_3)(\mu\text{-}OEt)Cl_2(NH_2CMe_3)}]_2$. Hydrogen atoms have been omitted. Reproduced with permission from [140], P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron* 4 (1985) 1391.

The reaction of $\mathrm{TaCl_5}$ with $\mathrm{Me_3SiNHAr}$ ($\mathrm{NAr = N\text{-}2,4\text{-}C_6H_3\text{-}(Pr^{\mathit{i}})_2}$) in the presence of donor solvents L provides the imido complexes $[\mathrm{Ta(NAr)Cl_3}L_2]$ in high yield (L = tetrahydrofuran, *di*methoxyethane, pyridine, tetrahydrothiophene, *etc.*) [470]. The properties of these imido complexes and their reactions with alkynes were studied. The crystal structure was solved for the complex $[\mathrm{Ta(NAr)(O\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_2}]$, which turned out to confirm the octahedral geometry predicted by NMR data. The bonding in the complexes are discussed [470].

2.7 Nb(V) and Ta(V) oxyhalide complexes with N-donor ligands

$\mathrm{NbOCl_3}$ reacts with acetoxime (HL, $\mathrm{(H_3C)_2C{=}NOH}$) in $\mathrm{CH_3CN}$ to give oximates, $\mathrm{NbOCl_3(H}L)_2$, $\mathrm{NbOCl_2}L(\mathrm{H}L)_2$ and $\mathrm{NbOCl}L_2(\mathrm{H}L)$, in which L^- is N-bonded [122].

Niobium(V) in hydrochloric and sulphuric acid media, in the presence of an excess of chloride or thiocyanate ions, reacts with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HR) to give complexes, $\mathrm{Nb(OH)_3Cl}R$ or $\mathrm{Nb(OH)_3(NCS)}R$, which are extractable into chloroform [146]. The experimental conditions for quantitative extraction of niobium(V) into the organic phase are given, permitting a separation from zirconium(IV) and hafnium(IV). The identity of the complexes was determined spectrophotometrically.

Niobium *penta*chloride reacts with *tri*chloromethane, forming CCl_4 and $NO^+[NbOCl_4]^-$, which latter complex in acetonitril solution reacts with *tri*phenylmethylphosphonium chloride to form $PPh_3Me[NbOCl_4(CH_3CN)]$ [91]. The crystal structure solution of this complex (and the IR and Raman vibrational spectra) show that the niobium is octahedrally coordinated with O and N-bonded CH_3CN in *trans* positions to each other, see Figure 18.

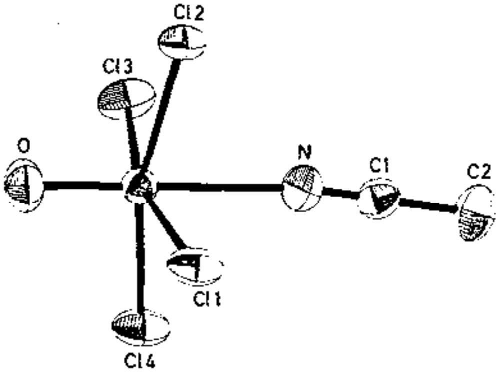
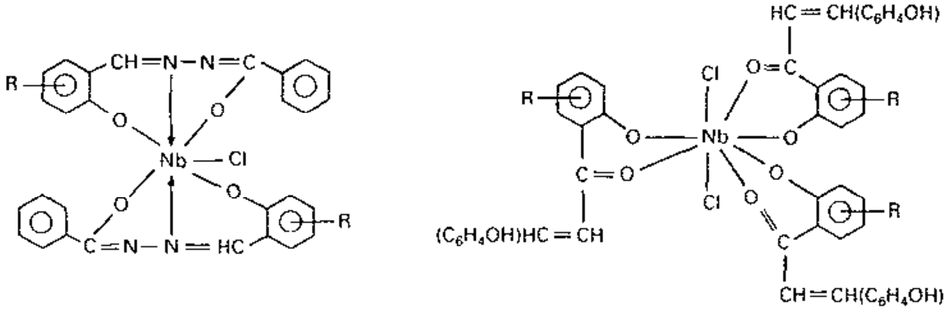


Figure 18. The crystal structure of the $PPh_3Me[NbOCl_4(CH_3CN)]$ complex. Reproduced with permission from [91], W. Hiller, J. Strähle, H. Prinz and K. Dehnicke, Z. *Naturforsch.* **39 b** (1984) 107.

Substituted 2-hydroxy-benzalbenzoyl hydrazones (*L*) react with $NbCl_5$ forming complexes of the type $Nb(L)_2Cl$ [147]. Infrared spectra were interpreted to indicate (*1*) enolisation of the C=O followed by deprotonation and complexation with Nb, and (*2*) azomethine nitrogen complexation with Nb and (3) deprotonation of phenolic OH and complexation with Nb. The central metal ion acquires a coordination number of seven, see Figure 19 (A).

Tantalum(V)-[*bis*-(8-hydroxyquinoline)] coordination compounds $[TaCl_3(BHQ)]$, $[TaOCl(BHQ)]$ and $[TaO(HBHQ)_3]$, with $H_2(BHQ)$ = *bis*-(8-hydroxyquinoline) = $C_{18}H_{10}(OH)_2N_2$, are yellow and insoluble in common organic solvents [148]. Probable structures of the three complexes are given, based on chemical analyses, magnetic measurements, IR spectra and thermograms. The O and N atoms of ligands coordinate to tantalum, forming chelate rings and giving tantalum coordination numbers of 7, 6 and 7, respectively [148].

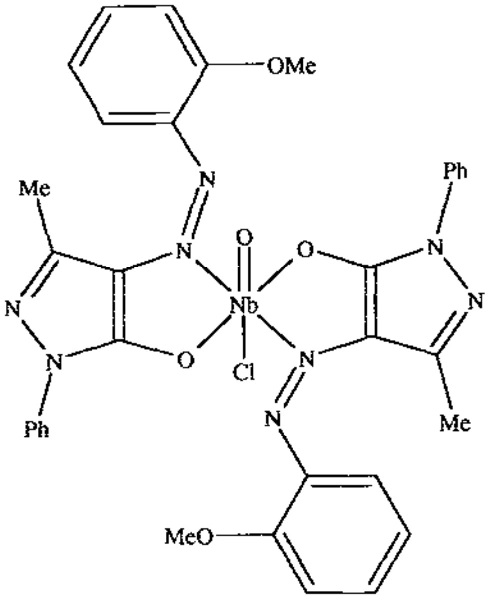
*Di*hydroxychalcones, i.e. substituted 2,2'-*di*hydroxy-benzalacetophenones (L), react with $NbCl_5$ forming complexes of the type $Nb(L)_3Cl_2$ [147]. Infrared spectra were interpreted to indicate complexation to niobium in such a way that the metal acquires a coordination number of eight, see Figure 19 (B).



(A) (B)

Figure 19. The estimated structure of A: benzalbenzoyl hydrazone *mono*mer complexes $Nb(L)_2Cl$ with seven-coordination; B: *di*hydroxychalcone *mono*mer complexes $Nb(L)_3Cl_2$ with eight-coordination. Reproduced with permission from [147], N.S.Biradar, V.L.Roddabasanagoudar and T.M.Aminabhavi, *Indian J.Chem.* **24 A** (1985) 703.

In *di*methylformamide (DMF), niobium*penta*chloride and 1-phenyl-3-methyl-4-(2-methoxybenzeneazo)-5-pyrazolone (PMMBP, an azo-dye) were found to react in a ratio of 1:2 [149]. Based on chemical analysis and IR-spectra the following possible structure, **8**, was proposed for the complex.



8

The complexation reaction of 5,5'-methylene-*bis*-salicylaldoxime (MBSO) with $TaCl_5$ was studied under various conditions (in DMF solution in dry nitrogen or ambient air or in oxalate solution) [127]. The 1:1 compounds obtained were *dia*magnetic and insoluble in common organic solvents. Probable structures (see Figure 20) were proposed on the basis of elemental analysis, magnetic measurements and infrared spectra [127].

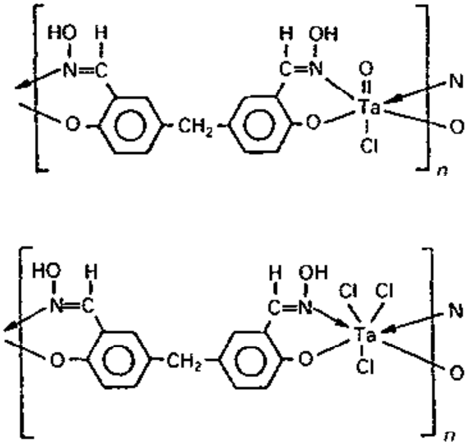


Figure 20. Probable structures of tantalum MBSO complexes $[TaCl_3C_{15}H_{12}O_4N_2]$ and $[TaClC_{15}H_{12}O_5N_2]$ with five and seven-coordinated Ta. Reproduced with permission from [127], S. Chomal, A. S. Aazmi and G. C. Shivahare, *Acta Chim. Hung.* **122** (1986) 127.

The tantalum(V) *coordination polymers* of 5,5'-methylene-*bis*-salicylaldehyde-aniline Schiff-base (MBSASB), 5,5'-methylene-*bis*-salicylaldehyde-o-phenylenediamine Schiff-base (MBSOPDSB) or 5,5'-methylene-*bis*- salicylaldehyde-*tri*ethylenetetramine Schiff-base (MBSTETASB) have been prepared and characterized [150]. The Schiff-bases are double-acting *bi*dentate ligands which coordinate to tantalum via nitrogens and oxygens on both sides. Tantalum is in turn 6 or 7 coordinated and form polymeric chains:

$$\cdots\text{- Schiff-base - }TaO_xCl_y\text{ - Schiff-base - }TaO_xCl_y\text{ - }\cdots$$

2.8 Nb(V) and Ta(V) thiohalide complexes with N-donor ligands

$NbSBr_3$ reacts with ligands to give $NbSBr_3{\cdot}2L$ (for ligands L = CH_3CN, py, 1,4-thioxane, tetrahydrothiophene), $NbSBr_3{\cdot}3py$, and $NbSBr_3{\cdot}bpy$ (py = pyridine, bpy = 2,2'-*bi*pyridine) [115]. $NbSeBr_3$ reacts only with CH_3CN to give $NbSeBr_3{\cdot}2CH_3CN$. The complexes were characterized by IR, ^{1}H NMR, and diffuse reflectance spectra and electrical conductivity [115].

Complexation of thiopicolinamides TPMA and TPA with niobium(V) was studied in dry DMF-methanol medium (TPMA = thiopicolinmethylamide and TPA = thio-picolinanilide) [151]. Insoluble nine-coordinated *bi*-nuclear [$Nb_2Cl_4L_6$] compounds were formed, having two Cl bridges and three pairs of NS coordinated chelate rings, according to chemical analyses and IR-spectra, see Figure 21.

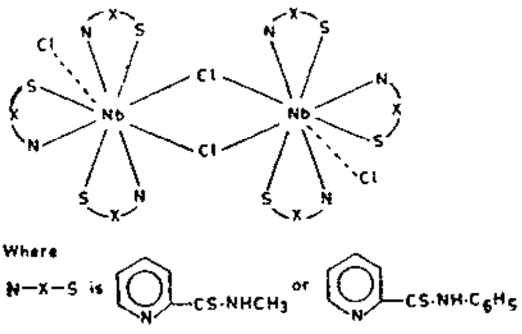


Figure 21. Proposed structures of thiopicolinanilide and thiopicolinmethylamide niobium(V) complexes. Reproduced with permission from [151], R. K. Sharma and G. C. Shivahare, *J. Indian Chem. Soc.* **62** (1985) 18.

2.9 Nb(V) and Ta(V) halide complexes with C-donor and other ligands

Because of the short Nb-C and Ta-C bond lengths observed experimentally, the complexes in this section can be taken to be in the oxidation state +V.

The d^0-d^0 *di*tantalum complex [$TaCl_2(SMe_2)(N\text{-}C_6H_5)]_2(\mu\text{-}Cl)_2$ can be prepared from the reaction of $Ta_2Cl_6(Me_2S)_3$ and azo-benzene in benzene-toluene solution (like the *iso*-structural niobium compound) [152]. Single crystal X-ray data show a *di*nuclear compound, adopting a distorted edge-sharing *bi*-octahedral structure, see Figure 22. The Ta=N-Ph distance is 1.747(8) Å. IR data are given [152].

After the first characterization in 1980 of a η^2 -alkyne complex (the anion [$TaCl_4(py)(PhCCPh)]^-$ with py = pyridine and PhCCPh = *di*phenylacetylene), several similar complexes have now been described. By use of $NbCl_4(THF)_2$ (THF = tetrahydrofuran) as a starting material, the following compounds have been obtained and characterized by means of their crystal structures (PhCCMe = 1-phenyl-1-propyne): $NbCl_3(PhCCPh)$ [153],

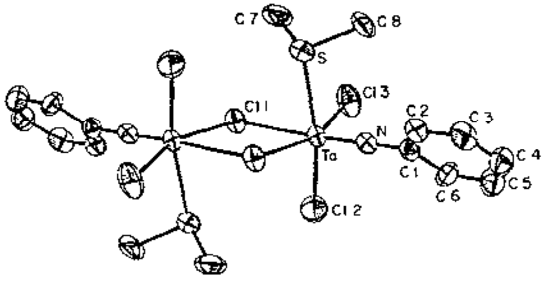


Figure 22. Drawing of the $[TaCl_2(SMe_2)(N\text{-}C_6H_5)]_2(\mu\text{-}Cl)_2$ molecule. Reproduced with permission from [152], J. A. M. Canich, F. A. Cotton, S. A. Duraj and W. J. Roth, *Polyhedron* **5** (1986) 895.

and $NbCl_3(PhCCPh)(THF)_2$ [154], $NbCl_3(PhCCMe)(THF)_2$ [154], $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot 0.5(THF)$ [154],and $Nb_2OCl_{43}(PhCCPh)(THF)_4$ [154]. The structures are illustrated in Figures 23 and 24. It is evident that a sevenfold coordination around the metal atom is preferred. Note also the threefold coordination around the Cl1 ligands in Figure 23.

Silaacyl derivatives of tantalum have been discovered: $(Cp^*)Cl_3Ta[\eta^2\text{-}COSiMe_3]$, with $Cp^* = \eta^5\text{-}C_5Me_5$ and Me = methyl [155-156], $(Cp^*)Cl_3Ta[\eta^2\text{-}OC\mathit{L}SiMe_3]$ where the Lewis donor *L* binds to the η^2-silaacyl carbon atom [156], $(Cp^*)Cl_3Ta\{\eta^2\text{-}OC(SiMe_3)[P(OMe)3]\}$ [157] and $(Cp^*)Cl_2Ta(\eta^4\text{-}OC(SiMe_3)P(OMe)_2O$ [157]. X-ray crystal structure, as well as spectroscopic and reactivity data of these six and seven coordinate complexes are given.

2.10 Nb(V) and Ta(V) pseudo-halide complexes with oxy-donors

Tri-alkoxy *di-pseudo*halide niobium(V) complexes, $Nb(OR)_3(Ps)_2$ (where $R = CH_3$, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$ and $Ps = CN^-$, NCO^-, NCS^- and N_3^-) have been prepared using chloride/pseudohalide exchange in hot dry tetrahydrofuran solution. The sixteen light-yellow to dark-brown compounds were characterized as $Nb(OR)_3(Ps)_2$ on the basis of chemical analyses and IR spectral data [118].

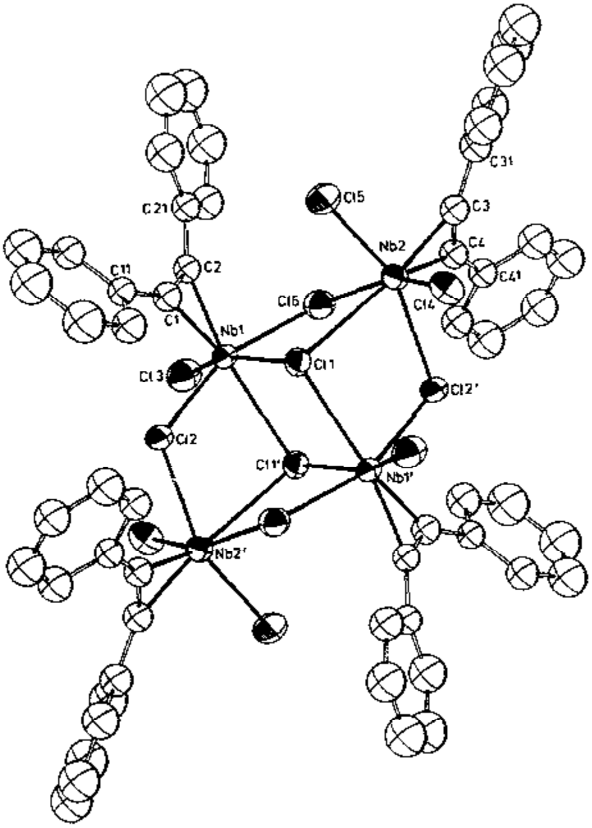
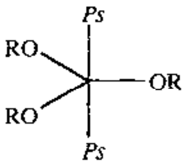


Figure 23. Structure of the tetrameric alkyne niobium(V) complex: $(NbCl_3(PhCCPh))_4$ [153]. Reproduced with permission from [153], E. Hey, F. Weller and K. Dehnicke, *Z. Anorg. Allgem. Chem.* **514** (1984) 25.

Also, belonging to the above series, seven *tri*-phenoxy *di-pseudo*halide niobium(V) complexes, $Nb(OR)_3(Ps)_2$ (where $R = C_6H_5$ (phenyl) and $Ps = CN^-, NCO^-, NCS^-, N_3^-, NH_2^-$ and $C_9H_6NO^-$ (oxine)) were prepared using chloride/pseudohalide exchange in hot dry acetonitrile or tetrahydrofuran solution [158]. These brown compounds were characterized as $Nb(OR)_3(Ps)_2$. Analytical data, conductance, and IR and pronton NMR spectral data were reported [158]. A *mono*meric trigonal *bi*pyramidal structure, **9**, was assumed:



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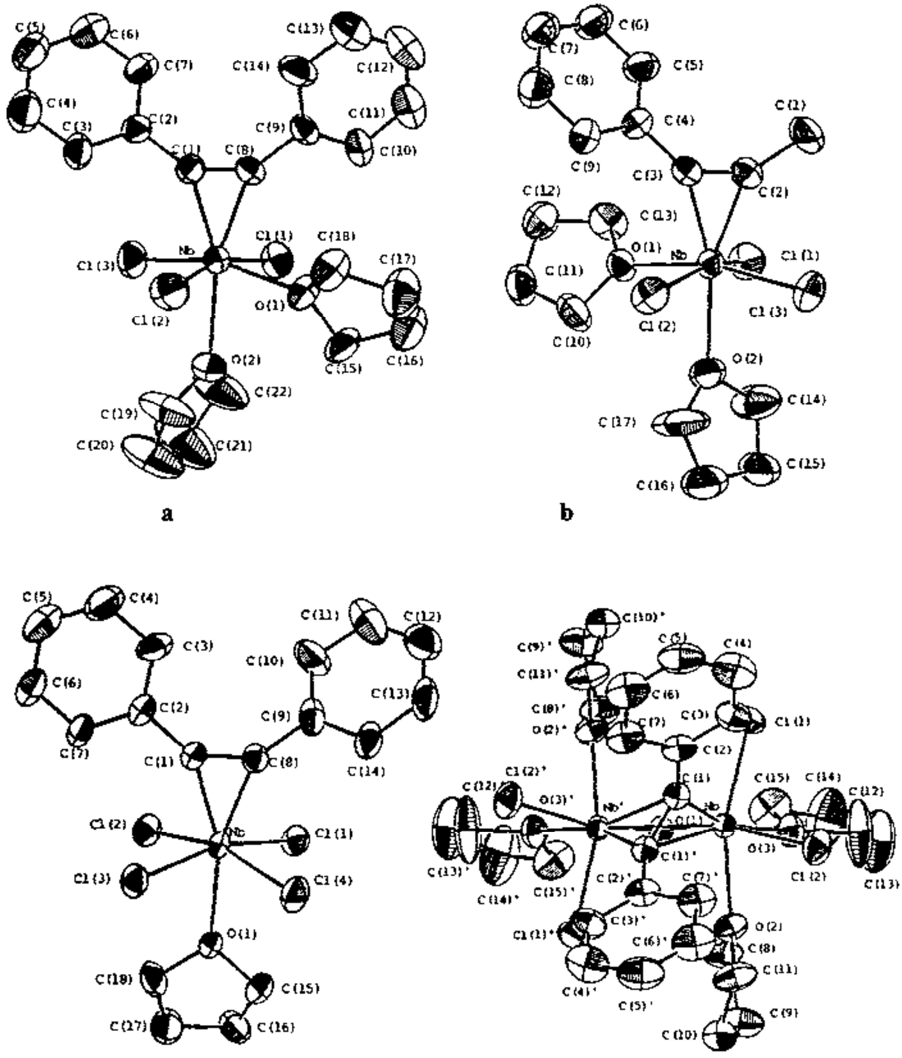


a

b

c

d

Figure 24. Structures of new alkyne niobium(V) complexes: (a) = $NbCl_3(PhCCPh)(THF)_2$, (b) = $NbCl_3(PhCCMe)(THF)_2$, (c) = $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot 0.5(THF)$, and (d) = $Nb_2OCl_{43}(PhCCPh)(THF)_4$ [154]. The crystal structures a. Reproduced with permission from [154], F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 508.

Reactions of acetyl *iso*thiocyanate, CH_3CONCS, with *iso*propoxides of Nb(V) and Ta(V) in dry benzene give products of the type $M(OPr^i)_{5-x}(NCS)_x$, $x = 1$ to 4 [159]. On the basis of IR spectra and molecular weight determinations, it was concluded that the *mono*- and *di*-thiocyanato derivatives are *di*meric with double alkoxy bridging; no information is given on the higher thiocyanates.

The *tri*-alkoxy (or *tri*-phenoxy) *di*-chloride niobium(V) complexes, $Nb(OR)_3Cl_2$, where $(OR)_3 = (OCH_3)_3$, $(OC_2H_5)_3$, $(i\text{-}OC_3H_7)_3$, $(n\text{-}OC_4H_9)_3$, $(OC_6H_5)_3$, $[(OC_6H_4O)+(OC_6H_4OH)]$, $[(O_2C_6H_3OH)+(OC_6H_3(OH)_2)]$, react with $NaNO_2$, $AgNO_2$ or $AgNO_3$ in dry tetrahydrofuran forming $Nb(OR)_3L_2$ with $L = NO_2^-$, ONO^- or ONO_2^- [119]. The 21 complexes formed were characterized by chemical analysis and IR spectroscopy [119].

New *pseudo*halide, oxine and amido derivates of niobium(V) *di*chloro *tri*-catecholoate or *tri*-pyrogallolate complexes, $[Nb(Ps)_2(X)]$, where $Ps = CN^-$, NCO^-, NCS^-, N_3^-, NH_2^- and $C_9H_6NO^-$ (oxine) and $X = (OC_6H_4O)(OC_5H_4OH)$ (*tri*-catecholate) or $(OC_6H_3O\text{-}HO)(OC_5H_3(OH)2)$ (*tri*-pyrogallolate), were isolated and characterized by chemical analysis and IR spectra [160]. Also, these 12 coloured solids are *mono*meric with an assumed trigonal *bi*pyramidal coordination geometry.

2.11 Oxides of niobium(V) and tantalum(V)

Niobium and tantalum oxides are numerous, and structurally very complicated and elaborate. Columbite-tantalite series of minerals of general composition $(Fe,Mn)(Nb,Ta)_2O_6$ and pyrochlore minerals are in this respect no exception. The pentoxides and many other phases are built of MO_6 octahedra sharing edges and corners, but this can be (and is) done in an almost unlimited number of ways (block structures). By partial oxygen loss various subvalent phases are formed, *e.g.* $Nb_{22}O_{54}$, NbO_2, NbO and so on.

The presence of the molecules Nb_2O_4, Nb_2O_5, Nb_4O_9, and Nb_4O_{10} were identified in the gas phase over lithium niobate [161]. The molecules were characterized thermochemically (atomization energies and standard heats of formation) [161].

Defect structures in non-stoichiometric Nb_2O_5 was treated statistically [162]. At high temperatures and pressures, Nb_2O_5 and Ta_2O_5 solids may be reduced by Ta metal foil to form NbO_2 and TaO_2 phases [163]. Shock-induced phases in Nb_2O_5 were studied by X-ray diffraction analysis and high-resolution electron microscopy [164-165].

Recrystallization experiments in closed silica glass ampoules with H-Nb_2O_5/$NbCl_5$ mixtures gave crystals of N-Nb_2O_5, B-Nb_2O_5 and T-Nb_2O_5 depending on circumstances [166].

The specific heat of the high temperature modification of α''-Ta_2O_5 were determined at 10-320 K [167]. Thermodynamic properties were reported. A phase transition was observed at 215.3 K [168]. The thermodynamic properties of rhombic β-Ta_2O_5 were redetermined by the e.m.f. method at high temperatures [169], and below room temperature by the method of adiabatic calorimetry [170]. The dependence of the electronic structure of Ta_2O_5 on coordination number and symmetry of nearest coordination sphere around Ta was determined [171]. A high temperature phase transition in Ta_2O_5 were found [172].

X-ray photoelectron spectroscopic analysis of 4 keV Ar^+-bombarded Nb_2O_5 and $NaNbO_3$ has revealed the formation of lower-valence oxides and even metallic niobium [173].

The structure of Nb_2O_5 phases [174] and the many Nb_2O_5, $LiNbO_3$ and $NaNbO_3$ polymorphs have been described, *e.g.* in relation to the phases within the Li_2O-Nb_2O_5 system [175-177], the Li_2O-Nb_2O_5-Ta_2O_5 system [178].

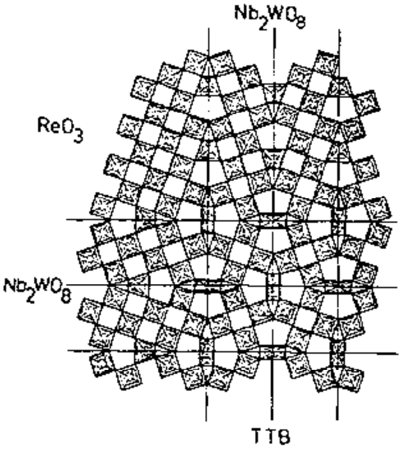


Figure 25. Twin planes relating the structure of ReO_3-type to the framework structures of Nb_2WO_8 and the tetragonal tungsten bronze (TTB), Na_xWO_3 [179]. Reproduced with permission from *Chemica Scripta* **26** (1986) 547, article by B.-O. Marinder.

The $NaNbO_3$-Nb_2O_5-WO_3 system was reviewed [179]; very complicated structures occur: $Na_2Nb_4O_{11}$, $NaNb_3O_8$, $Na_2Nb_8O_{21}$, $NaNb_7O_{18}$, $NaNb_{13}O_{33}$ [180], $WNb_{12}O_{33}$, $W_3Nb_{14}O_{44}$, $W_4Nb_{26}O_{77}$, Nb_2WO_8, $Nb_{26}W_{26}O_{143}$ [181-182], just to mention a few. Also,

$Na_2Ta_4O_{11}$ and $Ag_2Ta_4O_{11}$ were characterized [183-184]. Many of these structures are based on cumulated blocks of octahedra like in ReO_3, or related to the tetragonal tungsten bronze (TTB) structure, known from *e.g.* Na_xWO_3. One typical example is shown in Figure 25 for the case of Nb_2WO_8 [179].

A powder sample of $LiNbO_3$ was investigated by ^{93}Nb NMR two-dimensional spectroscopy [70]. $LiTaO_3$ single crystals were studied by Raman spectroscopy in ferro- and *para*-electric phases and extensive assignments of observed bands were given [185]. A lithium insertion compound $(Li,Cu)TaO_3$ with the $LiNbO_3$ structure was prepared [471]. $AgNbO_3$ single crystals were studied by Raman spectroscopy at different temperatures, revealing a complex sequence of phases [186].

Polymorphism at high temperatures was studied in the oxides Li_3NbO_4 and Li_3TaO_4 having nearly rock-salt structure [81], and these salts were characterized by X-ray powder diffracion and infrared spectroscopy [80,82]. Comments were given on the formation of $LiNb_3O_8$ [176]. The binary systems Li_2O-M_2O_5 were reinvestigated and phases like *e.g.* $Li_{16}M_4O_{18}$ (M = Nb or Ta) [177], $Li_2Nb_6O_{16}$ [187] and $Li_2Nb_{28}O_{71}$ [188] found. Compound formation among Li_3NbO_4 and Li_2WO_4 or $LiNb_3O_8$ and TiO_2 was studied in the solid state [189-190]. The reaction of Ta_2O_5 and Li_2CO_3 was studied by mass spectra, thermogravimetry, and X-ray phase analysis to establish the mechanism of the $LiTa_3O_8$ formation [191]. If tantalic acid was used in stead of Ta_2O_5, similar results were obtained [192]. The *ortho*tantalate Li_3TaO_4 has been protolysed to form $Li_{1.2}H_{1.8}TaO_4$ and $Li_{1.1}H_{1.9}TaO_4$ having rock-salt related structures [193]. Proton motion in solid $HNbO_3$ and $HTaO_3$ (obtained by H^+-Li^+ ion exchange) was determined by proton NMR relaxation [194]. The electric conductivity of $HNbO_3$ powder was measured by impedance spectroscopy [195]. $LiNbO_3$ and $LiTaO_3$ phases have been substituted in part with the pair Cu(II)-Ti(IV) [196]. Ferroelectric tungsten-bronze single crystals $K_3Li_2Nb_5O_{15}$ have been grown [197].

$NaTaO_3$ and $Na_2Ta_4O_{11}$ phases were prepared by decomposition of pyrochlores obtained under hydrothermal conditions [183].

To the already known structures of crystals formed from mixtures of potassium oxide and niobium pentoxide, (*e.g.* $KNbO_3$, KNb_3O_8 and $K_8Nb_{18}O_{49}$ and the long list of non-stoichiometric K_2O:Nb_2O_5 mixtures), $K_3Nb_7O_{19}$ has now been added. It forms white triclinic crystals with a structure, solved by X-ray diffraction methods, consisting of edge-shared pairs of octahedra. As Figure 26 shows, the pairs of octahedra are corner-shared to one another to form double strings seven pairs long, and the strings are corner-shared to other strings forming tunnels [198]. A high-resolution electron microscopic study of the $KNbO_3$-Nb_2O_5 system has confirmed the existence of layer structures $K_4Nb_6O_{17}$ and *L*-KNb_3O_8, three tetragonal tungsten-bronze related structures and a block structure $KNb_{13}O_{33}$ [199].

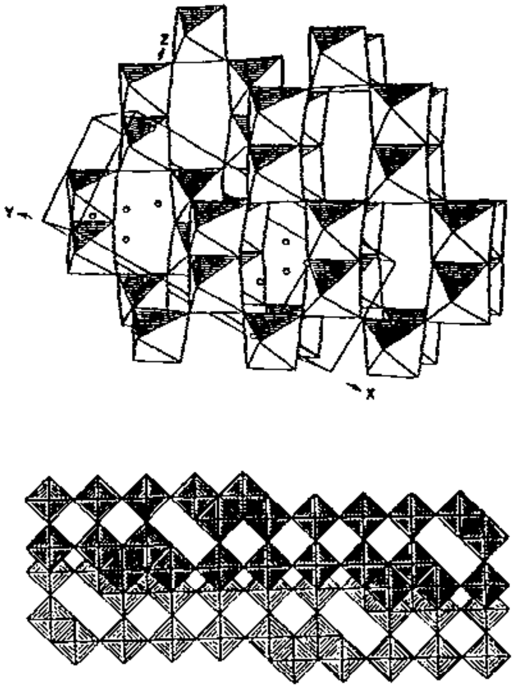


Figure 26. View of the structure of $K_3Nb_7O_{19}$ showing one of the sets of tunnels. Open circles represent K in the unit cell. Also shown is an idealized diagram of the block structure. Reproduced with permission from [198], G. D. Fallon, B. M. Gatehouse and L. Guddat, *J. Solid State Chem.* **61** (1986) 181.

The compounds $LiNbWO_6$ and $LiTaWO_6$ have been protolysed to form $HNbWO_6$ and $HTaWO_6$ in hot aqueous H_2SO_4 [200-201]. The reaction is accompanied by a structural transformation from the rutile to the ReO_3 structure. Compounds were characterized by chemical analysis, X-ray powder diffraction, thermogravimetry and IR spectroscopy [200].

Methods for synthesis of *anti*ferroelectric bismuth *ortho*tantalate, $BiTaO_4$, [202] and *di*electric antimony *ortho*tantalate, $SbTaO_4$ [203], were studied.

In the Cu_2O-Ta_2O_5 system, $Cu_5Ta_{11}O_{30}$ and $Cu_3Ta_7O_{19}$ phases were prepared *in vacuo* at high temperatures and studied by X-ray diffraction [204]. They have similar structures, based on layers of α-U_3O_8 type (containing pentagonal *bi*pyramids) and layers composed of octahedra, only differing in the sequence of these layers [205].

The $CaTa_2O_6$ and $CaTa_4O_{11}$ phases were prepared at high temperature and studied by high-resolution transmission electron microscopy. The resulting structure was compared with computer simulated images [205]. In $CaTa_2O_6$ tantalum is octahedrally, in $CaTa_4O_{11}$ pentagonal *bi*pyramidally and octahedrally coordinated [205]. X-ray powder diffraction data were given for *mono*clinic $2TiO_2 \cdot 5Nb_2O_5$, prepared by simultaneous hydrolysis of titanium and niobium alkoxides [206].

The crystal structure has been found for a new kind of lamellar niobate, $Ba(Nb_3O_8)_2 \cdot H_2O$. The layers are similar to those of KNb_3O_8, but one layer out of two is displaced [207].

Iron niobate crystals form an ordered super-structure of α-PbO_2, the Columbite-type, $FeNb_2O_6$, see Figure 27(c), according to a neutron powder diffraction stydy (Rietveld profile-refinement method) [209]. During preparation, it appears to be essential to control the partial pressure of oxygen; low pressures favour the formation of *tri*-rutile structure phases with high content of Fe^{2+}, according to X-ray and Mössbauer data [210]. The *tri*-rutile $FeNb_2O_6$ structure was solved by single crystal X-ray diffraction and found to consist of chains of MO_6 octahedra (M = Fe or Nb, disordered), in which each octahedron shares a pair of opposite edges [211]. The *tri*-rutile structure was confirmed for $FeTa_2O_6$ in an investigation covering X-ray and neutron diffraction, magnetic susceptibility, heat capacity and Mössbauer techniques [212]. The magnetic structures of this Fe(II)-compound was also described. Iron tantalates $FeTaO_4$, $FeTa_2O_6$ and $Fe_4Ta_2O_9$ have a considerable range of non-stoichiometry [213].

Crystals of Sr_4FeTaO_8 and Sr_4CoTaO_8 with K_2NiF_4 structure were examined by X-ray and electron diffraction and magnetic susceptibility measurements [214]. The crystals were unstable in air. The structures and electronic spin states were discussed [214]. Rutile phases related to $CrNbO_4$ (which contains Nb(V)) have been prepared and characterized in terms of the structural, magnetic and electronic properties [215]. Thermal interaction between Ta_2O_5 and Co_3O_4 at high temperatures, led to the formation of $CoTa_2O_6$ and other phases [216].

Single crystals of $NiTa_2O_6$ were prepared and investigated by X-ray methods [208]. The structural relationships were systematised between the different ordered and disordered AB_2O_6 and ABO_4 oxo-metallates, *e.g.*the α-PbO_2 and Columbite structures, see Figure 27. Mixed phases, $Zn(Nb_xTa_{1-x})_2O_6$ are known also [217].

In the CaO-Nb_2O_5-P_2O_5 system, $CaNb_2O_6$, $Ca_3Nb_2O_8$, β-Nb_2O_5, NbO_2 and $NbO(PO_4)$ are formed at 1400 °C [218-219], and in the BaO-Nb_2O_5-P_2O_5 system, $BaNb_2P_2O_{11}$ is formed [220]. By heating, the latter compound decomposes into oxides and $NbOPO_4$. The crystal structures were solved for $BaNb_2P_2O_{11}$ (isomorphous with $BaNb_2V_2O_{11}$) and $NbPO_5$ (NbO_6 octahedra joined to PO_4 tetrahedra, forming a framework) [220]. Other phosphates are mentioned in a later section.

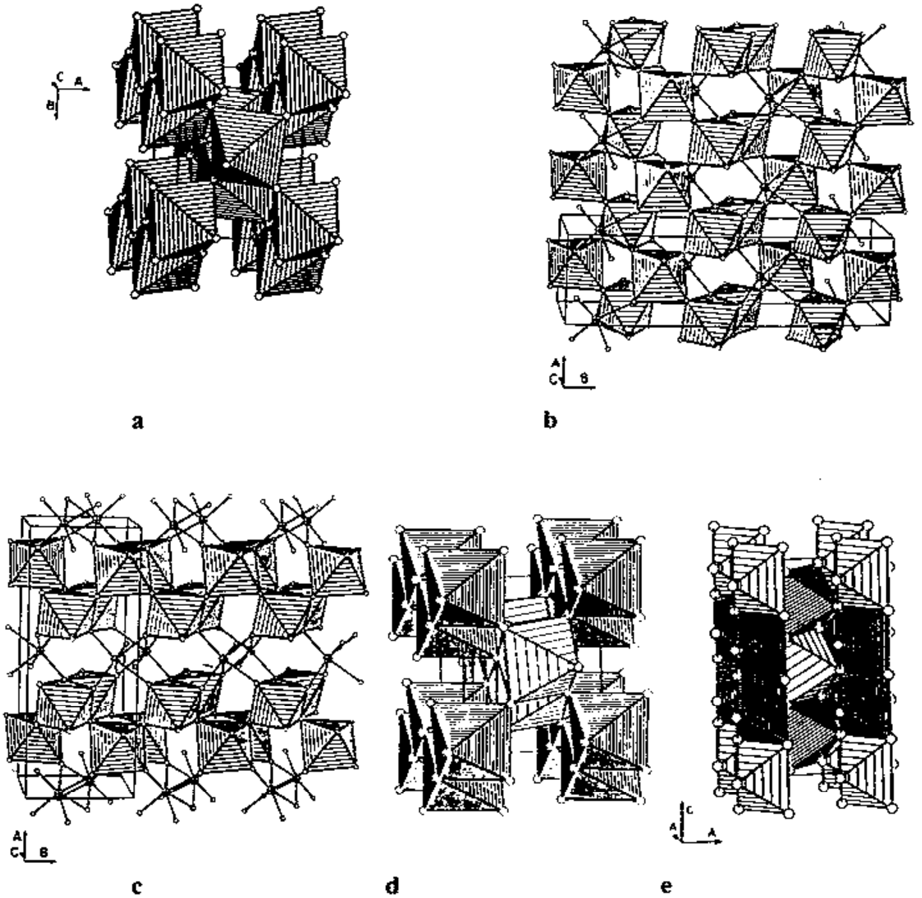


Figure 27. Crystal structures of (**a**): α-PbO_2, (**b**): $ZnTa_2O_6$ in the α-PbO_2 type structure with Zn^{2+} and Ta^{5+} octahedra (the latter are hatched), (**c**): $ZnNb_2O_6$ belonging to the Columbite type structure, with $Nb5^{+}$ octahedra hatched, (**d**): $FeNbO_4$ in the Wolframite type structure, with Fe^{3+} and Nb^{5+} differently hatched and (**e**) $NiTa_2O_6$ in the rutile SnO_2 type structure, with Ta^{5+} densely hatched. Reproduced with permission from [208], H. Müller-Buschbaum and R. Wichmann, *Z. Anorg. Allgem. Chem.* **536** (1986) 15.

Compounds formed in the BaO-Nb_2O_5, BaO-Nb_2O_5-TiO_2, BaO-Nb_2O_5-V_2O_5, CaO-Nb_2O_5-P_2O_5 and BaO-Nb_2O_5-P_2O_5 systems have been studied by X-ray phase and structure analyses [218, 220-223]. In the BaO-Nb_2O_5 system, $Ba_4Nb_2O_9$ and $Ba_5Nb_4O_{15}$ were identified [221]. Compounds $Ba_6Ti_{14}Nb_2O_{39}$, $Ba_{14}Ti_{40}Nb_2O_{99}$, $Ba_{10}Ti_{28}Nb_2O_{72}$

and $Ba_{18}Ti_{54}Nb_2O_{132}$ were isolated and their structures studied [222]. In the BaO-Nb_2O_5-V_2O_5 system, at 700-850 °C tetragonal $Ba_4Nb_2V_2O_{14}$ and rhombohedric $BaNb_2V_2O_{11}$ were formed, among others [223]. The crystal structure of the latter was determined. It contained NbO_6 octahedra linked through vertices, forming ReO_3-type infinite layers of composition $Nb_2O_6^{2-}$ [223].

Compounds formed in the ZnO-Nb_2O_5 and ZnO-Nb_2O_5-A_2O systems (A = Na, K) have been studied by X-ray phase analyses [224]. In the ZnO-Nb_2O_5 system, $Zn_3Nb_2O_8$, $ZnNb_2O_6$ and other phases were identified [224]. Compounds $K_3Zn_{0.33}Nb_{7.67}O_{21}$, $K_2Zn_2Nb_4O_{13}$ and $K_2M_3Nb_3O_{13}$ where M is Al, Cr, Ga, Fe, Sc, Y, or In were isolated and their properties studied [224].

Compounds formed in the PbO-Nb_2O_5-K_2O system have been studied by thermal and X-ray phase analyses, and a compound, $K_{2x}Pb_{1-x}Nb_2O_6$, was found [225]. The formation of sodium and potassium lead niobates, $Na_2Pb_4Nb_{10}O_{30}$ and $K_2Pb_4Nb_{10}O_{30}$, by the method of heating mixtures of Na_2CO_3 or K_2CO_3, Nb_2O_5 and PbO powders were studied by thermogravimetry and X-ray diffraction [226]. The $K_2Pb_4Nb_{10}O_{30}$ phase melts congruently at 1600 K [227].

A series of oxides, $AM_3O_9(M_2O_4)_n$, has been made and characterized by X-ray and electron diffraction. The series was derived from the rutile structure by chemical twinning (*e.g.* A = Na, K; M = Ba, Fe, Ti, Nb; n = 2 and 4) [228]. The *penta*valent oxidation state of niobium is counterbalanced by the presence of *tri*-valent ions (*e.g.* Ti(III), Fe(III)) in the rutile structure.

A topotactic dehydration of the lamellar oxide $HK_2Ti_5NbO_{14}\cdot H_2O$ to the oxide $K_4Ti_{10}Nb_2O_{27}$ was performed, and the process studied by electron and X-ray diffraction [229]. The structural model of $K_4Ti_{10}Nb_2O_{27}$ involved intergrowth of $K_3Ti_5NbO_{14}$ layers with the $K_2Ti_6O_{13}$ tunnel structure [229].

The compound $LiNbGeO_5$, recently prepared [230], have been found to give a strong blue luminescence when irradiated with UV light at low temperatures [231]. The crystal structure is similar to that of sillimanite (Al_2SiO_5) with octahedrally coordinated Nb^{+5}, distorted in a way similar to that of α-$NbPO_5$, i.e. with one shorter and one longer Nb-O distance (1.78 and 2.32 Å, respectively). The Raman spectrum of $LiNbGeO_5$ was reported [231].

The formation of calcium pyroniobate, $Ca_2Nb_2O_7$ (as well as $Sr_2Nb_2O_7$ and $Ca_2Ta_2O_7$), in a sodium chloride/sulphate melt at 800-850 °C was reported [232]. Substitutions in $Ca_2Nb_2O_7$, $(Ca_xM_{1-x})_2(Ti_{1-x}Nb_x)_2O_7$, with pyrochlore and perovskite-type layer structures, were also studied for M = La, Pr, Nd, Sm, Dy, Bi and $0 < x < 1$ [233].

The self-diffusion of ^{89}Sr, ^{140}Ba and ^{95}Nb cations in strontium and barium niobates $BaNb_2O_6$, $SrNb_2O_6$, $Sr_2Nb_2O_7$, $Sr_6Nb_2O_7$ and $Sr_5Nb_4O_{15}$ has been studied in an effort to understand the solid-state high-temperature reactive-diffusion processes between $SrCO_3$

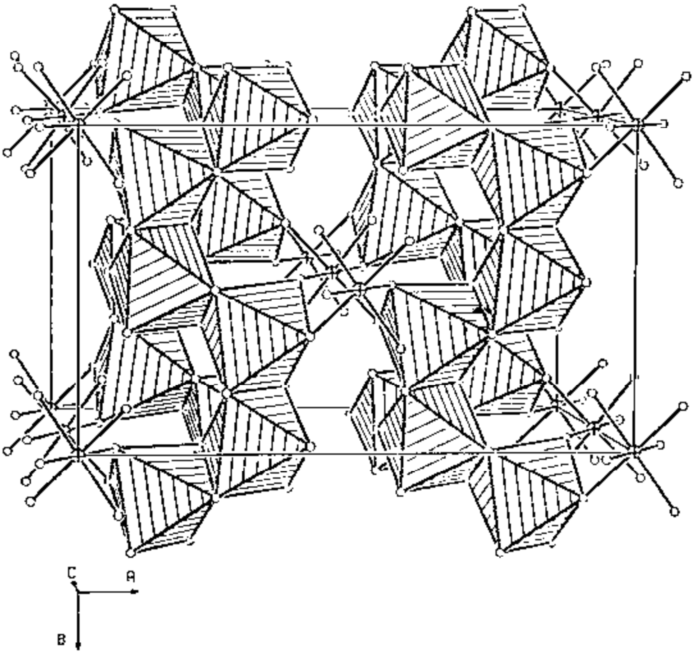


Figure 28. Crystal structure of $Zn_4Ta_2O_9$, showing edge-linked TaO_6 and $Ta_{0.5}Zn_{0.5}O_6$ octahedra (hatched) and chains of TaO_6 octahedra (not hatched). Reproduced with permission from [242], M. Waburg and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **522** (1985) 137.

(SrO) and Nb_2O_5 [234]. The X-ray crystal structure of $SrNb_2O_6$ and $SrNb_6O_{16}$ was solved by the Rietveld powder diffraction profile technique [235]. The crystallization of $BaNb_2O_6$ was described in [236].

The luminescence in $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ were compared with other luminescing perovskite-like niobates and tantalates with structures based on corner-sharing NbO_6 and TaO_6 octahedra, and with the associated electronic delocalization playing an important role for the luminescense [237]. The X-ray powder diffraction diagrams of $TiNb_2O_7$, $ZrNb_2O_7$ and mixed phases thereof were given in [238].

The X-ray single crystal structure of $Ni_4Nb_2O_9$ was shown to consist of a three-dimensional framework of NiO_6-octahedra, between which isolated pairs of NbO_6-double octahedra $[Nb_2O_9]$ are deposited [239]. The structure is much more complicated (480 atoms *per* cell) than those of similar compounds with Co, Fe, Mn or Mg substituting Ni; compounds which also have cumulated NbO_6-double octahedra.

Mixed oxides $Nb_2Te_2O_9$ and $Ta_2Te_2O_9$ were prepared by solid state reactions between oxides TeO_3 and Nb_2O_5 or Ta_2O_5. Crystal data, IR spectra and thermal decomposition processes were given [240]. The crystal structure of $Ta_2Te_2O_9$ was solved [241]. It contains two different kinds of TaO_6 octahedra, sharing oxygens with each other and with TeO_4 tetrahedra.

A new compound, $Zn_4Ta_2O_9$, was synthesized by high temperature reaction. The structure was solved and found [242] to consist of a Zn/O-network with incorporated one-dimensional TaO_6-chains, see Figure 28.

Also $Sr_4Ta_2O_9$ has been studied and it seems to have a complex perovskite super-structure which manifests itself on X-ray diffraction photographs and electron micrographs [243].

Single crystals of *mono*clinic $Ta_2Te_2O_9$ were grown from Ta_2O_5-TeO_2 melts [244]. The solved X-ray crystal structure showed infinite puckered layers of composition $(Te_4O_{12})_n$ alternating with layers of nearly regular TaO_6 octahedra sharing corners. The Ta-O bond distances ranged between 1.88 and 2.07 Å [244].

New complex F_{d3m}-pyrochlore $A_2(M'_{1-x}M''_x)_2O_7$ type oxides have been made, with A = Y and $M'_{1-x}M''_x = Mn_{2/3}^{2+}Nb_{4/3}^{5+}$, $Mn_{2/3}^{2+}Ta_{4/3}^{5+}$, $Mn^{3+}Nb^{5+}$ or $Mn^{3+}Ta^{5+}$. Oxidation states were obtained from the measured magnetic susceptibility, and hexagonally indexed powder X-ray diffraction patterns were given [245]. Bronzoid and pyrochlore phases $A_xNb_xW_{1-x}O_3$ have been characterized in the $KNbO_3$-WO_3 and $CsNbO_3$-WO_3 systems (A = K, Cs; $x < 0.5$) [246]. Pyrochlore type compounds $KMWO_6{\cdot}H_2O$ (M = Nb, Ta), or perhaps more correctly $(KH_2O)(MW)O_6$, were synthesized and characterized by thermogravimetry, differential scanning calorimetry and X-ray powder diffraction [247].

Complex oxides of the type $La(M'_{0.67}M_{0.33})O_3$, for M' = Mn, Co, Ni and Mg and M = Nb and Ta, with a perovskite structure, have been made and studied by X-ray diffraction [248].

The system La_2O_3-Li_2O-Nb_2O_5 was studied, and a new phase, $La_3Li_7Nb_2O_{13}$, was found [249]. X-ray diffraction diagrams of this compound and of La_2LiNbO_6 are given [249-250]. In the system La_2O_3-Li_2O-Ta_2O_5, two new phases, La_2LiTaO_6 and $La_3Li_7Ta_2O_{13}$, were identified by X-ray diffraction [250-251]. La_2LiNbO_6 and La_2LiTaO_6 are ordered *ortho*rhombic perovskites, whose vibrational spectra are known [252].

In the system Bi_2O_3-Nb_2O_5, complicated ordered solid solution structures, being related to those of fluorite, pyrochlore and perovskite, were studied by high-resolution electron microscopy and electron diffraction in order to elucidate structural principles [253]. Very impressive pyrochlore-like units of cumulated octahedra were found [254]. A high resolution electron micrograph of $Bi_4Nb_2O_{11}$ was given in [255]. The systems Bi_2O_3-GeO_2-Nb_2O_5 and Bi_2O_3-GeO_2-Ta_2O_5 were studied separately [256].

In the BaO-R_2O_3-Nb_2O_5 systems (R = *tri*valent Sc, In, Lu, Yb, Tm, *etc.*), a new 18R stacking *poly*type $Ba_6R_{0.5}Nb_{4.5}O_{18}$ has been prepared at *ca.* 1200 °C [257]. The stability of the new *poly*type decreases with increasing radius of the R ion (for Y, Tb, Gd, and Eu), but for R = Sm and Nd no 18R phase was observed. For R = Er, Ho, and Dy there was a small contamination with $Ba_5Nb_4O_{15}$. Unit cell data are given, based on X-ray diffraction [257]. Also, BaO-R_2O_3-Ta_2O_5 systems [258] and systems containing titania have been studied. Perovskite-type structures were found, like *e.g.* $Ba_8Ti_3M_4O_{24}$ with M = Nb or Ta [259] and $Ba_7Nb_4Ti_2O_{21}$ [260]. A yellow 11H hexagonal perovskite $Ba_{11}Re_{7/4}Nb_{7/4}W_{7/2}O_{32}$ has been characterized [261].

Lead zink niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$, is an excellent ferroelectric perovskite. It has been obtained by a sol-gel process involving the complex $Zn[Nb(OEt)_6]_2$, followed by an *in situ* sintering process [262]. Crystal growth and properties of Pb_2FeNbO_6 [263] and Pb_2ScTaO_6 [264] were studied.

The Nb-O bond lengths in $NdNbO_4$ and niobium-vanadium mixed $NdNb_{1-x}V_xO_4$ crystals of Fergusonite structure, see Figure 29, were studied by extended X-ray absorption (EXAFS) [265]. The Nb-O distances, 1.89 ± 0.03 Å, were unexpectedly almost independent of composition and essentially unchanged from the values exhibited in $NdNbO_4$.

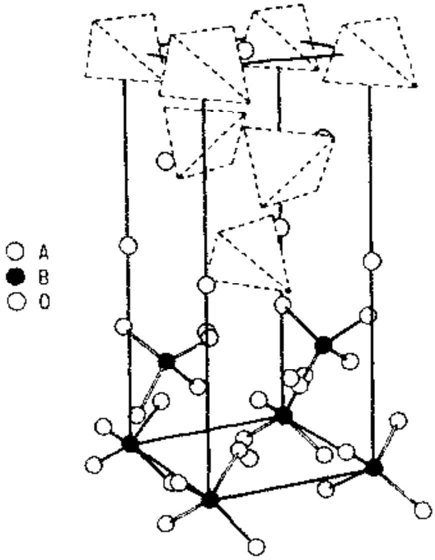
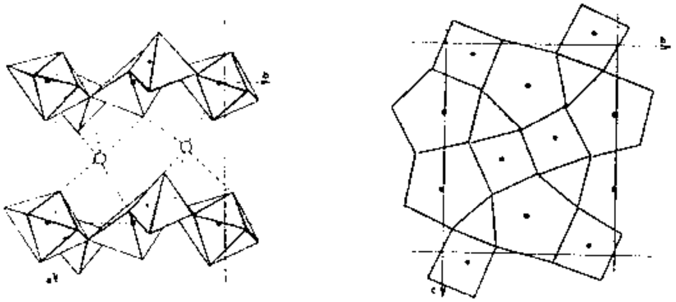


Figure 29. Tetragonal structure of $NdNb_{1-x}V_xO_4$ crystals. A = Nd, B = Nb or V. Reproduced with permission from [265], G. S. Knapp, M. V. Nevitt, A. T. Aldred and T. K. Klippert, *J. Phys. Chem. Solids* **46** (1985) 1321.

The high-melting fluorite-related rare earth tantalum oxides $3R_2O_3{\cdot}Ta_2O_5$ or R_3TaO_7, R = rare earth = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb have had their melting (solidification) points redetermined (range *ca.* 1900-2500 °C), and the correlation of the temperatures with rare earth ionic radii and crystal structures was examined [266]. Temperature and treatment dependent polymorphism in these oxides was studied by X-ray powder diffraction [267-268].

$KNbUO_6$, $RbNbUO_6$, $CsNbUO_6$ and $TlNb_2UO_{11.5}$ single crystals were made from U_3O_8, Nb_2O_5 and the *mono*valent carbonates [269-270]. Their X-ray crystal structures were solved and show complicated systems of UO_7 and NbO_5 (or NbO_6) *poly*hedra sharing edges and corners and with the *mono*valent ions in tunnels or between slabs [269-270], see Figure 30.



a b

Figure 30. The $CsNbUO_6$ structure seen in two projections, showing (a) the layered structure and (b) the NbO_5 and UO_7 *poly*hedral network within a layer. Reproduced with permission from [270], M. Gasperin, *Acta Cryst.* **C43** (1987) 404.

The compounds UNb_2O_7, UNb_4O_{12} and UNb_3O_{10} were examined by magnetic susceptibility, XPS and ESR methods and all were found to contain *penta*valent niobium [271].

The series of perovskite compounds $A^{I}A^{II}{}_2Nb_3O_{10}$ with A^{I} = H, Na, K, Rb, Cs and A^{II} = Ca have been made and characterized structurally by X-ray diffraction [272].

Plate-like green crystals of α-$PrNb_3O_9$ have been obtained hydrothermally [273]. The structure was solved and shown to consist of double and single zig-zag chains of corner-shared distorted NbO_6-octahedra which sometimes also share edges, see Figure 31.

$LaTa_3O_9$ crystals were obtained and studied by X-ray and electron diffraction and electron microscopy [274]. The structure is containing ribbons of pentagonal TaO_7-*bi*pyramids in one direction, connected by planes of TaO_6-octahedra. The tunnels formed in this way are occupied by La atoms [274].

Ternary perovskite oxides $La(Mn_{2/3}Nb_{1/3})O_3$, $La(Co_{2/3}Nb_{1/3})O_3$, $La(Ni_{2/3}Nb_{1/3})O_3$, $La(Mn_{2/3}Ta_{1/3})O_3$, $La(Co_{2/3}Ta_{1/3})O_3$ and $La(Ni_{2/3}Ta_{1/3})O_3$ have been made. IR spectra and X-ray diffraction crystal structures of these highly ordered compounds were studied [275]. Also, the crystal structure of $La_3(Ga_{5.5}Nb_{0.5})O_{14}$ was solved [276].

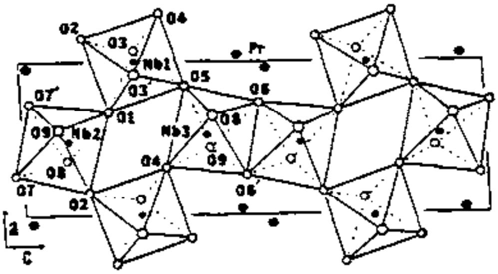


Figure 31. Projection of the view along α-$PrNb_3O_9$ structure showing connected NbO_6-octahedra and Pr^{3+} ions (small filled circles) in tunnels. Reproduced with permission from [273],C. C. Torardi, L. H. Brixner and C. M. Foris, *J. Solid State Chem.* **58** (1985) 204.

Thermal stability of rare-earth element niobates was studied in the high-temperature region [277]. Thermodynamic data, melting points and electric conductivity data were given for the following compounds: La_3NbO_7, Nd_3NbO_7, $LaNbO_4$, $NdNbO_4$, $EuNbO_4$, $TbNbO_4$, $YNbO_4$, $NdNb_3O_9$ [277].

The crystal structures of Sr_2RNbO_6 (R = Sm and Tm) have been determined and were found to be of a distorted cryolite-type containing octahedra sharing corners [278].

New hexagonal perovskite-like compounds $Sr_3LnNb_3O_{12}$ (with Ln = La, Pr or Nd) and $Sr_3LaTa_3O_{12}$ and $Sr_3PrTa_3O_{12}$ have been prepared by long-time sintering of mixtures of lanthanide oxides, niobium or tantalum oxides and strontium carbonate at 1350 °C [279]. The unit-cell parameters of the single-phase materials were determined [279]. Also, transparent $Ba_3LaNb_3O_{12}$ single crystals have been grown [280].

The crystal structure of $(Cs_{0.75}K_{0.25})(Nb,Ti)U_2O_{11}$ was shown to contain niobium-titanium pairs in *tri*angular *bi*pyramidal coordination joined by a corner [281].

High resolution electron microscopy was used to study the structures of $K_7Nb_{15}W_{13}O_{80}$ and $Bi_4Nb_5O_{18}F$ [282]. The Fourier-processed images gave atomic coordinates near those of the refined X-ray structures.

Solid state reactions have lead to single crystals of new kinds of tetragonal tungsten bronze-types whose X-ray structures could be solved: The $Ba_6FeNb_9O_{30}$ structure has a statistical distribution of Fe^{3+} and Nb^{5+} in the corner-linked octahedral framework with *penta*gonal tunnels [283]. $SrNb_6O_{16}$ is *iso*structural with $NaNb_6O_{15}F$ according to results found by the Rietveld powder diffraction profile technique [235]. A new compound, $Ba_4FeTa_{10}O_{30}$ with a tunnel structure is also related to $NaNb_6O_{15}F$ [284]. The complicated structures of *e.g.* $Ba_4CoTa_{10}O_{30}$ [286], $Ba_4MgTa_{10}O_{30}$ and $Ba_4NiTa_{10}O_{30}$ have been determined [285]. The $Ba_4CoTa_{10}O_{30}$ structure conforms to the network of the $Na_2Nb_{12}O_{30}F_2$ type [286].

The PbO-Nb_2O_5-WO_3 system contains solid solutions of composition $PbNb_2O_6 \cdot xWO_3$ and $Pb_4Nb_4O_{11} \cdot xWO_3$, both with the high temperature $PbNb_2O_6$ tetragonal tungsten bronze-type structure [287].

Heat treatments of mixtures of Ta_2O_5, WO_3 and W metal at high temperatures resulted in the formation of Ta_2WO_8 [288-289]. The structural properties of this and other bronzes, containing pentagonal tunnels, were studied by X-ray diffraction and by optical and electron microscopic methods [288-289].

Phase equilibria at 1300 °C have been studied for the SrO-La_2O_3-Nb_2O_5 system [290]. An indexed X-ray pattern was given for the $Sr_3La_2Nb_{12}O_{36}$ phase [290]. Analogous ternary lanthanide phases $Sr_3Ln_2Nb_{12}O_{36}$ with Ln = La - Lu were studied as well, and the crystal structure of $Sr_3Nd_2Nb_{12}O_{36}$ (tetragonal tungsten-bronze type) was solved [291].

In the system Ta_2O_5-La_2O_3, a new compound, $LaTa_7O_{19}$, has been made [292]. High resolution transmission electron microscopy and X-ray diffraction methods were used to study its crystal structure [292]. It can be considered to be built from two kinds of coordination *poly*hedra, octahedral TaO_6 and double layers of pentagonal TaO_7-*bi*pyramids.

The products of the reaction between Eu_2O_3 and Nb_2O_5 in the presence of reducing agents like EuO, Nb, NbO, and NbO_2 have been characterized by X-ray L_{III} absorption spectroscopy [293]. The oxidation states were found to be Eu^{3+} and Nb^{5+} in Eu_3NbO_7, whereas Eu_3NbO_6 contains also Eu^{2+}. On the other hand, $EuNbO_3$ clearly was proven to contain Eu^{2+} and Nb^{4+} [293]. In the presence of SrO, $Sr_6Nb_2O_{11}$ and Eu_3NbO_6 may be formed, but a number of previously described Eu-Nb-O phases were proved to be non-existing [294].

Single crystals of $Sr_6Nb_{34}O_{91}$ were prepared by CO_2-laser technique [295]. The structure, solved by X-ray diffraction techniques, consists of a network of corner-sharing NbO_6-octahedra similar to the known $[M_{10}O_{30}]^{12-}$ tetragonal tungsten-bronze (see Figure 32). The tunnels of the network are partly filled by Sr^{2+}, Nb^{5+} and O^{2-} -ions.

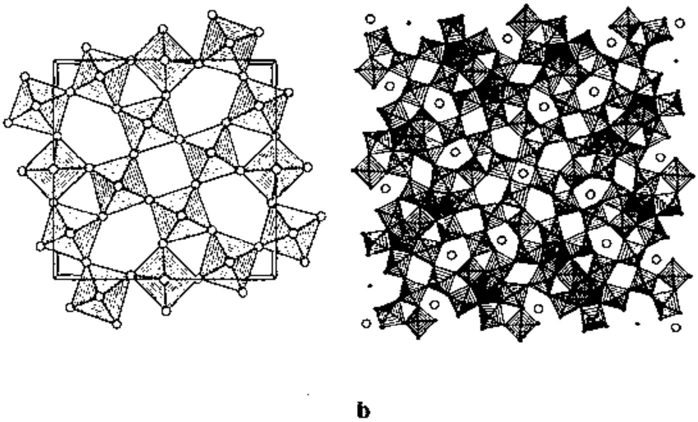


Figure 32. Perspective drawing of the $[M_{10}O_{30}]^{12-}$ tetragonal tungsten bronze network (a) and the new $Sr_6Nb_{34}O_{91}$ structure (b), both viewed along the direction [001]. Reproduced with permission from [295], K. Schückel and H. Müller-Buschbaum, *Rev. Chim. Minérale* **23** (1986) 154 and Gauthier-Villars, Publisher (Paris).

The compound $La_3Ga_{5.5}Nb_{0.5}O_{14}$, having the $Ca_3Ga_2Ge_4O_{14}$ structure, has been prepared during a study of the phase relations in the La_2O_3 - Ga_2O_3 - Nb_2O_5 system [296]. Also, the compounds $GaNbO_4$ and $GaNb_{11}O_{29}$ were formed.

In the systems R_2O_3-V_2O_5-Ta_2O_5, with R = a rare earth metal (Y, La, Ce, Pr, Nd, Sm, and Eu), new compounds of the type $RVTa_2O_9$ have been discovered and characterized by their X-ray powder diffraction diagrams, and in some cases, IR spectra were given [297-299].

2.12 Heteropolycompounds of Nb(V) and Ta(V)

The structures, properties and uses of metal-oxygen "*hetero*poly"clusters in aqueous solutions and in solids were reviewed [300]. A polyeder model illustrating the discussed kind of structures obtainable with niobium or tantalum is given in Figure 33. The $[Mn^{IV}O_6Nb_{12}O_{32}]^{12-}$ anion depicted can be thought of as containing two $[Nb_6O_{19}]^{8-}$ basic building units, known *e.g.* from the $[HNb_6O_{19}]^{7-}$ anion [300].

A new niobium-vanadium *iso*polycompound has been prepared and assigned the formula $\{Na_5H[NbV_5O_{18}]\}_2$ [301].

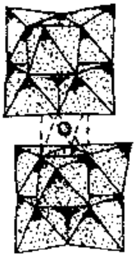


Figure 33. The *hetero*poly anion $[Mn^{IV}O_6Nb_{12}O_{32}]^{12-}$with octahedrally coordinated Mn^{4+}. Reproduced with permission from [300], H.-J. Lunk, S. Schönherr and V. I. Spitzin, *Z. f. Chem.* **27** (1987) 157.

2.13 Perchlorates, sulphates, phosphates and other oxy-complexes of Nb(V) and Ta(V)

Anhydrous Niobium(V) *per*chlorate, $Nb(ClO_4)_5$, and the *per*chlorato-niobates, $Cs[Nb(ClO_4)_6]$ and $Cs_2[Nb(ClO_4)_7]$, were prepared and characterized by chemical analysis, X-ray powder diagrams and IR-spectra [302]. $Nb(ClO_4)_5$ is a crystalline hygroscopic substance, which decomposes endothermally at about 70 °C, forming $NbO(ClO_4)_3$ and Cl_2O_7. Above 115 °C, $NbO(ClO_4)_3$ is transformed exothermally to $NbO_2(ClO_4)$ with the liberation of Cl_2 and O_2. The reaction of $Nb(ClO_4)_5$ with $CsClO_4$ in $HClO_4$ gives the *per*chloratoniobates $Cs[Nb(ClO_4)_6]$ and $Cs_2[Nb(ClO_4)_7]$ [302]. The IR-spectrum of $Nb(ClO_4)_5$ contains sets of bands characteristic of *uni*dentate and *bi*dentate *per*chlorato-groups, whereas the complexes in $Cs[Nb(ClO_4)_6]$ and $Cs_2[Nb(ClO_4)_7]$ are *uni*dentately bound [302].

Anhydrous Tantalum(V) *per*chlorate, $Ta(ClO_4)_5$, and the *per*chlorato-tantalates, $Cs[Ta(ClO_4)_6]$ and $Cs_2[Ta(ClO_4)_7]$, have been prepared and characterized similarly [303]. $Ta(ClO_4)_5$ is a colourless, crystalline, hygroscopic substance, which looses Cl_2O_7 at about 90 °C, to give $TaO(ClO_4)_3$. Above 130-140 °C, $TaO(ClO_4)_3$ is transformed exothermally to $TaO_2(ClO_4)$ with the liberation of Cl_2 and O_2. The reaction of $Ta(ClO_4)_5$ with $CsClO_4$ in $HClO_4$ gives the *per*chloratotantalates $Cs[Ta(ClO_4)_6]$ and $Cs_2[Ta(ClO_4)_7]$ [303]. $Ta(ClO_4)_5$ gives sets of IR bands characteristic of *uni*dentate and *bi*dentate *per*chlorato-groups, whereas $Cs[Ta(ClO_4)_6]$ and $Cs_2[Ta(ClO_4)_7]$ are *uni*dentate [303].

Electrode reaction equilibria of niobium complexes were studied by potentiometry and polarography in *per*chlorate and sulphate acidic solutions [304-305]. One- and two-electron reactions:

$$Nb(V) + e^- = Nb(IV)$$

$$Nb(V) + 2\,e^- = Nb(III)$$

occurred at the mercury electrode, Nb(V) probably being $NbO(OH)_2^+$, $NbO(OH)_2(SO_4)^-$, $NbOSO_4^+$ and $NbO(SO_4)_2^-$, and Nb(III) being Nb^{3+} and $NbSO4^+$, respectively. Equilibria kinetics were studied [304-305].

The complexation reaction of Nb(V) with SO_4^{2-} and HSO_4^- was studied using UV spectroscopy; it was found that freshly prepared solutions are in general non-equilibrium ones [306].

The crystal structures were solved for $K_7Nb(SO_4)_6$ and $K_7Ta(SO_4)_6$, prepared by precipitation from solutions of Nb_2O_5 or Ta_2O_5 in molten $K_2S_2O_7$. The coordination polyhedron consisted of six *uni*dentate sulphato ligands [307], see Figure 34.

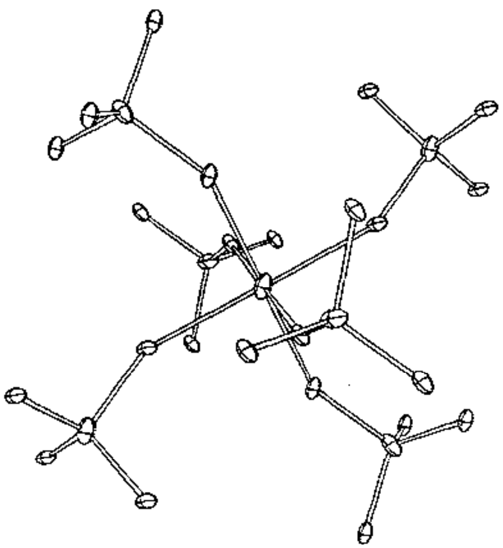


Figure 34. The structure of $[Nb(SO_4)_6]^{7-}$ and $[Ta(SO_4)_6]^{7-}$ ions with six *uni*dentate sulphato ligands [307-308]. Reproduced with permission from F. Borup and R. W. Berg.

The crystal structure of β-$NbPO_5$ (or $NbO(PO_4)$) contains PO_4 tetrahedra and strands of two NbO_6 octahedra, being connected in such a way that a ReO_3-bronze type of structure with pentagonal tunnels is formed [309]. New allotropic forms of niobium and tantalum phosphates, $NbPO_5$ and $TaPO_5$ [310], and hydrates thereof $NbOPO_4 \cdot nH_2O$ [311] were prepared and characterized by spectroscopy and by structural methods.

Preparation techniques for *ortho*tantalates $ATa(PO_4)_2$, with A = an alkali metal, have been developed [312]. Thermally induced solid state decomposition reactions, X-ray diffraction diagrams and IR-spectra were given [312]. In the crystal structure of $RbTa(PO_4)_2$, the tantalum atoms are in octahedral coordination with six PO_4 groups [313]. Infinite chains are formed by the TaO_6 and PO_4 groups. The results agree with earlier studies on $HTa(PO_4)_2$ and $CsTa(PO_4)_2$.

Sodium niobium phosphate $Na_4Nb(PO_4)_3$ exists in both crystalline and vitreous states [314]. Lattice data, EPR and optical absorption spectra were obtained. Vitrification seems to favour the formation of a niobyl group [314].

The crystal structure of niobyl tetraphosphate, $(NbO)_2P_4O_{13}$, has been solved, showing the Nb atom in octahedral coordination with five O atoms from different $P_4O_{13}^{6-}$ ions and one separate O atom [315].

Niobium(V)-containing phosphates with the general formula $Cu_xNb_{1-x}Ti_{1+x}(PO_4)_3$ ($0 \leq x \leq 1$) were made by sintering TiP_2O_7, Cu and oxides at high temperatures [316]. These compounds were recently shown to belong to the Nasicon type of structures, $NaA_2(PO_4)_3$ with A = Ti, Ge, Zr or analogous silicates. In such structures, three-dimensional lattice networks of cumulated octahedra and tetrahedra exist, forming large cavities, which are empty in $NbTi(PO_4)_3$ and in the new compounds [316]. Niobium is octahedrally coordinated to six oxygens.

The large family of niobium phosphate bronzes, $A_{4-x}Nb_6P_4O_{26}$ ($0 \leq x \leq 2$, A = K, Rb, Ba), has been studied, including $K_3Nb_6P_4O_{26}$ characterized by a mixed framework formed of corner-sharing NbO_6 octahedra and PO_4 tetrahedra and with K^+ located in between in intersecting tunnels [317], see Figure 35.

The crystal structure of $K_5[Nb_6Zr_2P_5O_{34}]$ has been solved [318]. It contains NbO_6 and ZrO_6 octahedra sharing corners and PO_4 tetrahedra sharing corners with octahedra to form a three-dimensional network with potassium ions situated in interconnected channel-like cavities [318].

Also, the structure of newly prepared crystals of $CaNb_2O(P_4O_{13})(P_2O_7)$ has been resolved [319]. The main outstanding feature of this compound is the coexistence in the same lattice of two kinds of phosphate anions with different degrees of condensation: a tetrameric one: $(P_4O_{13})^{6-}$ and a *di*meric linear one: $(P_2O_7)^{4-}$. Niobium atoms are in two octahedral NbO_6 coordination arrangements, one of which is nearly regular and another one less regular [319].

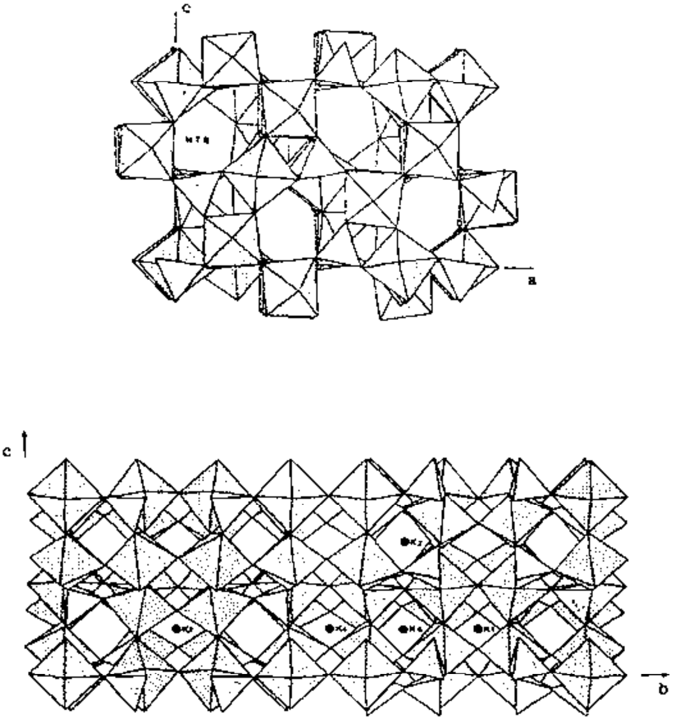


Figure 35. Projections onto (010) and (100) of the $K_3Nb_6P_4O_{26}$ framework structure [317]. Reproduced with permission from [317], M. M. Borel, A. Grandin, A. Benabbas, A. Leclaire and B. Raveau, *Mater. Res. Bull.* **24** (1989) 1485.

The 11-tungstoniobophosphoric acid, $H_4(PNbW_{11}O_{40})$, xH_20, was prepared and its UV absorption and IR spectral proterties examined [320].

The role of Nb_2O_5 and Ta_2O_5 in glass-forming systems were discussed in some detail [321-323]. Raman spectra of some NbO_6 containing glasses and crystals of $LiNbO_3$ or $MgNb_2O_6$ were compared [321,323]. NbO_6 and TaO_6 octahedra are capable of forming continuous networks in Cs_2O-Nb_2O_5-Al_2O_3 and P_2O_5-BaO-Ta_2O_5-Al_2O_3 system glasses [322-323]. Other phosphates are mentioned in the section on oxides.

2.14 Intercalation of molecules into Nb(V) and Ta(V) oxides

Many niobates and tantalates are well-suited frameworks for intercalation: Intercalation of primary *mono*amines $NH_2C_nH_{2n+1}$ with *n* ranging from 1 to 9 [324] and of *di*amines $H_2N\text{-}(CH_2)_n\text{-}NH_2$, with *n* ranging from two to ten [325], can be done into the lamellar niobate $HNb_3O_8{\cdot}H_2O$ with interesting results. The intercalated products can be dehydrated or hydrated at room temperature. If hydrated, they can - easily and reversibly - be dehydrated to compounds such as *e.g.*$[H_3N\text{-}(CH_2)_n\text{-}NH_3]_{0.5}[Nb_3O_8]$. Crystallographic investigations have revealed that the *di*amines tend to orient themselves transverse to the Nb_3O_8 layers, forming, for the larger values of *n*, dense organic layers [325]. A typical structure is shown in Figure 36. Similar results were found for the *mono*amines [324].

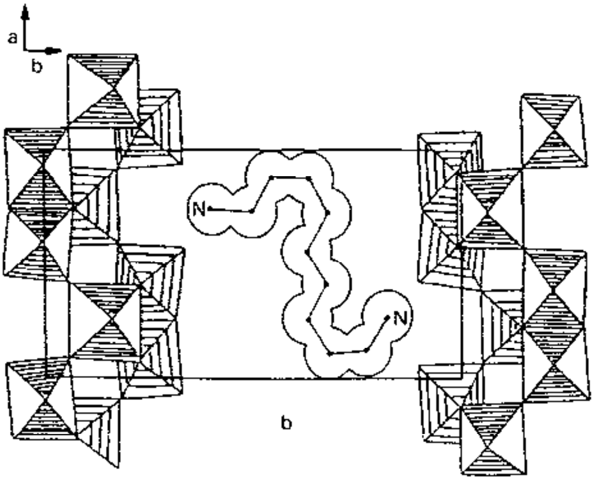


Figure 36. Structure of $[H_3N\text{-}(CH_2)_9\text{-}NH_3]_{0.5}[Nb_3O_8]$ (n = 9). The Nb_3O_8 layers and the organic layer are distinctly shown. Reproduced with permission from [325], R. Nedjar, M. M. Borel and B. Raveau, *J. Solid State Chem.* **71** (1987) 451.

The intercalation properties of $HTiNbO_5$ in the presence secondary and tertiary amines was also studied [326-327]. The $TiNbO_5$ layers, though different from the Nb_3O_8 layers of Figure 36, are able to form similar kinds of hydro-amine oxide layer compounds.

The layered solid acid $HCa_2Nb_3O_{10}$ can be intercalated with organic primary amines $C_nH_{2n+1}NH_2$, n = 1 to 16 [328].

2.15 Peroxy-niobates(V) and -tantalates(V)

The reactivity of the niobium *tetraperoxo* complex ion, $[Nb(O_2)_4]^{3-}$, was studied theoretically, using the multiple scattering X-α model as a basis for the calculation of molecular electrostatic potentials and electron deformation densities [329]. The electronic ground state configuration of $[Nb(O_2)_4]^{3-}$ is given as $^1A_1(2a_2)^2(2b_1)^2(8e)^4$ [330].

2.16 Nb(V) and Ta(V) sulphides and related S- and Se-containing compounds

Amorphous niobium sulphide, Nb_2S_5, was prepared by letting hexamethyl*di*silathiane $(CH_3)_3Si\text{-}S\text{-}Si(CH_3)_3$ react with $NbCl_5$ in acetonitrile at room temperature [331]. Acetonitrile was used because of high solubility of the intermediate $NbSCl_3$, and in this way a pure product could be obtained [331].

The structural chemistry of binary and ternary selenides of niobium and tantalum has been extensively studied. The four tetrachalcogenometalates K_3MX_4 (M = Nb, Ta, X = S, Se) have been obtained and characterized by *e.g.* single crystal X-ray diffraction methods [332]. They all contain discrete tetrahedral MX_4^{3-} ions. Single crystals of Tl_3MX_4 (M = Nb, Ta, X = S, Se) were synthesized and characterized by DTA, X-ray diffraction and infrared photographs [333]. Such crystals contain isolated, parallel-oriented MX_4 tetrahedra with metals M forming a body-centered cubic lattice. The ionicity of the chemical bonding in Tl_3MS_4 (M = Nb or Ta) was estimated to be intermediate between (*1*), a crystal consisting of ionicly bonded Tl^+ and MS_4^{3-}, and (*2*), an all covalent crystal. The bond ionicity increases from Nb to Ta [334-335]. Also, for Cu_3TaS_4 and Cu_3TaSe_4 the bond ionicity was studied and found to decrease from S to Se [336]. The compounds Tl_3TaX_4 (X = S, Se) were investigated by nuclear gamma resonance spectroscopy (isomer shifts of the 6.2 keV nuclear transition of ^{181}Ta) and the results compared with similar ones for Cu_3TaS_4 and Cu_3TaSe_4 [337]. When mixed, Tl_3TaS_4 and Tl_3TaSe_4 form continuous solid solutions, whose thermodynamic data were given [338].

Discrete anions $Ta_2S_{11}^{4-}$ and $Nb_4Se_{22}^{6-}$ of the metals in oxidation state +5 have been discovered in the newly solved crystal structures of the salts $K_4Ta_2S_{11}$ and $K_3Nb_2Se_{11}$ [472].

Black platy hexagonal crystals of approximate composition $Ba_2NbS_4(S_2)_{0.5}$ have been prepared from BaS, Nb and S at 1000 °C [339]. The solved X-ray crystal structure shows that Nb atoms occupy octahedral interstices in between layers of disordered S and S_2 ions [339]. Related compounds Nb_2PdSe_6, $Nb_2Pd_{0.71}Se_5$, $Nb_3Pd_{0.72}Se_7$, Ta_2NiS_5 and Ta_2NiSe_5 have been prepared and examined [16, 340-341].

In the Ba-Ta-S system, unstoichiometric compounds with tantalum vacancies exist. Hence, Ta can have a formal charge of +5, even when the formula looks otherwise. Thus, $BaTaS_3$ is $BaTa_{0.8}S_3$. The same seems to be the case for $BaTa_2S_5$, $Ba_3Ta_2S_8$, $Ba_9Ta_4S_{20}$ and now $Ba_{16.5}Ta_9S_{39}$, all of which have been characterized by means of their crystal structures [342].

Compounds Ta_2MSe_7 (M = Ni, Pt) have also been prepared and shown [343-344] to contain Ta(V)-centered *bi*capped trigonal prisms of Se^{2-} ions and Se-Se bonds analogous to $TaSe_3$. In addition to this, the structure also contains chains of Ta-centered octahedra and Pt- or Ni-centered square pyramids. The metallic versus non-metallic properties were examined by electronic structure calculations.

Following the earlier synthesis (and structure evaluation) of $Nb_2Pd_3Se_8$ [345], now also $Ta_2Ni_3S_8$ [346], $Ta_2Pd_3Se_8$ [347], $Ta_2Pt_3Se_8$ [346], $Co_2Nb_4PdSe_{12}$ [346], $Co_2Ta_4PdSe_{12}$ [347-348], $[Co_{1.5}Pt_{0.5}]Ta_6PtSe_{16}$ [349] and $Nb_2Pd_{0.71}Se_5$ [347] single crystal fibers or platelets have been prepared, by the method of long-time heating of the elements in closed quartz cells, placed in a temperature gradient and with bromine as transporting agent. The crystal structures have been solved and a review on these compounds and their structural chemistry has been published [16].

The basic $Nb_2Pd_3Se_8$ channel type structure, like that of $Ta_2Pd_3Se_8$, see Figure 37, contains niobium atoms in a trigonal prismatic environment of Se atoms and two types of Pd atoms - square planar and square pyramidal - each coordinated by Se atoms [345]. The structural results are consistent with the simple valence description: Nb(V), Pd(II) and Se(-II). The other structures contain columns of Nb or Ta in somewhat similar octahedral and trigonal-prismatic sites, surrounded by shared sulphur or selenium atoms. $Ta_2Ni_3S_8$ can be characterized as a semiconductor [346], whereas $Nb_2Pd_{0.71}Se_5$ is a metallic conductor along the needle axis [347].

$Ta_2P_2S_{11}$ is a new phase of the Ta-P-S system [350]. Single crystal X-ray diffraction studies on $Ta_2P_2S_{11}$, obtained from elements at high temperature, yielded a structure based on *bi*polyhedral $[Ta_2S_{11}]$ with *hepta*-coordinated tantalum(V) and tetrahedral $[PS_4]$. The $[Ta_2S_{11}]$ units are formed of two distorted $[TaS_7]$ groups sharing a triangular face made of *mono*- and *di*sulphide anions (in some positions disordered). The $[Ta_2S_{11}]$ units are shown in Figure 38.

The framework of the $[Ta_2S_{11}]$ units leaves three kinds of empty tunnels in the structure. The compound can be formulated as $Ta(V)_2P(V)_2S(-II)_9(S(-I)_2)$ and it is a *dia*magnetic semiconductor [350].

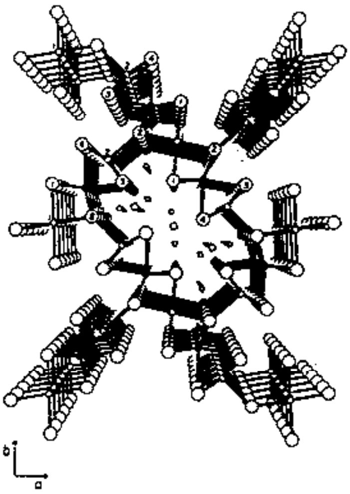


Figure 37. Perspective view along [001] of the structure of $Ta_2Pd_3Se_8$. Ta, Pd and Se atoms are small filled circles, small open circles, and large open circles, respectively. Reproduced with permission from [347], D. A. Keszler, J. A. Ibers, S. Maoyu and L. Jiaxi, *J. Solid State Chem.* 57 (1985) 68.

A new tunnel structure compound with inserted polymeric sulphur was found by X-ray diffraction study on single crystals of $Ta_4P_4S_{29}$, obtained from the elements by tempering under vacuum [351]. The structure is based on *bi*-prismatic, *bi*capped $[Ta_2S_{12}]$ units including sulphur pairs, bonded to each other through $[PS_4]$ tetrahedra sharing sulphurs with $[Ta_2S_{12}]$. The $[Ta_2S_{12}]$ unit is shown in Figure 39. The framework leaves large tunnels, in which $(S_{10})_\infty$ sulphur-chains are found to be inserted. The compound can be formulated as $Ta(V)_4P(V)_4S(-II)_{16}(S(-I)_2)_4S(0)_5$ and it is accordingly a *dia*magnetic semiconductor [351].

2.17 Nb(V) and Ta(V) complexes with O-donor ligands

2.17.1 Nb(V) and Ta(V) alkoxides

The complex salt $Li[Nb(OEt)_6]$ was obtained as a result of crystallization from an ethanolic solution of lithium ethoxide and niobium ethoxide [352]. The crystal structure was recently determined [353]. A partial hydrolysis product, $[Li_2Nb_2(OEt)_{10}(OH)_2]$, has a structure which was solved by single crystal X-ray diffraction analysis, see Figure 40. The structural unit is based on the *tetra*nuclear Li_2Nb_2 framework, similar to the $[Ti(OMe)_4]_4$ and $[W(OEt)_4]_4$

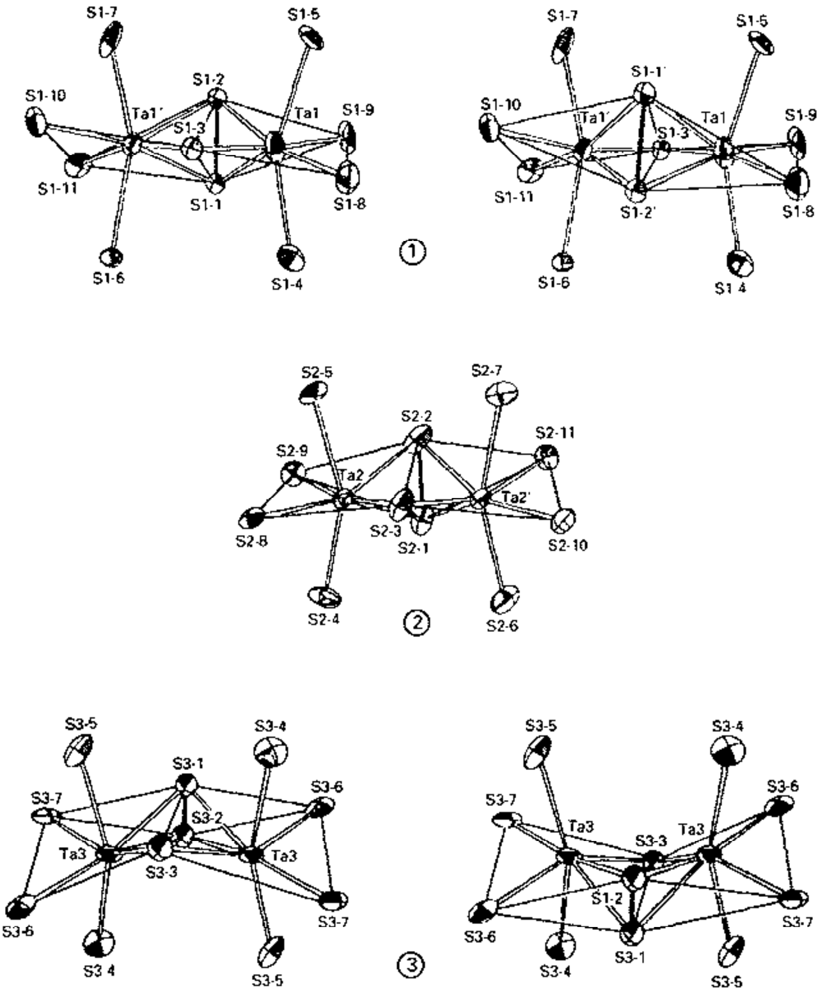


Figure 38. The three different $[Ta_2S_{11}]$ *bi*polyhedral units encountered in $Ta_2P_2S_{11}$. (1) and (3) have two arrangements due to disorder in the shared sulphur *tri*angle. Reproduced with permission from [350], M. Evain, S. Lee, M. Queignec and R. Brec, *J. Solid State Chem.* **71** (1987) 139.

tetramers; however, two of the four $[MO_6]$ octahedrons are replaced by $[LiO_4]$ tetrahedra. The interest in $Li[Nb(OEt)_6]$ is large, partly because of its possible application as a precursor-material for the preparation of $LiNbO_3$ optical components [353].

$Zn[Nb(OEt)_6]_2$, was obtained from treating $K[Nb(OEt)_6]$ with $ZnCl_2$ [262]. $K[Nb(OEt)_6]$ was obtained from dissolving potassium into dry ethanol (EtOH) and letting it react with $[Nb(OEt)_5]$. From $Zn[Nb(OEt)_6]_2$, a lead zink niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$, has been obtained by a sol-gel process [262].

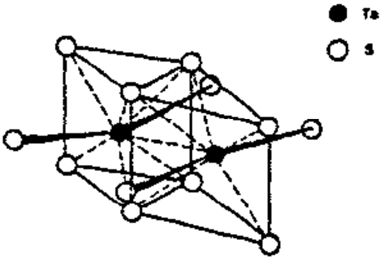


Figure 39. Perspective drawing of the $[Ta_2S_{12}]$ *bi*capped *bi*prismatic unit of the basic tunnel structure of $Ta_4P_4S_{29}$. Reproduced with permission from [351], M. Evain, M. Queignec, R. Brec and J. Rouxel, *J. Solid State Chem.* **56** (1985) 148.

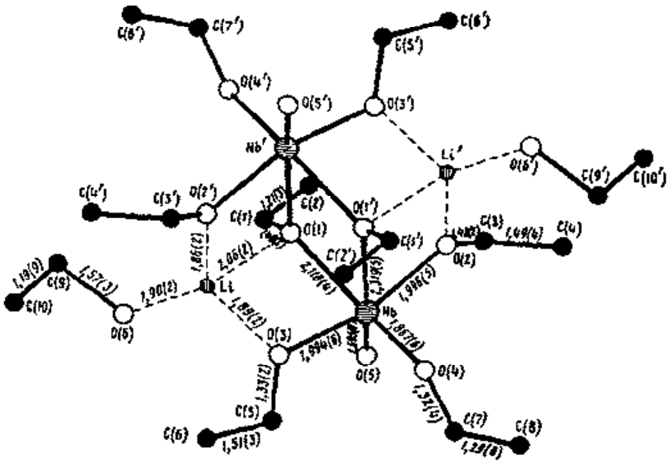
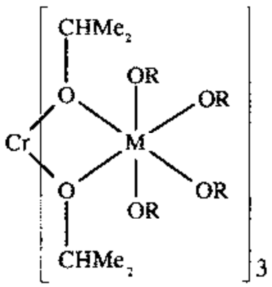


Figure 40. Structure of $[Li_2Nb_2(OEt)_{10}(OH)_2]$. Reproduced with permission from [352], A. I. Yanovskii, E. P. Turevskaya, N. Ya. Turova and Yu. T. Struchkov, *Sov. J. Coord. Chem.* **11** (1985) 63

The 3-methyl-1-pentene-3-oxy derivates, $M(OC(C_2H_5)(CH_3)CH{:}CH_2)_6$, with M = Nb or Ta, have been prepared [354]. They were characterized by elemental analysis, mol weight determinations, and IR and ^{1}H NMR spectral studies, and found to be *mono*meric colourless complexes, soluble in common organic solvents [354].

The penta-*iso*-propyloxide complex $[Nb(OPr^i)_5]$ reacts with $[La(OPr^i)_3]$ in alcoholic solution forming crystalline alkoxyniobates with formula $[LaNb_2(OPr^i)_{13}]$. The structure of the complexes was discussed in terms of the so-called "coordination polymerism" concept [355].

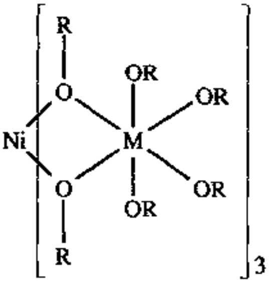
Iso-propyloxide complexes $K[M(OPr^i)_6]$ (M = Nb, Ta) react with $CrCl_3{\cdot}3THF$ (THF = tetrahydrofuran) in benzene in molar ratios 3:1 yielding soluble complexes of the type $Cr[M(OPr^i)_6]_3$ [356]. On heating under vacuum the green complexes tend to disproportionate into $Cr(OPr^i)_3$ and $M(OPr^i)_5$. A number of *bi*metallic alkoxides ($Cr[M(OR)_6]_3$ with R = Me, Et, Pr^i, and/or Am^t in varying combinations, and $Cr[M(OPr^i)_4(acac)_2]_3$ with acac = acetylacetonate) have also been synthesized by alcoholysis of $Cr[M(OPr^i)_6]_3$ with methanol, ethanol and *t*-amyl alcohol. The compounds were characterized by chemical analysis, by infrared, visible and electron spin resonance spectroscopy, and by magnetic susceptibility measurements [356]. This and the replaceability of only twelve out of eighteen *iso*propoxy groups were taken as evidence for the following structure, **10**:



10

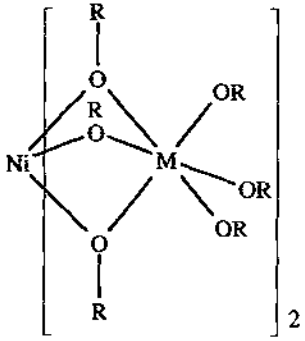
In the acetylacetonate complexes, $Cr[M(OPr^i)_4(acac)_2]_3$, niobium or tantalum achieve a coordination number of eight (acac is *bi*dentate) [356].

A new class of *bi*metallic *iso*propoxides of Ni(II) with the general formula $Ni[M(OPr^i)_6]_2$, with M = Nb or Ta, have been synthesized and characterized by elemental analyses, molecular weight determinations, IR and VIS spectroscopy, in addition to magnetic susceptibility measurements and alcohol exchange reaction studies [357]. An octahedral geometry was assigned to Ni(II) primary *bi*metallic alkoxides ($Ni[M(OR)_6]_2$, M = Nb or Ta, R = Me, Et, Pr^n or Bu^n), while in secondary derivatives, (*e.g.* $Ni[M(OR)_6]_2$, M = Nb or Ta, and R = Pr^i), an equilibrium between octahedral and tetrahedral forms seems to exist. The tetrahedral and octahedral structures deduced were **11** and **12** [357].



Tetrahedral

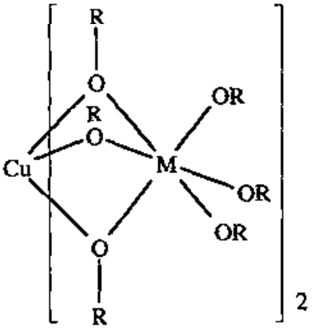
11



Octahedral

12

*Bi*metallic alkoxides of copper(II) of the type $Cu[M(OPr^i)_6]_2$ (M = Nb or Ta) have been obtained, by letting $CuCl_2$ interact with $K[M(OPr^i)_6]$ in the molar ratio 1:2 in benzene solution [358]. These blue-green complexes undergo facile alcohol interchange with primary alcohols such as methanol, ethanol, *n*-propanol and *n*-butanol, forming complexes of the type $Cu[M(OR)_6]_2$, R = Me, Et, Pr^n and Bu^n. With *t*-butanol, only $Cu[Ta(OPr^i)_2(OBu^t)_4]_2$ was obtained. Infrared, electronic and electron spin resonance spectral and magnetic susceptibility measurements indicated a distorted octahedral D_{4h} geometry, **13**, for Cu(II) [358].



13

Novel *ter*metallic *iso*propoxides $[(Pr^iO)_4M(\mu\text{-}OPr^i)_2 Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, M = Nb(V) and Ta(V) have been synthesized from $Pr^iOBe(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ and $M(OPr^i)_5$ and characterized by IR, NMR and mass spectroscopy [359]. The complexes have the structure shown in Figure 41, and they are soluble in anhydrous common organic solvents and can be volatilized without noticeable disproportionation.

A mixed alkoxide-aryloxide of tantalum, $Ta_2(OC_6H_3Pr^i{}_2)_4(OCH_3)_6$ has been isolated as white crystals, whose structure has been solved [360]. The structure, **14**, consists of an octahedral arrangement of oxygen donor atoms around two tantalum metal centers in an edge shared *bi*-octahedron with two methoxide ligands (R = the 2,6-*di*-*iso*propylphenoxy group) [360].

Some ethoxy-complexes are mentioned in the section on carboxylates.

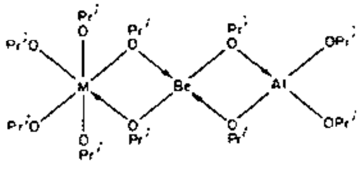
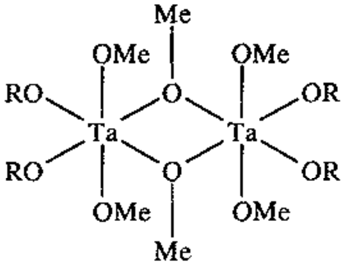


Figure 41. Structure of *ter*metallic *iso*propoxides $[(Pr^iO)_4M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, M = Nb(V) and Ta(V). Reproduced with permission from [359], M. Aggrawal and R.C. Mehrotra, *Polyhedron* 4 (1985) 845.



14

2.17.2 Nb(V) and Ta(V) alkenoxides

4-pentene-1-oxy derivatives of niobium and tantalum, $M(OCH_2CH_2CH_2CH{=}CH_2)_5$, have been prepared in dry benzene and characterized on the basis of elemental analyses, molecular weight determinations, IR and PMR spectral studies [361]. The presence of double bonds does not seem to have any marked effect on the properties of these compounds when compared with the corresponding alkoxides.

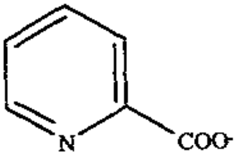
An X-ray study of the alkylidene complex $Ta(CHCMe_3)(S\text{-}2,4,6\text{-}C_6H_2\text{-}Pr^i{}_3)_3(SEt_2)$ have suggested why the complex is inactive for metathesis of ordinary olefins [362].

2.17.3 Nb(V) and Ta(V) carboxylates

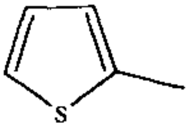
White crystalline compounds of the general formula $NbO_2(OOCR)$ and $TaO_2(OOCR)$ can be obtained from the *penta*chlorides and an excess of the carboxylic acids, *R*COOH with *R* = H, CH_3, C_2H_5, *n*-C_3H_7, CH_2Cl, $CHCl_2$ and CCl_3. The compounds were characterized by chemical analysis and IR spectroscopy [129].

A *tris*-complex of niobium(V), $NbOL_3$, with *L* = the pyridine-2-caboxylate anion, **15**, as a *bi*dentate ligand, was prepared by controlled oxidation of the *tetrakis*-niobium(IV) complex $Nb(L)_4$. The compound was characterized by electronic and IR spectra [363].

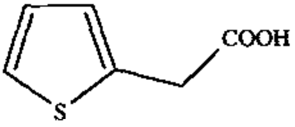
The preparation of *hetero*cyclic carboxylates of niobium(V) and tantalum(V) in dry benzene has been considered for the acids H*L* = HTCA = 2-thiophenecarboxylic acid and H*L* = HTAA = 2-thiopheneacetic acid.



15

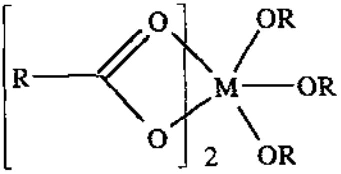


HTCA



HTAA

The ethoxy complexes of the type $M(OEt)_{5-n}L_n$ were obtained, with *M* = Nb, Ta, *n* = 1 to 3 and *L* = TCA or TAA [128]. The complexes were characterized on basis of chemical analysis as well as IR and ^{1}H NMR data. A tentative seven-coordinated structure, **16**, was assigned to the $M(OEt)_3L_2$ complexes:



16

$M(OEt)_3L_2$, with *M* = Nb or Ta and *L* = TCA or TAA [128].

A study of the mechanism of formation of mixed complexes of niobium(V) with 4-(2-pyridylazo)-resorcinol (PAR or H_2R) and hydroxy-acid ions (A^{2-} = oxalate and tartrate) was done [364]. The reaction was represented by a ligand-ligand replacement reaction and a ligand addition reaction:

$$NbOA_i^{(3-2i)+} + H_2R \dashrightarrow [NbOA(HR)_2]^- + (i-1)A^{2-} + 2H^+$$

$$NbO^{3+} + A^{2-} + H_2R \dashrightarrow [NbOA(HR)_2]^- + 2H^+$$

When the hydroxyacid residue A^{2-} is citrate, *tri*hydroxy-glutarate or mucate, the replacement of the residues by PAR anions were not possible due to steric hindrance [364]. In this case the mixed complexes can be made by the addition reaction [364].

The niobium(V)-4-(2-pyridylazo)-resorcinol (PAR) - tartaric acid - sodium chlorate complex system exhibits a catalytic polarographic wave which can be applied to sensitive determination of minute amounts of niobium in geological samples [365]. Further properties of 4-(2-pyridylazo)-resorcinol (PAR) complexes are described in the section on extraction.

A new seven coordinate *mono*meric complex, the oxo-*tris*-(tropolonato)niobium(V) *mono*hydrate, $NbOT_3 \cdot H_2O$ ($T = O_2H_5C_7$, the tropolonato seven-sided-ring group) was synthesized and its X-ray crystal structure determined [366]. The distorted pentagonal-*bi*pyramid configuration of oxygen atoms around niobium is shown in Figure 42. The terminal O atom occupies an axial position with a short Nb-O bond (1.71 Å). The analogous compounds $NbST_3$ and $NbSeT_3$ have been obtained by reaction of $NbOT_3$ with $[(Me_3Si)_2Y]$ (Y = S or Se).

The complexation reaction of 5,5'-methylene-*bis*-salicylaldehyde (MBS) with $TaCl_5$ was studied under various conditions (in DMF solution in dry nitrogen or ambient air or in oxalate solution) [127]. The 1:3 compound obtained was *dia*magnetic and insoluble in common organic solvents. A probable structure (see Figure 43) was proposed on the basis of elemental analysis, magnetic measurements and infrared spectra [127].

2.18 Nb(V) and Ta(V) complexes with S- and Se-donor ligands

By mixing $NbCl_5$, $LiSCH_2CH_2SLi$ (lithium 1,2-ethane *di*thiolate) and $(Et)_4NCl$ (tetraethyl ammonium chloride) in molar ratios 1:3:1 in acetonitrile it was possible [367] to prepare crystals of the composition $[(Et)_4N][Nb(SCH_2CH_2S)_3]$. $TaCl_5$ formed a similar compound. The anion

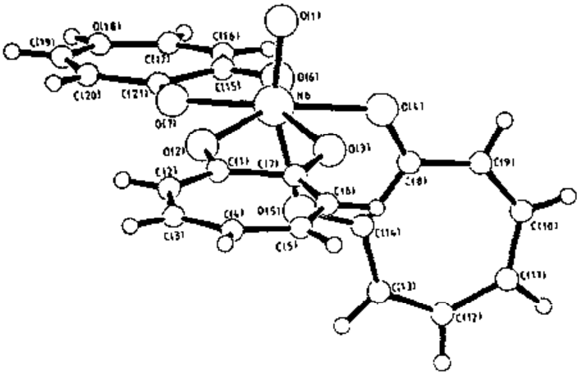


Figure 42. X-ray crystal structure of oxo-*tris*-(tropolonato) niobium(V) *mono*hydrate, $[NbO(O_2H_5C_7)_3]\cdot H_2O$. The distorted pentagonal-*bi*pyramid configuration is easily seen. Reproduced with permission from [366], M. G. B. Drew, D. A. Rice and D. M. Williams, *Inorg. Chim. Acta* **118** (1986) 165.

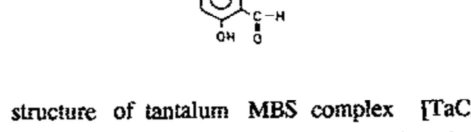


Figure 43. Probable structure of tantalum MBS complex $[TaC_{45}H_{33}O_{13}]$ with seven-coordinated Ta. Reproduced with permission from [127], S. Chomal, A. S. Aazmi and G. C. Shivahare, *Acta Chim. Hung.* **122** (1986) 127.

of the niobium complex was studied by X-ray crystal structure determination [367]. It has three chelate rings arranged like a propeller (C_3-symmetry, absolute configuration Λ, see Figure 44).

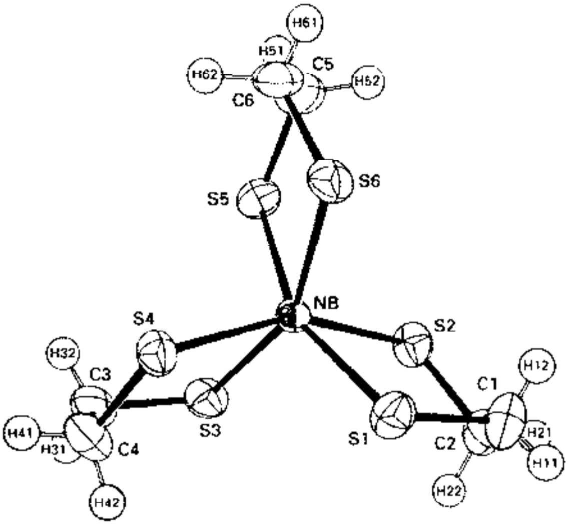


Figure 44. Structure of the anion Λ-$[Nb(SCH_2CH_2S)_3]^-$. Reproduced with permission from [367], K. Tatsumi, Y. Sekiguchi, A. Nakamura, R. E. Cramer and J. J. Rupp, *Angew. Chem.* 98 (1986) 95.

Also, the synthesis and IR and Raman spectroscopic studies of $[A][M(SCH_2CH_2CH_2S)_3]$ and $[A][M(SCH{=}CHS)_3]$ with A = Ph_4P, Et_4N and M = Nb, Ta and the crystal structure of $[Ph_4P][Nb(SCH_2CH_2CH_2S)_3]$ have been presented [473]. Electronic spectra and structure/bonding properties were discussed in relation to extended Hückel calculations [473].

High-coordination-number *di*ethyl-*di*thiocarbamate compounds have been obtained by letting the *penta*halides react with $Na(S_2CNEt_2)$ [368]. The following compounds were identified by means of their crystal structures: $[Nb(S_2CNEt_2)_4]Br$, $[Nb(S_2CNEt_2)_3S]$ and $[Ta(S_2CNEt_2)_3(S_2)]$. The (S_2CNEt_2) ligands are all chelating the metals. The first of these compounds is eight-coordinate with *mmmm* dodecahedral symmetry, the next one is seven-coordinate with an axial multiple Nb=S bond and a pentagonal *bi*pyramidal molecular geometry and the third one is eight-coordinate with the metal in a distorted dodecahedral environment [368].

The coordination chemistry of *poly*nuclear transition metal complexes with sulphur ligands has been reviewed recently [368A].

2.19 Nb(V) and Ta(V) complexes with O- and S-donor ligands

*Poly*sulphide anions S_x^{2-}, with $x = 2$ or more, have been incorporated into a red niobium(V) *di*nuclear complex salt, $(PPh_4)(NH_4)[Nb_2(OMe)_2(S_2)_3(S_5)O]$, see Figure 45. The ligands around Nb form a pentagonal *bi*pyramid, in which the bridging oxy group and the oxygen atoms of the methoxy groups are on axial positions and the S atoms of the S_5^{2-} and non-equivalent S_2^{2-} ligands are equatorially positioned. Preparative details, IR and Raman data are given [369].

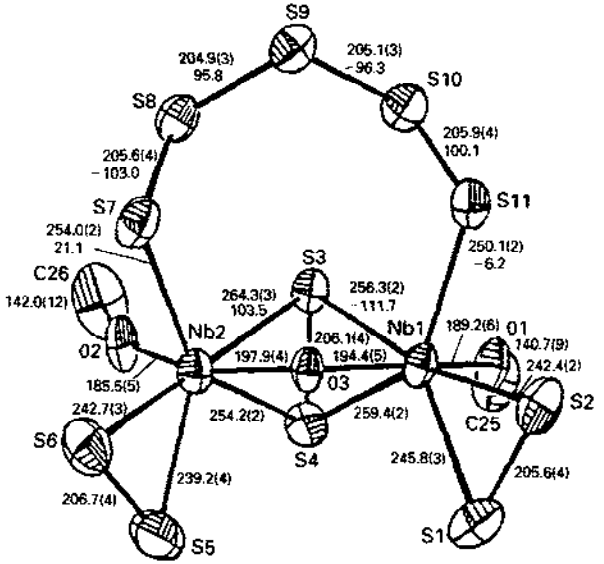


Figure 45. Structure of the anion $[Nb_2(OMe)_2(S_2)_3(S_5)O]^{2-}$. Reproduced with permission from [369], A. Müller, J. Schimanski, M. Römer, H. Bögge, F.-W. Baumann, W. Eltzner, E. Krickemeyer and U. Billerbeck, *Chimia* 39 (1985) 25.

The new seven coordinate *mono*meric complexes $NbST_3$ and $NbSeT_3$ have been obtained by reaction of $NbOT_3$ with $[(Me_3Si)_2Y]$ ($T = O_2H_5C_7$, the tropolonato seven-sided-ring group and Y = S or Se). X-ray crystal structures were determined [366], see the analogous oxide shown in Figure 42.

The Nb=S group has been examined in the *tris*-N,N-*di*ethyl *di*thiocarbamato compound $NbS(S_2CNEt_2)_3$ [370-371]. The X-ray structure solution of the yellow crystals showed two independent molecules with pentagonal *bi*pyramidal coordination, in which the terminal sulphide atom occupies an axial position and the other six positions are taken by sulphur of *di*thiocarbamate [370]. The results compare well with previously solved structures of $NbO(S_2CNEt_2)_3$ [372] and $TaS(S_2CNEt_2)_3$ [373].

*Di*thiolato *di*nitrogen (or hydrazido (4-)) tantalum(V) complexes, $[Ta(SAr)_3(THF)]_2(\mu\text{-}N_2)$ with $Ar = 2,6\text{-}C_6H_3(Pr^i)_2$, $2,4,6\text{-}C_6H_2(Pr^i)_3$ and phenoxide analogues (S replaced by O) have been made (pr^i = *iso*propyl) [374]. Also, crystal structural comparisons have been made of

$[Ta(S\text{-}2,6\text{-}C_6H_3(Pr^i)_2)_3(THF)]_2(\mu\text{-}N_2)$ and $[Ta(O\text{-}2,6\text{-}C_6H_3(Pr^i)_2)_3(THF)]_2(\mu\text{-}N_2)$. The compounds contain nearly linear Ta=N-N=Ta cores and the Ta coordination is five-coordinate [374].

The preparation of $(PPh_4)[NbS(SPh)_4]$ was described, and the crystal structure of the compound was solved, giving a square-pyramidal geometry at the metal with a multiply-bonded sulphur at the apex (Nb-S = 2.171(2) Å) [112].

2.20 Nb(V) and Ta(V) oxynitrides and complexes with O- and N-donors

New oxynitrides ANbO$_2$N and ATaO$_2$N with A = Ba, Sr, Ca were prepared and shown to have a ABO_3 perovskite type structure [375].

$Ta(OPr^i)_{5-x}(SB)_x$ coordination compounds of tantalum(V) have been synthesized in boiling anhydrous benzene solution, OPr^i being the *iso*propoxide radical, $x = 0, 1, 2$ or 3 and SBH is aldimines of the type o-HO-C_6H_4-CH:N-C_6H_4-CH_3-o, o-HO-C_6H_4-CH:N-C_4H_9-n, C_6H_5-CH:N-NH-$CONH_2$ or C_6H_5CH:N-NH-$CSNH_2$ [376-377]. The aldimines were obtained by condensation of salicylaldehyde with *o*-methylaniline or *n*-butylamine and of benzaldehyde with semicarbacide hydrochloride or thiosemicarbacide. The complexes were fully characterized by their analytical data, conductances, magnetic data, IR, VIS and PMR spectra and molecular weights determined by the cryoscopic method in benzene. The complexes are all *mono*meric, with coordination numbers six, seven and eight for the x = 1-, 2- and 3-derivatives, respectively, with the aldimines acting as *bi*dentate ligands, using O, N or S atoms for chelating to tantalum [377].

Complexation of niobium(V) and tantalum(V) with 4-oximino-3-methyl-2-pyrazolin-5-one takes place via oximino N and pyrazolone carbonyl O, resulting in the *bi*nuclear compounds $LM(O)(\mu\text{-}O)_2M(O)L$, ($M$ = Nb or Ta, HL = 4-oximino-3-methyl-2-pyrazolin-5-one), according to elemental analysis, magnetic and IR spectral methods [378].

The complexation reaction of 5,5'-methylene-*bis*-salicylaldoxime (MBSO) with $TaCl_5$ was studied under various conditions (in DMF solution in dry nitrogen or ambient air or in oxalate solution) [127]. The 1:3 compound obtained was *dia*magnetic and insoluble in common organic solvents. A probable structure (see Figure 46) was proposed on the basis of elemental analysis, magnetic measurements and infrared spectra [127].

Niobium and tantalum *penta*ethoxides react with *mono*functional benzoyl hydrazones, BHyH [379], or *bi*functional benzoyl hydrazones, BH_2 [380], in refluxing benzene to give *mono*meric red or brown products of the type $M(OEt)_{5-x}(BHy)_x$, x = 1, 2 or 3 [379], or yellow to orange $M(OEt)_{5-2x}(B)_x$, x = 1 or 2 and M = Nb, Ta, respectively [380]. The *bi*functional benzoyl

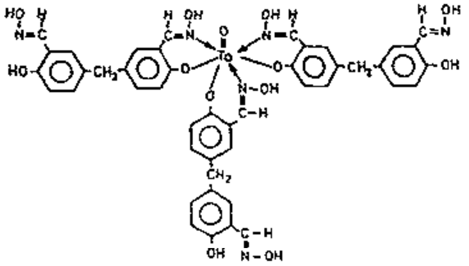
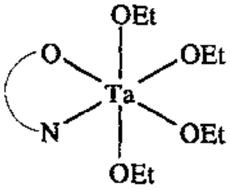


Figure 46. Probable structure of tantalum MBSO complex, $[TaC_{45}H_{39}O_{13}N_6]$, with seven-coordinated Ta. Reproduced with permission from [127], S. Chomal, A. S. Aazmi and G. C. Shivahare, *Acta Chim. Hung.* **122** (1986) 127.

hydrazones are *tri*dentate [380]. The benzoyl hydrazones employed were prepared by condensing an amine with an aldehyde or ketone, *e.g.* benzaldehyde, acetophenone and furfural. On the basis of elemental analysis, IR and NMR spectra and molecular weight determinations, it was concluded that the *mono*functional hydrazones behave like *bi*dentate ligands coordinating to the metal through deprotonated enolic and azamethine groups [379]. The following 6, 7 and 8 coordinate structures, **17**, **18** and **19**, were tentatively assigned to the complexes.



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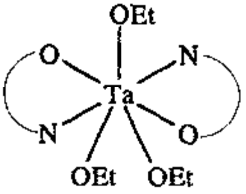

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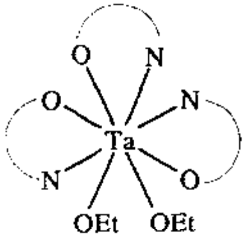

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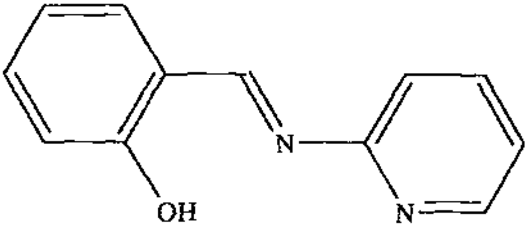
Niobium(V) Schiff-base complexes of the type $Nb(OEt)_{5-x}(L)_x$ where $x = 1$ or 2 and LH is the Schiff-base salicylidene-2-aminpyridine, **20**, have been isolated as liquids from niobium *penta*ethoxide /Schiff-base mixtures in dry benzene [381].



20

The Schiff-base salicylidene-2-aminopyridine.

The compounds were *mono*meric in boiling benzene. IR spectra indicated coordination through azomethine nitrogen and phenolic oxygen. Also tantalum alkoxides are known to react with certain Schiff-bases [382].

Niobium(V) forms a ternary complex $[Nb(BPHA)_2(DCTA)]$ (BPHA = N-benzoyl-N-phenylhydroxylamine and DCTA = 1,2-*di*amino-*cyclo*hexane-tetraacetic acid) which can be used for analytical purposes (polarographic determination of traces of Nb) [383].

A comparative characterization was given of glycinato-niobates and glycinato-tantalates, synthesized in basic media [384]. Both the carboxylate and the amino groups of the glycinic acid were coordinated to the metal, according to IR-spectral evidence [384].

The synthesis has been performed and the crystal structure solved of $Nb(OAr\text{-}2,6\text{-}Ph_2)_3(NMe)(HNMe_2)$ and the corresponding Ta methylimide complex ($OAr\text{-}2,6\text{-}Ph_2$ is 2,6-*di*phenylphenoxide) [385].

2.21 Nb(V) and Ta(V) complexes with As-ligands

A new kind of complex anion, $[NbAs_8]^{3-}$, see Figure 47, was discovered in crystals containing also rubidium and a rubidium cryptate. The new ion of symmetry $\bar{8}2m - D_{4d}$ participates in the formation of one-dimensional chains with stacked crown-forming $(As^-)_8$ *poly*anions containing Nb^{5+} in their centers separated by Rb^+ cations. Some data on the crystal structure and the molecular orbital diagram are reported [386].

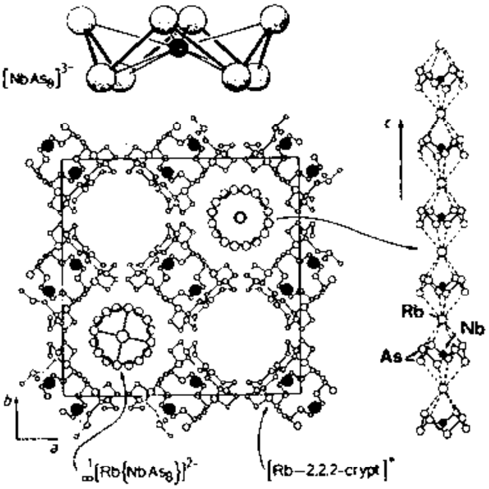


Figure 47. Structure of the new complex anion, $[NbAs_8]^{3-}$, and the crystal in which it was found. Reproduced with permission from [386], H.-G. von Schnering, J. Wolf, D. Weber, R. Ramirez and T. Meyer, *Angew. Chem.* **98** (1986) 372.

2.22 Nb(V) and Ta(V) carbides and complexes with C-donor ligands

Niobium carbide NbC has unusual properties such as being hard and brittle. Its electronic structure has been studied by high-energy electron energy-loss spectroscopy [387].

The reaction between the Nb(V) cyclo*penta*dienyl derivate $[(\eta^5\text{-}t\text{-}BuC_5H_4)_2Nb]BH_4$ and sulphur in toluene solution has been studied [388]. In this way, a new Nb(V) compound, $\{(Cp')_2Nb(\eta^2\text{-}S_2)\}_2(\mu\text{-}S_5)$ ($Cp' = \eta^5\text{-}t\text{-}BuC_5H_4$ = *tert*-butyl-substitued cyclo*penta*dienyl), has been synthesized and its crystal structure determined, see Figure 48.

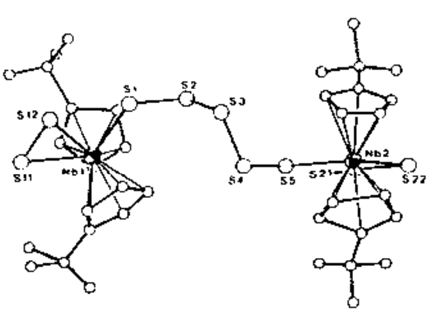


Figure 48. Structure of $(t\text{-BuC}_5H_4)_4Nb_2S_9$. Reproduced with permission from [388], H. Brunner, U. Klement, J. Wachter, M. Tsunoda, J.-C. Leblanc and C. Moise, *Inorg. Chem.* **29** (1990) 584.

2.23 Biological complexes of Nb(V) and Ta(V)

Chelate macrocyclic complexes of the extended π-bonding type have been little studied in the period. Acid-base properties of the *meso*-nitrogen atoms of a substituted tetrazaporphyrin metallate(V) ring system (*tetra*-4-*tert*-butylphtalocyanine, OTaPc') were studied in anhydrous acetic and sulphuric acids, for the case of niobium [389] and for tantalum [390]. The kinetic stabilities (stepwise protonation constants [389]) were determined by visible absorption spectroscopy. Niobium and tantalum phtalocyanine complexes belong to the group of stable phtalocyanines in proton-donor media [390].

The syntheseis, properties and crystal structures of some phtalocyaninato complexes have recently been reported: The *di*nuclear Br_3^- salt μ-bromo-μ-*di*oxo-*bis*(phtalocyaninatoniobium(V))*tri*bromide [390A], and the *mono*nuclear *tri*chloro(phtalocyaninato)Tantal(V) [390B], both having coordination numbers of seven.

Complexes [Nb(por)(O)(OAc)] and [Nb(por)(X)$_3$], (in which por is a porphyrinate^{2-} anion: oep = *octa*ethylporphyrinate, tpp = tetraphenylporphyrinate or tptp = tetra*para*tolylporphyrinate and X = Cl or Br), have been prepared and characterized on the basis of IR, UV-VIS, electrochemical and EPR data [391].

Ascidians (sea squirts) are able to extract niobium from sea-water containing 0.1 ppb of Nb, but the complexes responsible for the binding of niobium are not known. Recently, it was shown [392] *in vitro* that amino-acids like glycine, alanine, serine, tyrosine, cysteine cannot be responsible, but certain α-hydroxy carboxylic acids (lactic, malic, glycollic, and tartaric acids) are able to candidate, and suggestions are made for the mechanism [392].

2.24 Solvent extraction of Nb(V) and Ta(V)

The extraction of niobium from ores and the refinements needed to obtain high-purity niobium complexes and niobium metal have been reviewed [13-14]. The distribution coefficients for extraction of various elements into the commonly used solvent methyl-*iso*butyl-ketone (MIBK) are given, according to reactions similar to *e.g.*

$$4\ HF + NbF_7^{2-} + 3\ MIBK \longrightarrow H_2NbF_7 \cdot 3(MIBK) + 2\ HF_2^-$$

Separation coefficients of niobium and tantalum in various ketones and other details are also given [14-15]. In the extraction/separation process, MIBK can be replaced by *tri*-butyl phosphate (TBP) forming a soluble complex $H_2NbF_7{\cdot}3(TBP)$ [15].

The extraction of niobium(V) and tantalum(V) from >4 molar sulphuric acid solutions by *di*-2-ethylhexylhydrogen phosphate (D_2EHHP) has been studied by chemical analysis, infrared spectroscopy and other methods [393]. The extracted compounds did not contain any sulphate group, and corresponded to the formulae $NbO(D_2EHHP)_3$ and $TaO(D_2EHHP)_3$, tending to polymerize in the organic phase, perhaps forming $MO(D_2EHHP)_3(H\text{-}D_2EHHP)_3$, M = Nb or Ta [393].

Niobium(V) in hydrochloric and sulphuric acid media, in the presence of an excess of chloride or thiocyanate ions, reacts with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (H*R*) to give complexes, $Nb(OH)_3ClR$ or $Nb(OH)_3(NCS)R$, which are extractable into chloroform [146]. The experimental conditions for quantitative extraction of niobium(V) into the organic phase are given, permitting a separation from zirconium(IV) and hafnium(IV) [394]. The identity of the complexes was determined spectrophotometrically [146].

A spectrophotometric study was made on the extraction of mixed complexes of niobium(V) and tantalum(V) with 4-(2-pyridylazo)-resorcinol (PAR or H_2R) and hydroxy-acids (oxalate, tartrate, citrate, *tri*hydroxy-glutarate and mucate) by a chloroform solutions of *tri*-*n*-octylamine

(TOA) [395]. The Nb(V)-PAR-oxalate, Nb(V)-PAR-tartrate and Ta(V)-PAR-oxalate compounds go into the basic organic phase, probably forming the singly charged anions $[NbO(C_2O_4)(HR)_2]^-$, $[NbO(C_4H_4O_6)(HR)_2]^-$ and $[Ta(OH)_2(C_2O_4)(HR)_2]^-$, respectively [364, 395].

Re-extraction of $NbOF_5^{2-}$ and TaF_7^{2-} from solvents with C=O, S=O and P=O functional groups has been studied by means of chemical analysis and Raman spectroscopy [46].

3. Niobium(V) and (IV) mixed complexes (d^0 and d^1)

The knowledge of the complicated phase relationships within the system NbO_2-Nb_2O_5, some of which have already been mentioned, has been extended through the preparation of 1-2 mm large crystals of $Nb_{22}O_{51}$, $Nb_{47}O_{116}$, $Nb_{25}O_{62}$ and $Nb_{53}O_{132}$, all belonging to the NbO_x type with $2.4 < x < 2.5$ [396]. Many systems with NbO_2-Nb_2O_5 and a third metal oxide have been studied. $Nb_{12}O_{29}$ has been modified to form $V_3Nb_9O_{29}$, the block-structure of which was studied by electron microscopy [397]. A new kind of block structure was found in the crystal structure of $V_8Nb_5O_{29}$ [398]. Lithium metal has been inserted into $V_3Nb_9O_{29}$ forming *e.g.* $Li_{13.6}V_3Nb_9O_{29}$ [399].

Non-stoichiometric phases $Hf_2Nb_{20}O_{51}$, $Zr_3Nb_{44}O_{116}$, $Hf_3Nb_{44}O_{116}$, β-$ZrNb_{24}O_{62}$ and β-$HfNb_{24}O_{62}$ have block structures, according to high resolution transmission electron microscopy [400].

A new mixed-valence oxoniobate compound, $Sr_5Nb^{4+}{}_3Nb^{5+}{}_2O_{16}$, was synthesized from Sr and Nb oxides in a hydrogen plasma at about 2000 °C. The complicated crystal structure was solved and found [401] to contain four different kinds of NbO_6 octahedra (two Nb(IV) and two Nb(V)) and one relatively strongly distorted NbO_4 tetrahedron, see Figure 49. Hence, niobium(IV) then can be octahedral as well as tetrahedral coordinated within the same framework.

Another new mixed-valence oxy-niobate compound, $Sr_7Nb_6O_{21}$, has been prepared [402]. The method involved a mixture of 4 $SrCO_3$, 2 Nb and 1 Nb_2O_5 which was pressed and heated to about 2500 °C by means of the thermal power of a CO_2 laser. Single crystals produced were investigated by X-ray diffraction techniques and proved to have a structure consisting of layers of perovskite-type, with a width of about 13 Å, and containing 6 layers of corner-linked NbO_6 octahedra and Sr^{2+} ions in between, see Figure 50. The three different kinds of niobium atoms all have trigonal symmetry with three long Nb - O bonds (2.09 - 2.18 Å) and three short ones (1.85 - 1.96 Å). The formula $Sr_7Nb_6O_{21}$ can be given as $Sr_{1.167}Nb^{+4}{}_{0.333}Nb^{+5}{}_{0.667}O_{3.5}$, showing the close relationship of the structure to the already known perovskites $CaNbO_{3.5}$ and $Ba_{1.25}TaO_{3.75}$ [402].

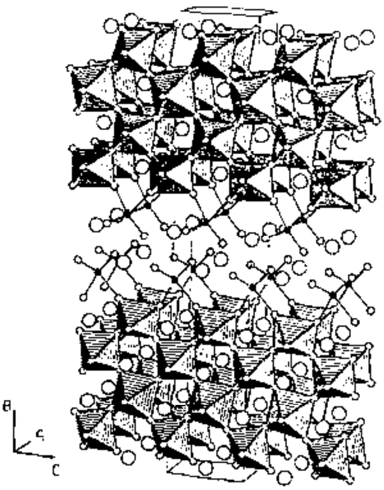


Figure 49. Structure of the mixed-valence oxy-niobate compound, $Sr_5Nb^{4+}{}_3Nb^{5+}{}_2O_{16}$, showing four kinds of NbO_6 octahedra (hatched) and one kind of deformed NbO_4 tetrahedra (small filled circles). Reproduced with permission from [401], K. Schückel and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **528** (1985) 91.

4. Nb(IV) and Ta(IV) compounds (d^1)

Low valent complexes of niobium and tantalum were described in a 275 pages long thesis [403].

4.1 Nb(IV) and Ta(IV) halide complexes

Thermodynamic data for gaseous tantalum halides, TaF_4, $TaCl_4$, $TaBr_4$, and TaI_4 were reviewed, and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20]. Crystals of $NbCl_4$ have been obtained by chemical vapour transportation [404].

The vapour pressures of solid $NbCl_4$ and $NbBr_4$ have been determined by a spectrophotometric method, as function of temperature near 600 K [405]. $NbCl_4$ is *mono*meric in the gaseous state. Gas phase visible/near-IR spectra of $NbCl_4$ and $NbBr_4$ are given [405]. The stability of gaseous $NbCl_4$ was studied by tensimetry, DTA and TG methods [25, 406], and the enthalpies of formation of solid $NbCl_4$, $NbBr_4$ and NbI_4 were given [407-408]. A possible

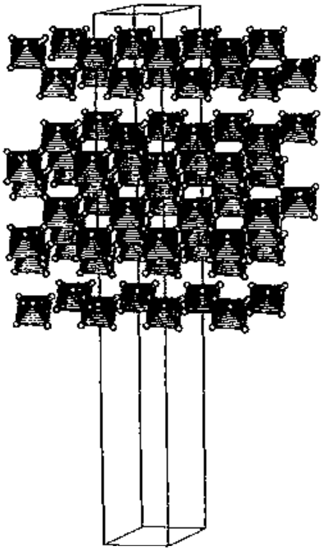


Figure 50. Unit cell of the mixed-valence oxyniobate compound, $Sr_7Nb^{4+}{}_2Nb^{5+}{}_4O_{21}$, showing a perovskite layer of corner-linked NbO_6 octahedra (hatched) and the beginning of the next layers. Strontium ions (in the cavities between octahedra) are not shown. Reproduced with permission from [402], K. Schückel and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **523** (1985) 69.

disproportionation of $NbCl_4$ into $NbCl_3$ and $NbCl_5$ occurred at *ca.* 320 °C [406]. The photoelectron spectrum (AlKα, HeI) of NbI_4 (or rather Nb_2I_8) was studied in an attempt to find the relation between the energy of the niobium core levels and the oxidation number [42].

The magnetic properties of crystals of Li_2NbF_6 and Na_2NbF_6 were determined from 4.2 to 293 K [409]. The crystals exhibit *para*magnetic behaviour as a result of the presence of Nb(IV) cations at the centers of independent octahedra, which are distorted from the ideal octahedral O_h-symmetry. The standard enthalpy of formation was determined for the Rb_2TaBr_6 crystal and for the $TaBr_6{}^{2-}$ ion in the gas state [410]. The ferri-magnetic behaviour of trigonal $MnNbF_6$ was studied in order to obtain information on the Mn^{2+}-F^--Nb^{4+} super-exchange interaction in this structure of corner-sharing NbF_6 and MnF_6 octahedra [411].

Niobium and tantalum in K_2NbF_7 and K_2TaF_7 will be partly reduced to oxidation state IV after being bombarded in a 4 keV Ar^+ ion beam [412].

A ternary chloride of tin(II) and tantalum(IV), Sn[Ta_2Cl_9], has been prepared as a green *dia*magnetic solid [413]. The X-ray crystal structure of this compound has several surprising features: discrete face-sharing *bi*octahedral [Ta_2Cl_9]$^-$ units that show a chiral distortion from D_{3h} symmetry, see Figure 51.

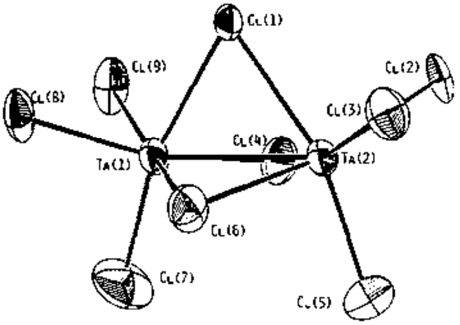


Figure 51. Structure of the [Ta_2Cl_9]$^-$ unit as found in the Sn^{2+} salt. Reproduced with permission from [413], F. A. Cotton, E. Babaian-Kibala, L. R. Falvello and M. Shang, *Inorg. Chem.* **29** (1990) 2591.

4.2 Nb(IV) and Ta(IV) oxyhalide complexes

Thermodynamic data for gaseous tantalum oxyhalides, $TaOF_2$, $TaOCl_2$, $TaOBr_2$, and $TaOI_2$ were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20]. Solid $NbOF_2$ has been synthesized and found to crystallize in space group *Pm3m* with one formula in the cell. Nb is on an octahedral site. Visible and UV spectra and magnetic behaviour between 77 and 300 K are reported [414].

$NbOCl_2$ and $TaOCl_2$ powders have also been examined by X-ray diffraction; the two compounds were found to be *iso*-structural and indexed powder diagrams were given, as well as structural and IR spectral data for the grey-green niobium compound [32]. $NbOBr_2$, $TaOBr_2$ and $TaOI_2$ crystals have further been prepared and examined by X-ray diffraction [34].

4.3 Nb(IV) and Ta(IV) halide complexes with O-donors

*Di*nuclear niobium(IV) complexes, $Nb_2Cl_4(OMe)_4(MeOH)_2 \cdot 2MeOH$ and $Nb_2Cl_4(OMe)_4(CH_3CN)_2$, have been prepared and studied by X-ray crystallography and proton NMR spectroscopy [415]. The complexes have an edge-sharing *bi*octahedral geometry and possess a single Nb-Nb bond and two bridging methoxy groups, see Figure 52. Axial and equatorial terminal ligands seem to interchange easily [415].

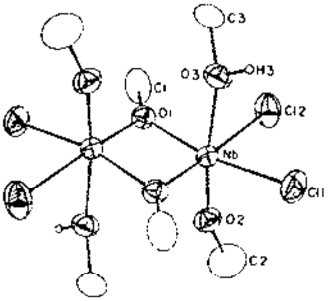


Figure 52. Structure of the centrosymmetric *di*nuclear niobium(IV) molecule, $Nb_2Cl_4(OMe)_4(MeOH)_2$. Reproduced with permission from [415], F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chem.* **26** (1987) 3319.

The compound *trans*-$NbCl_2(Bu^tC(O)CHC(O)Bu^t)_2$ or, in short notation, *trans*-$NbCl_2(dpm)_2$ with Hdpm = dipivaloylmethane = 2,2,6,6-tetramethylheptane-3,5-*di*one, has been prepared in two polymorphs [416]. The X-ray crystal structures have been solved, and they show the same kind of molecule, see Figure 53. The UV-visible spectrum for this octahedral or rather D_{2h}-symmetry niobium^{4+} chromophore (the d^1 electron system) shows a doublet band at 588.4 and 626.7 nm. High formal oxidation states of the metal in many cases lead to charge transfer transitions obscuring the d-d transitions. By combining VIS and EPR spectral measurements with a molecular orbital calculation (the Fenske-Hall procedure), a reasonable and consistent picture of the electronic structure of the molecule was obtained [416]. The doublet in the spectrum was assigned to the *d-d* transitions $yz \dashrightarrow xz$ and $yz \dashrightarrow x^2 - y^2$ (at *ca.* 16000 and 17000 cm^{-1}). The EPR spectrum with the expected 10-line signal, with $<g> = 1.930$ and with $<A_{iso}> = 149$ G also were explainable.

The new *bi*nuclear Nb(IV) compound, $Nb_2Cl_2(OEt)(O_2CMe)_5$, has been shown to have a crystal structure in which two $(\eta^2\text{-}CH_3COO)_2Nb$ groups are joined by $\mu\text{-}OC_2H_5$, two μ-Cl atoms and $\mu_2\text{-}\eta^2\text{-}CH_3CO_2$. In this complex the Nb-Nb distance indicates the presence of a single bond [117].

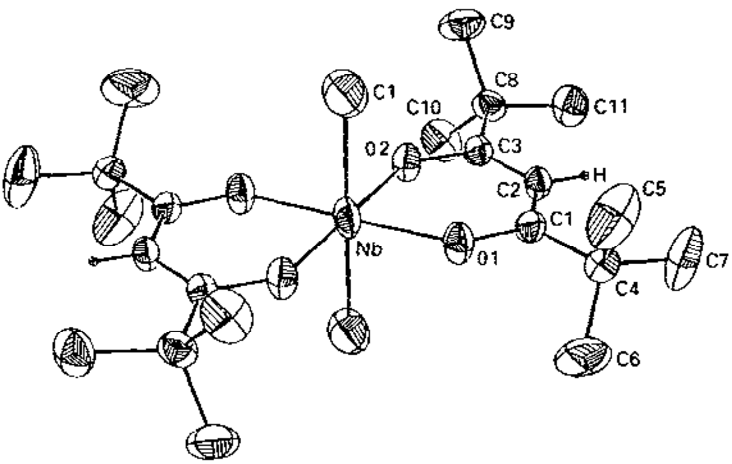


Figure 53. Structure of *trans*-$NbCl_2(dpm)_2$ with Hdpm = dipivaloylmethane in its *mono*clinic phase. Reproduced with permission from [416], F. A. Cotton, M. P. Diebold and W. J. Roth, *Polyhedron* 4 (1985) 1485.

4.4 Other Nb(IV) and Ta(IV) halide complexes

Solid NbS_2Cl_2 was obtained by letting Nb react with S_2Cl_2 [114]. It contains $Nb_2(S_2)_2^{4+}$ groups linked with one another by Cl^- ions in a layered lattice [417] and is unstable when heated [418]. Its electronic, vibrational, resonance Raman spectra and the crystal valence force field were reported [419]. The compound underwent oxidation forming NbS_2Cl at 160-200 °C in an electrochemical cell using a $NaAlCl_4$ molten salt as an electrolyte [114]. It can be intercalated with lithium to form $Li_{0.7}NbS_2Cl_2$ [420].

The tantalum *di*mer $Ta_2Cl_6(SMe_2)_3$ has been found to react with the bulky chelating ligand 1,3-*bis*(*di*isopropylphosphino)propane (dippp) to form $[(dippp)TaHCl]_2(\mu\text{-}S)(\mu\text{-}H)_2$ [474]. The bonding was deduced form spectroscopic data and the solved X-ray structure.

Dark brown *para*magnetic, *triangulo* niobium(IV) clusters, $(Cp')_3Nb_3Cl_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}O)(\mu_3\text{-}X)$, with Cp' = C_5H_4Me (methylcyclo*penta*dienyl) and X = OH or Cl have been prepared. X-ray structure determinations show that these clusters contain a Nb_3 triangle bridged by Cl atoms along each edge and capped by a μ_3-oxo ligand and a μ_3-X ligand on opposite sides of the Nb_3 plane. Terminal Cp' and Cl ligands complete the coordination sphere about each Nb atom. Bonding in the clusters is discussed, based on their 10-line ESR spectra (the three d^1 electrons form an $S = 1/2$ system, coupled to one Nb nucleus with $I = 9/2$) [421-423].

Tantalum(IV) complexes, $(Cp')_2Ta_2X_4(\mu_2\text{-}X)_2$, with Cp' = *e.g.* C_5H_4Me (methylcyclo*penta*dienyl) and X = Cl or Br have been prepared. X-ray structures were determined, including their reactivity as precursors to the doubly bonded $(Cp')_2Ta_2(\mu\text{-}X)_4$ tantalum(III) complexes. Bonding in the clusters is discussed [475].

4.5 Nb(IV) and Ta(IV) oxides

By use of mass spectrometry and a Knudsen cell, the gaseous molecule NbO_2 has been characterized thermodynamically with respect to dissociation stability [424]. Thermodynamic data for gaseous tantalum(IV) oxide, TaO_2, were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20].

Solid NbO_2 was studied theoretically by molecular orbital model calculations on small clusters in order to explain the photo-electron spectra [425]. MO level schemes and atomic charges of $[NbO_5]^{6-}$ and $[NbO_6]^{8-}$ have been given [425]. Thermogravimetric measurements have shown that solid NbO_2 is a metal-deficient oxide, whose main defects are neutral niobium vacancies in the rutile structure [426]. Rutile $Nb_{0.94}O_2$ was prepared by shock reduction of Nb_2O_5, like previously rutile TaO_2 was prepared from Ta_2O_5 [427]. Recovered products were examined by X-ray powder diffraction analysis [427]. TaO_2 is unstable, but can be studied in $(Ti,Ta)O_2$ rutile solid solutions. Crystal field splittings for Ta have been studied in such phases [428].

A new mixed-oxidation-state compound $NaNb(II)Nb(IV)_2O_5F$ has been prepared. Single crystals are *dia*magnetic and black with metallic luster. The structure was determined and it shows short Nb-Nb distances [429].

The compound $(Ti^{3+})_2(Ti^{4+})_{1-x}(Nb^{4+})_xO_5$ with $x = 0.075$ was examined magnetically versus temperature [430]. Nb(IV)-Nb(IV) pairs were discovered in new mixed valence oxides $KTi_{2-x}Nb_{5+x}O_{17}$ rutile crystals ($0 \leq x \leq 1.75$) [431].

The product $EuNbO_3$ of the reaction between EuO and NbO_2 has been characterized by X-ray L_{III} absorption spectroscopy. The oxidation states were proven to be Eu^{2+} and Nb^{4+} [293].

4.6 Nb(IV) and Ta(IV) complexes with O-donors

A red *tetrakis*-complex of niobium(IV), NbL_4, with L = the pyridine-2-caboxylate anion, **15**, was prepared in dry benzene. The compound was analysed and characterized as a non-ionic *mono*mer Nb(IV) complex by iodine titration, by molecular weight and conductivity determinations. Electronic and IR spectra as well as magnetic susceptibility were reported [363].

Crystallographic analyses of two salts, $K_2(H_3NCH_2CH_2NH_3)[Nb(C_2O_4)_4]\cdot4H_2O$ and $K_4[Nb(C_2O_4)_4]\cdot3H_2O$, have shown that the *tetrakis*(oxalato)niobium(IV) anion, $Nb(C_2O_4)_4{}^{4-}$, can be either square *anti*prismatic or dodecahedral in the solid state [432].

The new niobium(IV) nonamethoxide anion, $[Nb_2(OMe)_9]^-$, has been characterized in three X-ray crystallographic structure solutions; it has a confacial *bi*octahedral geometry of virtual D_{3h} symmetry with Nb-Nb bonding and three O-bridging methoxy groups [433].

4.7 Nb(IV) and Ta(IV) sulphides and selenides

The layered compounds MX_2, with M = Nb, Ta and X = S, Se tend to be of interest in many contexts. The M atoms and the chalcogen atoms are in hexagonal close-packed layers; layers of M are sandwiched between layers of chalcogen, see Figure 54. Nb and Ta atoms display both octahedral and trigonal-prismatic coordination [16].

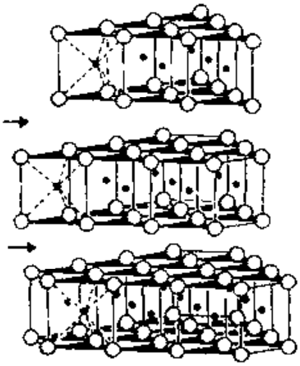


Figure 54. Schematic representation of the MX_2 type structure. Intercalation can take place as indicated by arrows. The drawing is adapted with permission by [347], D. D. Keszler, J. A. Ibers, S. Maoyu and L. Jiaxi, *J. Solid State Chem.* **57** (1985) 68.

Phases NbS_x with x = *ca.* 1.5 or 1.7 are obtained often when preparing NbS_2 from Nb_2O_5 and H_2S at 700 °C [434]. NbS_xSe_{2-x} layer crystals, with different *poly*type-structures depending on x, for $0 \leq x \leq 2$, were prepared and studied by X-ray diffraction [435].

The properties of NbS_2 were studied by X-ray photoelectron spectroscopy and by magnetic susceptibility [436]. The kinetics of the oxidation of NbS_2 to Nb_2O_5 has been studied thermogravimetrically as a function of the partial pressure of oxygen [437].

Inner-shell-electron energy-loss spectroscopy [438], scanning tunneling microscopy [439] and ^{181}Ta Mössbauer spectroscopy [440] were used to obtain information on electronic structure and atomic arrangements of 2*H*-TaS_2. In Li intercalated 2*H*-TaS_2, the electronic configuration of Ta changes form $Ta^{4+}(5d^1)$ toward $Ta^{3+}(5d^2)$ [440]. Electronic structures of other 2*H*-TaS_2 intercalates are given in [441]. Preparational details for 2*H*-TaS_2 intercalates have been reported in [442] and ^{181}Ta Mössbauer spectra given in [443]. The superstructure in 4*Hb*-TaS_2 was studied by high resolution electron microscopy [444].

A phase transition in 1*T*-TaS_2 involving charge density waves has been studied by X-ray scattering [445-446], electron diffraction [447], ^{181}Ta NMR and NQR spectroscopy [448], magnetic methods [449], thermal methods [450], and high resolution electron and scanning tunneling microscopy [439,451-452]. The transition is hydrogen impurity dependent [453-454]. The special interest of the study is that the phase transition which clearly could be followed on precession photographs does not involve the underlying crystalline structure, only the waves. Similar waves occur in 1*T*-$TaSe_2$, see *e.g.* [455].

It has been shown that silver ions can be intercalated between the layers in 2*H*-MS_2 [456] (M = Nb, Ta). In such crystals, grown using vapour transport with chlorine as transport agent, short Ag-Nb or Ag-Ta distances, determined by X-ray diffraction methods, suggest interaction between the 5s-orbital of silver and the lowest unoccupied (or partly occupied) d_z2-orbital of the trigonal-prismatically coordinated transition metal. The stability of intercalated phases Ag_xMS_2 was studied [456] by EMF measurements and compared with the similar alkali metal intercalates. Also, lithium, copper, silver, iron, tin, zink and many others [457] have been intercalated into NbS_2 [458] [459-464] and $NbSe_2$ [465-466] and into molybdenum substituted niobium *di*chalcogenides [467].

TaS_2 has been intercalated with hydrogen [468], lithium [441-442,469,476], sodium [442-443], lead [441], tin [441] and substituted with molybdenum [477], and with rare earth metals (La and Ce), forming several new phases with interesting superconductivity [478]. TaS_2 can be intercalated with ammonia [479-480], pyridine [481-482] and with metalhydroxides [483].

Co-intercalation of alkali metal hydroxides and water molecules into NbS_2 and TaS_2 can be made, according to chemical analyses, X-ray diffraction and NMR spectroscopic investigations [484].

Crystals of Nb_2Se_9 have been re-examined by structure solution and classified as containing Nb(IV); hence the formula can be specified as $2Nb^{4+}2(Se_2)^{2-}(Se_5)^{4-}$, in accordance with the one-dimensional semiconducting properties. The structure is based on chains of niobium in *bi*capped trigonal prismatic coordination with selenium and has short Nb-Nb bonds [485].

Also, the $CuTaS_3$ crystal structure solution has given the valence description as $Cu^{2+}Ta^{4+}3S^{2-}$ [485]. A new ternary chalcogenide, $Ta_2Cu_{0.80}S_6$, has been prepared and its crystal structure solved [486]. It contains S_2^{2-} pairs and the Ta atoms must then have a formal valency of IV. It shows a close relation to the $CuTaS_3$ structure, containing units of infinite chains of CuS_4 tetrahedra and TaS_6 octahedra [486].

The compounds Nb_2PdSe_6, $Nb_2Pd_{0.71}Se_5$, $Nb_3Pd_{0.72}Se_7$, Ta_2NiS_5 and Ta_2NiSe_5 have been prepared and examined [16, 340-341]. They contain new kinds of layered and channel structures, see *e.g.* Figure 55. They have interesting electric and magnetic properties, and exhibit structural phase transitions. Ta_2NiS_5 have been intercalated topotactically with hydrazine, 1,2-*di*amino-ethane and 1,3-*di*amino-propane and the inter-layer distance enlargements studied by X-ray diffraction [487].

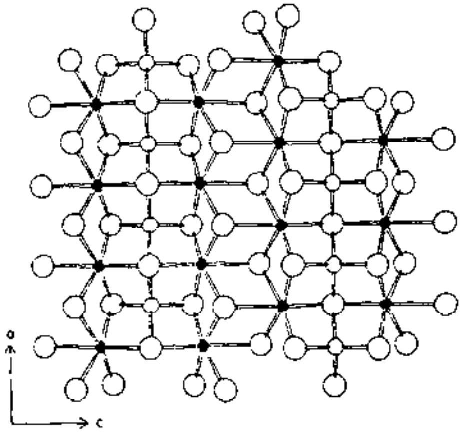


Figure 55. The *ortho*rhombic *Cmcm* Ta_2NiS_5 structure in the (a,c) plane. Octahedral tantalum and tetrahedral nickel are shown, surrounded by sulphur (or selenium) in layers three atoms thick. Reproduced with permission from [340], F. J. Di Salvo, C. H. Chen, R. M. Fleming, J. V. Waszczak, R. G. Dunn, S. A. Sunshine and J. A. Ibers, *J. Less-Comm. Met.* **116** (1986) 51.

Furthermore, it was found that *e.g.* the reaction of Ta_2NiSe_5 and Ta_2PdSe_6 with *n*-butyllithium affords the compounds $Li_2Ta_2NiSe_5$ and $LiTa_2PdSe_6$ which have layered structures [488].

A *para*magnetic compound, $NbNiTe_5$, with metallic conductivity and a new kind of layer structure has been prepared [489]. Each layer consists of *bi*capped trigonal prismatic niobium atoms and octahedral nickel atoms coordinated by tellurium atoms, see Figure 56. For comparison, note the structure of Ta_2NiS_5 and Ta_2NiSe_5, Figure 55.

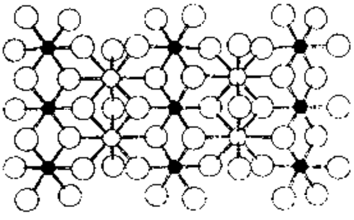


Figure 56. View of one layer of the layer structure of $NbNiTe_5$, showing the coordination around the Nb atoms (small open circles) and Ni atoms (small filled atoms). Reproduced with permission from [489], E. W. Liimatta and J. A. Ibers, *J. Solid State Chem.* **71** (1987) 384.

In the compounds $NbTe_2$ and $TaTe_2$ the metals occupy octahedral positions [16]. $NbTe_2$ reacts with PCl_5, giving $NbCl_5$ and PCl_3 [490].

4.8 Other Nb(IV) and Ta(IV) complexes

Complexes [Nb(por)(O)] and [Nb(por)(X)$_2$] (in which por is a porphyrinate^{2-} anion: oep = *octa*ethylporphyrinate, tpp = tetraphenylporphyrinate or tptp = tetra*para*tolylporphyrinate and X = Cl or Br) have been prepared, by reduction of [Nb(por)(X)$_3$] or [Nb(por)(O)(OAc)] [391]. The compounds were characterized on the basis of IR, UV-VIS, electrochemical and EPR data [391]. The [Nb(por)(X)$_2$] complexes have axial symmetry [391].

4.9 Nb(IV) and Ta(IV) complexes with N- and C-donors

Ammonolysis of tantalum alkyls has been studied in order to obtain a safe procedure for preparing solid state materials. In this way cubic TaN and a *tri*meric nitride, $((Cp')MeTaN)_3$ (Cp' = methylcyclo*penta*dienyl and Me = methyl) were obtained. The crystal structure of the latter compound was solved, see Figure 57, and other properties elucidated. The compound can be reduced to form $[K(n Et_2O)]^+[((Cp')MeTaN)_3]^-$. Molecular orbital diagrams are given [491].

The formation of vacancies in niobium carbides has been studied theoretically [492].

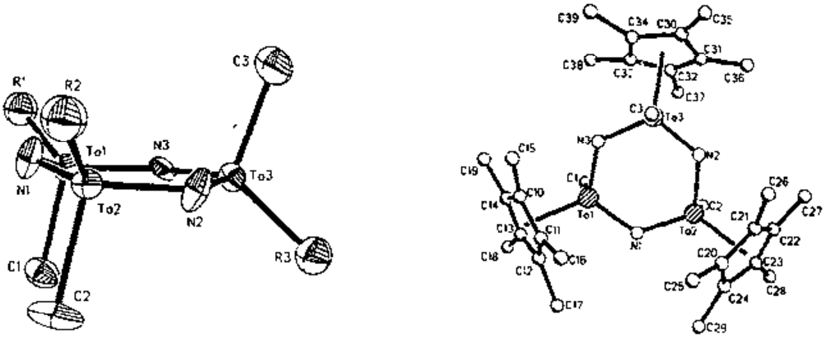


Figure 57. Crystal structure of the *tri*meric nitride molecule, $((Cp')MeTaN)_3$ (Cp' = methylcyclo*penta*dienyl and Me = methyl) [491]. Reproduced with permission from [491], M. M. B. Holl, M. Kersting, B. D. Pendley, and P. T. Wolczanski, *Inorg. Chem.* **29** (1990) 1518.

5. Mixed Nb(IV) and Nb(III) complexes (d^1 and d^2)

A new mixed valence (Nb(III) and Nb(IV)) compound of unknown structure, $(C_5Me_5)_3Nb_3S_7)$, has been obtained by letting the Nb(I) cyclo*penta*dienyl derivate (η^5 $-C_5Me_5)Nb(CO)_4$ and sulphur react in tetrahydrofuran solution under irradiation [388].

6. Nb(III) and Ta(III) complexes (d^2)

6.1 Nb(III) and Ta(III) halides and halide complexes

Thermodynamic data for gaseous tantalum halides, TaF_3, $TaCl_3$, $TaBr_3$, and TaI_3 were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20].

The thermodynamic properties of crystalline $TaCl_3$ were studied, and the composition of the vapour phase in equilibrium with it was determined. The vapour contained $TaCl_5$, $TaCl_4$, $TaCl_3$, $TaCl_2$, TaCl, Ta, Cl, and Cl_2. The heats, free energies and entropies of sublimation were determined [493].

It has been shown that electrochemically formed $[TaCl_4]^-$ ions, in LiCl-KCl-$TaCl_5$ molten mixtures at 400-550 °C, by fluoride ion addition are unstable and disproportionate to primarily $[TaF_7]^{2-}$ and metallic tantalum [60].

6.2 Nb(III) and Ta(III) chalcogenohalide complexes

Thermodynamic data for gaseous tantalum(III) oxyhalides, TaOF, TaOCl, TaOBr, and TaOI were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20].

The selenoiodide NbSeI has been prepared and classified as $Nb_4Se_4I_4$, a cubic cluster compound containing tetrahedral Nb_4Se_4 units with niobium-niobium bonding, according to the results of a crystal structure solution [494]. The structure has a close relation to the new $GaNb_4Se_8$ structures, see Figure 69. $Nb_4Se_4I_4$ can be intercalated with lithium to form $Li_{2.8}Nb_4Se_4I_4$ [420].

6.3 Nb(III) and Ta(III) halides with O- and chalcogen-donors

With $Nb_2Cl_6(THT)_3$ as starting material (THT = tetrahydrothiophene), *di*meric Nb(III) alkoxide compounds, $Nb_2Cl_5(OR)(HOR)_4$ (R = Me, Et, Pr^i), have been made [495]. According to crystallographic examination, these compounds have edge-sharing *bi*octahedral geometries in which the Nb atoms are bridged by one chloride and one alkoxide ligand. $Nb_2Cl_5(OMe)(MeOH)4$ has a short Nb-Nb distance, indicative of a metal-metal double bond [495]. For R = Et and Pr^i, the compounds are unstable in THF, forming tetranuclear Nb(IV) complexes, $[Nb_2OCl_4(OR)_2(THF)_2]_2$ [495], see Figure 58. The compounds have been further characterized in solution by proton NMR spectroscopy [495].

A *di*nuclear Nb(III) complex salt, $(NMe_4)[Nb_2Cl_2(THT)(CH_3CO_2)_5]\cdot CH_2Cl_2$ with THT = tetrahydrothiophene has been characterized by NMR, IR, cyclic voltammetry and X-ray crystallography [496]. The Nb-Nb distance and the *dia*magnetism indicated a double metal-metal bond. Acetate is coordinated in three different modes: Bridging *bi*dentate, chelating, and bridging *uni*-dentate, see Figure 59.

Niobium and tantalum face-sharing *di*mers $M_2Cl_6(SMe_2)_3$ (M = Nb or Ta, and with two bridging Cl) have been found to react with *di*methylsulphide, SMe_2, to form edge-sharing *bi*octahedra $M_2Cl_6(SMe_2)_4$ [497]. The crystal structures were compared to those of similar complexes in which *di*methylsulphides were replaced by 3,6-*di*thiaoctane, in an attempt to understand the *M-M* bonding schemes in these complexes [497]. Also, single crystal structures of *di*-μ-chloro-tetrachloro-*bis*--(tetrahydrofuran)-[μ-(*di*methylsulphide)]-*di*-niobium(III),

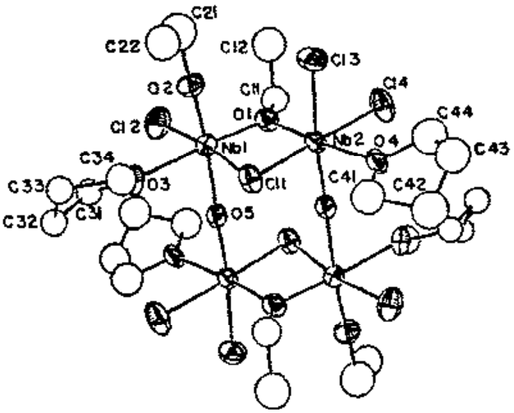


Figure 58. Crystal structure of the tetranuclear $[Nb_2OCl_4(OEt)_2(THF)_2]_2$ molecule [495]. Reproduced with permission from [495], F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chem.* **26** (1987) 3323.

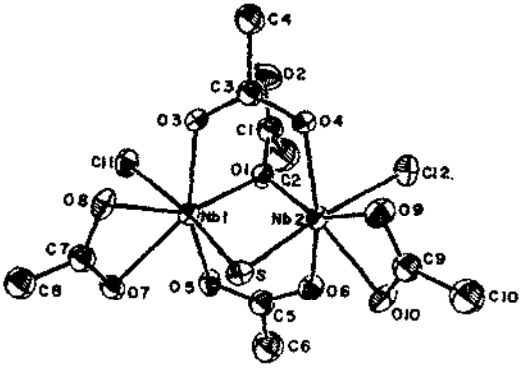


Figure 59. View of the $[Nb_2Cl_2(THT)(CH_3CO_2)_5]^-$ anion. Carbon atoms in the bridging THT ligand have been omitted for clarity. Reproduced with permission from [496], F. A. Cotton, M. P. Diebold, M. Matusz and W. J. Roth, *Inorg. Chim. Acta* **112** (1986) 147.

$[Nb_2Cl_6(C_4H_8O)_2(C_2H_6S)]$, and the analogous tantalum compound have been solved [498]. The coordination geometry can here be described as confacial-*bi*octahedral, see Figure 60, with a double metal-to-metal bond and a coordination number of 7 around the metal.

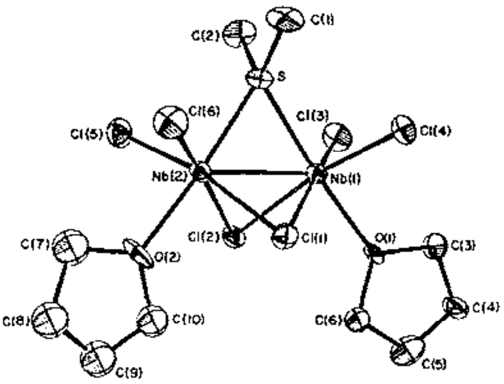


Figure 60. View of the $[NbCl_2(THF)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$ molecule. Reproduced with permission from [498], F. A. Cotton, S. A. Duraj and W. J. Roth, *Acta Cryst.* C41 (1985) 878.

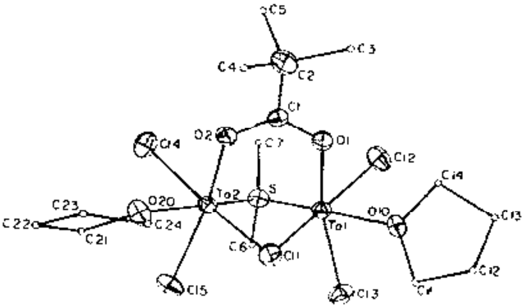


Figure 61. Structure view of the $[TaCl_2(THF)]_2(\mu\text{-}SMe_2)\text{-}(\mu\text{-}O_2CC_4H_9)$ molecule. Reproduced with permission from [499], F. A. Cotton, M. P. Diebold, S. A. Duraj and W. J. Roth, *Polyhedron* 4 (1985) 1479.

A *bi*nuclear tantalum(III) complex with a bridging carboxylato ligand, $Ta_2Cl_5(O_2CC_4H_9)(SMe_2)(THF)_2$, has been obtained by letting $Ta_2Cl_6(SMe_2)_3$ react with $C_4H_9CO_2Li$ [499]. The complex is a *di*mer with a distorted octahedra-sharing-an-edge geometry and some Ta=Ta bonding, see Figure 61. It is interesting to note that the existence of this green compound proves that low-valent tantalum can be stable in contact with oxygen-donor ligands, and moreover that this is the case even when the *di*mer contains a bridging *bi*dentate ligand.

For the crystal structure of *di*-μ -chloro-tetrachloro-*bis*-(tetrahydrofuran)-[μ-(*di*methylsulphide)]-*di*-tantalum(III), $[Ta_2Cl_6(C_4H_8O)_2(C_2H_6S)]$, see the analogous niobium compound and Figure 60 [498].

6.4 Nb(III) and Ta(III) halides with N- and P-donors

Relativistic MS Xα molecular orbital calculations have been performed under C_{2v} symmetry on *di*-μ-chloro-tetrachloro-*tetra*-ammine tantalum(III) compounds $[Ta_2Cl_6(NH_3)_4]$ and $[Ta_2Cl_6(NH_3)_4]^-$ [500]. These complexes were used as models for $Ta_2Cl_6(\gamma\text{-pic})_4$ and short-lived anion species obtained from this [501] by pulse radiolysis reduction (γ-pic = γ-picoline = 4-methylpyridine). Calculated electronic transitions compared to experimental absorption spectra have lead to the conclusion that the transient Ta *di*mer has a formal bond order of 2.5 or 1.5 (electronic configuration $\sigma^2\pi^2\delta^*$) [135, 500].
Bis-nitrogen-chelated, edge-sharing *bi*octahedral molecules $[M_2Cl_6(Et_2NCH_2CH_2NEt_2)_2]$ (M = Nb, Ta) with two bridging chlorides and four *uni*-planar terminal chlorides have been isolated, and their crystal structures determined [502]. These molecules have five membered M-N-C-C-N rings and are in the achiral *meso* conformation of C_{2h} symmetry with one ring of λ and the other ring of δ conformation, and the twofold axis passing along the metal-metal vector. For the phosphorous substituted analogous molecules $[M_2Cl_6(Et_2PCH_2CH_2PEt_2)_2]$ (M = Nb, Ta) chiral conformations of D_2 symmetry have been isolated [502-503], see Figure 63.

Ions Nb(III) and Ta(III) in the presence of hydroxide form *bi*nuclear complexes with nitrogen, in which the N_2 molecule is significantly activated and can be converted to hydrazine and ammonia [504].

A *di*nuclear organoimido niobium(III) complex, $Nb_2Cl_6(NPh)_2(SMe_2)_2$, has been synthesized by adding *tri*phenylazide to a solution of the metal-metal double bonded *di*mer $Nb_2Cl_6(SMe_2)_3$ in toluene at 0 °C [505], in a simpler way than previously [506]. The compound is air-sensitive and can be described as $[NbCl_2(NPh)(SMe_2)]_2(\mu\text{-}Cl)_2$ (see the analogous tantalum compound depicted in Figure 22). Its reactivity was investigated, see reference [505].

An exeptionally reactive 16 electron tantalum(III) *mono*mer, $TaClH_2(PMe_3)_4$, has been made and characterized with respect to its neutron structure, IR-, ^1H- and $^{31}P[^1H]$ NMR spectra, and reactivity [507]. In the solid state, the coordination polyhedron is a slightly distorted pentagonal *bi*pyramid with two axial phosphines and the hydride ligands in *cis* coordination, see Figure 62.

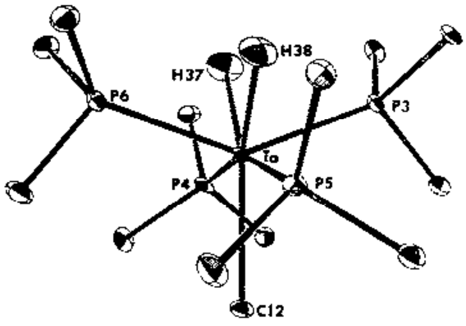


Figure 62. The neutron diffraction structure of the Ta(III) compound $TaClH_2(PMe_3)_4$ [507]. Methyl hydrogens have been omitted for clarity. Reproduced with permission from [507], M. L. Luetkins, Jr., M. D, Hopkins, A. J. Schultz, J. M. Williams, K. C. Fair, F. K. Ross, J. C. Huffman and A. P. Sattelberger, *Inorg. Chem.* **26** (1987) 2430.

$TaClH_2(PMe_3)_4$ reacts with 1,2-*bis*(*di*methylphosphino)ethane ($Me_2PCH_2CH_2PMe_2$ = dmpe) to give $TaClH_2(dmpe)_2$, with ethylene to give $TaCl(C_2H_4)(PMe_3)_4$, with *di*nitrogen to give the μ-*di*nitrogen complex $[TaClH_2(PMe_3)_3]_2(\mu\text{-}N_2)$ and with carbonmonoxide to give $TaCl(CO)_3(PMe_3)_3$ [507]. The crystal structure of $TaCl(CO)_3(PMe_3)_3$ has been solved based on X-ray data [507].

Bis-phosphorous-chelated, edge-sharing *bi*octahedral molecules $[Ta_2Cl_6(Et_2PCH_2CH_2PEt_2)_2]$ with two bridging chlorides and four *uni*-planar terminal chlorides have been isolated, in diastereomeric forms, and their crystal structures determined [503]. The difference between these molecules is in the conformations of the five membered Ta-P-C-C-P rings. Form *1* is the achiral *meso* compound of C_{2h} symmetry with one ring of λ and the other ring of δ conformation, and the twofold axis passing along the metal-metal vector. Form *2* is chiral of D_2 symmetry, with both rings in λ conformation and the twofold axes intersecting at the midpoint of the Ta-Ta bond. Form *2* has also been isolated for the case of niobium [502-503], see Figure 63.

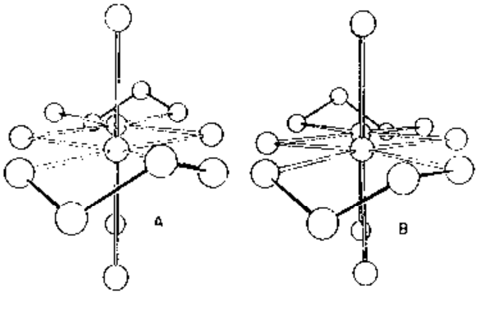


Figure 63. The structure of the two different ligand conformations in the *di*nuclear $[Nb_2Cl_6(Et_2NCH_2CH_2NEt_2)_2]$ (A) and $[Nb_2Cl_6(Et_2PCH_2CH_2PEt_2)_2]$ (B) molecules [502]. Reproduced with permission from [502], J. A. Canich and F. A. Cotton, *Inorg. Chem.* **26** (1987) 4236.

Discrete *tri*nuclear complexes of niobium(III) and tantalum(III) have been described: $(PEt_3H)^+[Nb_3Cl_{10}(PEt_3)_3]$ and $(PEt_3H)^+[Ta_3Cl_{10}(PEt_3)_3]$ [508]. A related compound, $Nb_3Cl_7(PMe_2Ph)_6$, with a nonintegral oxidation state was also described. The structures have been established by X-ray crystallography, see Figure 64. In each case there is an $M_3(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_3$ core surrounded by the remaining nine ligands. Six and eight electrons are available for *M-M* bonding, according to Fenske-Hall molecular orbital calculations [508].

Finally, a discrete tetranuclear tetrahydrothiophene ethylene-*bis*(*di*phenylphosphine) complex of tantalum(III) has been described: $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2 \cdot C_7H_8$ [509]. The structure consists of two confacial *bi*-octahedral units of $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)]$ (with Ta=Ta double bonds, see Figure 60), bridged by two $Ph_2PCH_2CH_2PPh_2$ ligands to form the unusual tetrameric units. The structure was established by X-ray crystallography on the red crystals [509].

6.5 Nb(III) and Ta(III) halides with C-donors

The reaction between niobium(V)chloride and phenyl-acetylene was investigated in carbon tetrachloride [510]. Two mols of phenylacetylene were found to react with one mol $NbCl_5$ forming first a five-coordinated complex (Figure 65, I) which in turn reacts with more

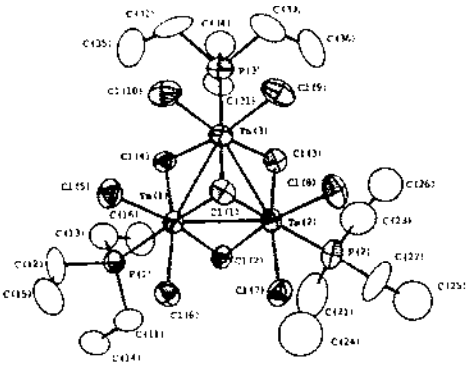


Figure 64. The structure of the $[Ta_3(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_3Cl_6(PMe_3)_3]^-$ ion [508]. Reproduced with permission from [508], F. A. Cotton, M. P. Diebold, X. Feng and Wieslaw J. Roth, *Inorg. Chem.* **27** (1988) 3413.

phenyl-acetylene to form an unstable π-bonded complex (Figure 65, **II**), and finally catalytically produces $NbCl_3$ and oligomerized (mainly *tri*merization) of the phenylacetylene.

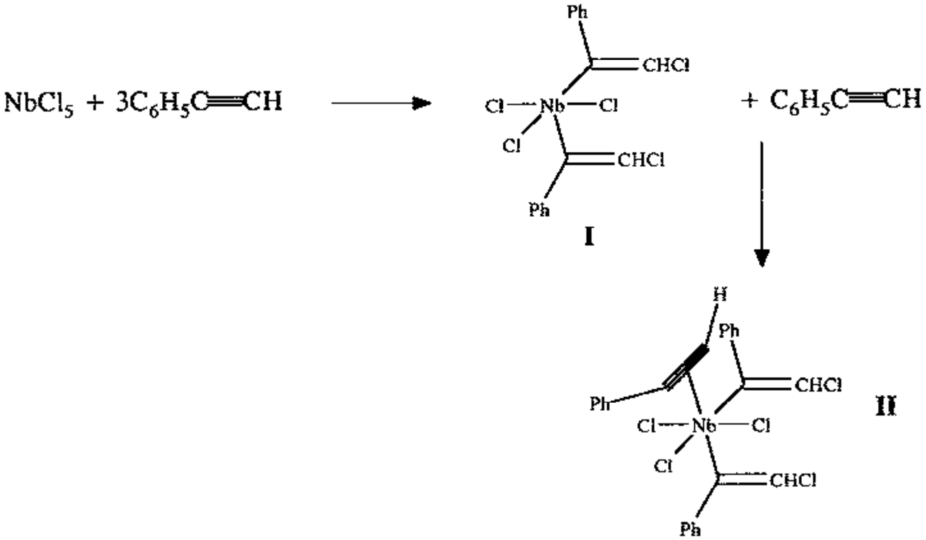
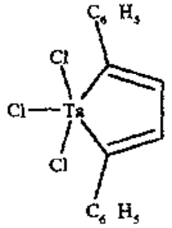


Figure 65. *Cyclo*trimerization of phenylacetylene by $NbCl_5$. Adapted from [510] C. J. du Toit, J. A. K. du Plessis and G. Lachmann, *S. Afr. J. Chem.* **38** (1985) 195.



21

A tantalum(III) species, probably $Cl_3Ta[(C_6H_5)C{=}C(H)Cl]_2$, **21**, is formed during the $TaCl_5$-catalysed *cyclo*trimerization of phenyl-acetylene $C_6H_5C{\equiv}CH$ [40]. The complex **21** shown above is assumed to react with more phenylacetylene forming *tri*phenylbenzene and $TaCl_3$ [40].

A new unique *di*nuclear Niobium(III) cation, $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]^+$, has been prepared and characterized by solving the X-ray crystal structure of a salt [511]. The cation has a short (2.695 Å) Nb=Nb double bond and bridging as well as terminal chlorine atoms. A C-shaped PhC-C(Ph)C(Ph)-CPh chain clasps the Nb=Nb bond. The structure is shown in Figure 66.

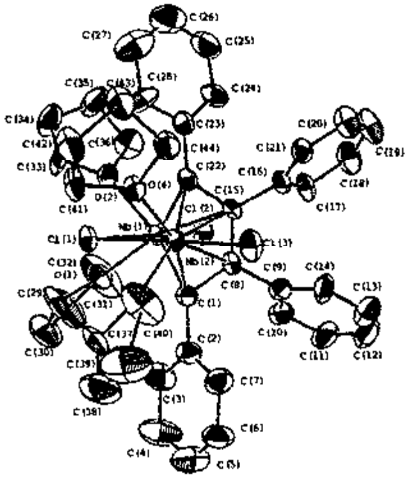


Figure 66. The structure of the unique *di*nuclear Nb(III) cation, $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]^+$ [511]. Four tetrahydrofuran groups (left side) and four C-phenyl groups (right side) are shown in full. Reproduced with permission from [511], F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 2619.

Another new unique tetranuclear Nb(III) anion, $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$, has been prepared and characterized by solving the X-ray crystal structures of several different salts [511-512]. The anion consists of a planar, rectangular Nb_4 group with an oxygen atom at the center. The long Nb··Nb edges are doubly bridged by Cl atoms, and there is one terminal Cl atom on each

Nb atom. A C-shaped PhC-C(Ph)C(Ph)-CPh chain clasps each short Nb··Nb edge. The mode of bonding is shown in Figure 67. The oxidation state of Nb is most likely to be +III, and hence two Nb=Nb double bonds can be formed *per* tetramer unit, in accordance with the short (2.611 Å) Nb-Nb distance. The central oxygen atom in this anion has an environment that is without precedent. Note the relation between the two ions in Figures 67 and 66.

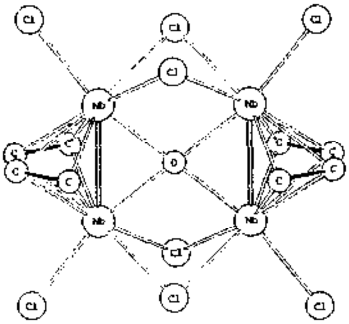


Figure 67. The structure of the unique tetranuclear Nb(III) anion, $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$, as found in several salts [511-512]. Phenyl groups are omitted for clarity. Reproduced with permission from [511], F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 2619.

Finally, a hexanuclear Nb(III) compound of composition $(Bu)_3Sn[Nb_6Cl_{19}(PhC)_{12}]\cdot C_7H_8$, has been made and characterized by its X-ray crystal structure [513]. The hexanuclear entity consists of a central triangular $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3$ cluster with a $Cl_3NbCl_2(c\text{-}C_4Ph_4)$ unit of roughly octahedral shape (if $c\text{-}C_4Ph_4$ is considered as one ligand) attached to each central Nb atom by three mutually *cis* Cl atoms. The Nb-Nb distances in the central cluster (2.87 Å) are indicative of Nb-Nb single bonds and there is no further Nb-Nb bonding. The mode of bonding is shown in Figure 68. The oxidation state of Nb is considered to be +III.

6.6 Nb(III) and Ta(III) oxides, sulphides and selenides

Electrode reaction equilibria of involving niobium(III) complexes were studied potentiometrically and polarographically in perchlorate and sulphate acidic solutions [304-305]. A two electron reaction:

$$Nb^{5+} + 2e^{-} = Nb^{3+}$$

occurred at the mercury electrode, the Nb(III) complexes probably being Nb^{3+}, $NbSO_4^{+}$ or $Nb(OH)_2^{+}$. Equilibrium constants were given [304]. An intermediate Nb(IV) complex might also be formed [305].

Several *bis*-oxo-capped M_3X_{17} clusters (M = Nb and X = O) have now been obtained and their crystal structures solved [117]. These complexes have a core of three Nb atoms and two oxygens forming a triangular *bi*pyramid. Each niobium are further bound to five outer-sphere ligands. The structures have been solved for the cases of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$, $[Nb_3O_2(O_2CBu^t)_6(THF)_3]^{+}$, and $[Nb_3O_2(O_2CCH_3)_6(THF)_3]^{+}$. In all these compounds, six chelating groups provide twelve ligands, and three *mono*dentate groups provide the last three oxygens [117].

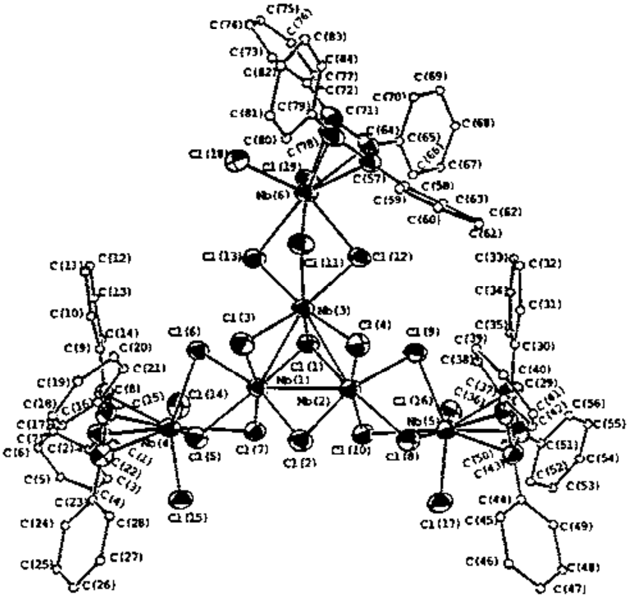


Figure 68. The unique hexanuclear Nb(III) compound $(Bu)_3Sn[Nb_6Cl_{19}(PhC)_{12}]\cdot C_7H_8$, characterized by its X-ray crystal structure [513]. The entity consists of a central triangular $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3$ cluster with three roughly octahedral $Cl_3NbCl_2(c\text{-}C_4Ph_4)$ units attached to central Nb atoms by Cl atoms. Reproduced with permission from [513], F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 2614.

The preparation and crystal structure of Nb_2S_3 are discussed in [514].

New $GaNb_4S_8$ and $GaNb_4Se_8$ cluster compounds of Niobium(III), have been prepared by heating the elements in closed silica tubes [494]. According to the results of crystal structure solutions, the compounds contain tetrahedral Nb_4S_4 or Nb_4Se_4 units with a Nb_4 cluster as the core and with niobium-niobium bonding, see Figure 69. The structure has a close relation to the AB_2X_4 spinel structures and the new $Nb_4Se_4I_4$ structure [494].

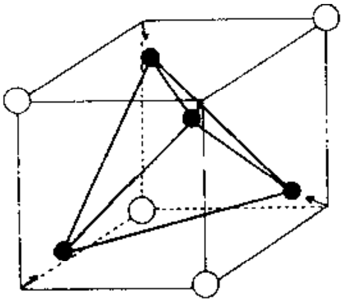


Figure 69. New $Nb_4Se_4I_4$, $GaNb_4S_8$ and $GaNb_4Se_8$ cluster compounds of Niobium(III) contain tetrahedral Nb_4S_4 or Nb_4Se_4 units with a Nb_4 core. Filled circles = Nb, open circles = S or Se. Reproduced with permission from [494], H. B. Yaich, J. C. Jegaden, M. Potel, M. Sergent, A. K. Rastogi and R. Tournier, *J. Less-Comm. Met.* **102** (1984) 9.

6.7 Nb(III) and Ta(III) nitrides

In the vapour phase, NbN, molecules have been characterized by spectroscopy (molecular constants for upper $^3\Phi$ and ground $^3\Delta$ states, obtained from vibrational and rotational spectra) [515-516].

Solid niobium nitride, NbN, has unusual properties such as being hard, brittle and a superconductor below 16 K. Its electronic structure has been studied by high energy electron energy loss spectroscopy [387].

The formation of vacancies in niobium nitrides has been studied theoretically [492]. Non-stoichiometric compact cubic δ-NbN_{1-x} phases with small x values were prepared and investigated [517]. Energy band structure studies have been performed on NbN single crystals using the linearized augmented-plane-wave method [518].

6.8 Nb(III) and Ta(III) C-donor complexes

The reaction between the Nb(III) cyclo*penta*dienyl derivate $(\eta^5\text{-}C_5Me_5)_2NbBH_4$ and sulphur has been studied [388].

7. Niobium and tantalum clusters of oxidation state < III

The electronic bonding in Nb_6Cl_{14}, and, in general, in $Nb_6Cl_{12}L_6{}^{2+}$ clusters (with L as a ligand) was described using graph theory, by means of 76 valence electrons including 16 in eight face-localized three-center bonds [519].

In acidic aqueous solution, green $[Ta_6Cl_{12}]^{2+}$ cluster ions can be oxidized by nitrate, bromate, dichromate or Ce^{4+} to form $[Ta_6Cl_{12}]^{3+}$ and $[Ta_6Cl_{12}]^{4+}$ clusters in separate potentiometric steps, before the formation of $Ta_2O_5{,}xH_2O$ starts [520]. $[Ta_6Br_{12}]^{2+}$, $[Nb_6Cl_{12}]^{2+}$ and $[Nb_6Br_{12}]^{2+}$ behave in a rather similar way [520-521].

The ligand replacement reactions in $(pyH)_2[Ta_6Br_{12}]Cl_6$ at elevated temperature were followed by chemical analyses in steps; the chloride atoms penetrate into the interior of the cluster gradually, forming the ions $[Ta_6Br_6Cl_6]^{4+}$, $[Ta_6Br_2Cl_{10}]^{4+}$ and $[Ta_6Cl_{12}]^{4+}$ in agrement with theoretical predictions [522].

The mixed oxidation state cluster ions $[Nb_6Cl_{12}]^{2+,3+}$ and $[Ta_6Cl_{12}]^{2+,3+}$ have been used for incorporation into Na-montmorillonite as a first step in obtaining new oxide materials by calcination [523].

Dark red solid cluster hydroxides $M_2[Ta_6Cl_{12}](OH)_6{\cdot}nH_2O$ with M = Na, K, Rb, $(CH_3)_4N$ and $(C_2H_5)_4N$ and n = 12 to 20 were prepared, and their stability towards air oxidation in alkaline methanol-water solution examined [524]. Insoluble $[Ta_6Cl_{12}](OH)_4{\cdot}10H_2O$ and soluble clusters $[Ta_6Cl_{12}]X_4{\cdot}nH_2O$ and $[Ta_6Cl_{12}]X_6{}^{2-}$, X = Cl, Br are the products of acidification with HCl and HBr [524]. The are no evidence that the OH^- ions enter into the inside coordination sphere of the cluster unit.

A new dodeca-μ-bromo-hexabromo-*octahedro*-hexaniobate(4-) salt, $KGd[Nb_6Cl_{18}]$, containing $(Nb_6Cl_{12})Cl_6$ clusters has been studied by crystal structure solution [525]. The average oxidation state of Nb is 7/3. The found geometry of the cluster is shown in Figure 70. A similar structure was found for the case of $K_4[(Nb_6Br_{12})Br_6]$ [526], *iso*typic with the previously found $K_4[(Nb_6Cl_{12})Cl_6]$ [527].

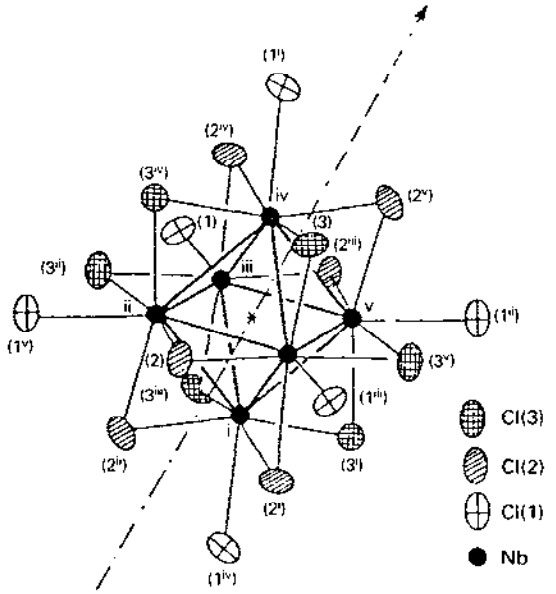


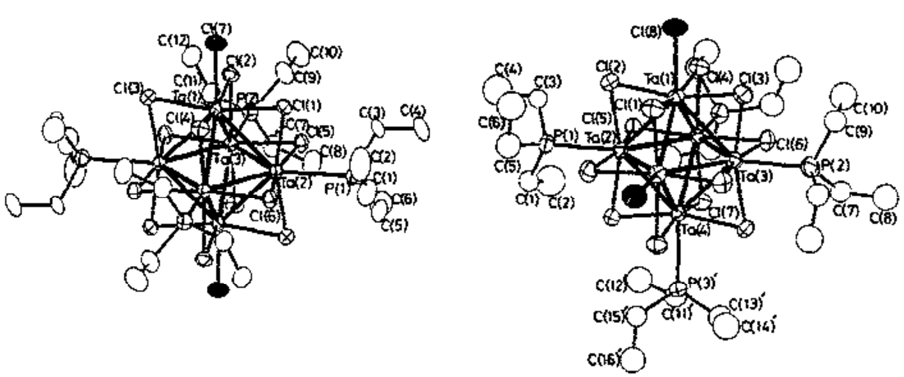
Figure 70. Structure of octahedral $(Nb_6Cl_{12})Cl_6$ clusters surrounded by K^+ and Gd^{3+} in the trigonal crystal. Reproduced with permission from [525], S. Ihmaïne, C. Perrin and M. Sergent, *Acta Cryst.* **C43** (1987) 813.

Other salts, $R[Nb_6Cl_{18}]$, $R[Ta_6Cl_{18}]$, $MR[Nb_6Cl_{18}]$ and $MR[Ta_6Cl_{18}]$ with M = a *mono* valent ion and R = a rare earth, have been made [528]. All of these compounds crystallize in the trigonal system (rhombohedral space group $R\bar{3}$), except when M = Cs, for which cases the lattices are hexagonal (space group $P\bar{3}1c$) [528].

Alkoxides of the hexanuclear niobium and tantalum cluster units have now been made and studied: $[M_6X_{12}](OMe)_2 \cdot 4MeOH$ and $M'_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$, M = Nb, Ta, X = Cl, Br, Me = methyl and M' = alkali metal [529]. Physical and spectral data are reported.

The photoelectron spectra (AlKα, HeI) of Nb_3I_8 (with trigonal Nb_3 groups) and the Nb_6I_8 cluster compounds Nb_6I_{11}, HNb_6I_{11}, $Nb_6I_8(CH_3NH_2)_6$ and $Nb_6I_8(C_3H_7NH_2)_6$ were studied in an attempt to find the relation between the binding energy of the niobium core levels and the oxidation number [42].

Clusters with chloro and *tri*alkylphosphine ligands, $[(M_6Cl_{12})Cl_2\{P(R)_3\}_4]^{n+}$, M = Nb, Ta, $R = C_2H_5$, C_3H_7 and C_4H_9, and n = 0, 1 or 2 have been isolated in *cis* and *trans* isomers by column chromatography; structure determinations have shown that bond distances between the metals in the cluster depend not only on the oxidation state of the cluster but also on the kind of terminal ligands on each metal, see Figure 71. Electronic spectra of the charged clusters (n = 1 or 2) show bands indicating splittings of a metal cluster orbital (t_{1u} or t_{2g}) due to lowering of the symmetry from O_h [530].



trans *cis*

Figure 71. Structure of octahedral *trans* and *cis* isomers of $[(Ta_6Cl_{12})Cl_2\{P(C_2H_5)_3\}_4]^+$ ions (from BF_4^- salts), isolated by column chromatography. Reproduced with permission from [530], H. Imoto, S. Hayakawa, N. Morita and T. Saito, *Inorg. Chem.* **29** (1990) 2007.

A new mixed-oxidation-state compound $NaNb(II)Nb(IV)_2O_5F$ has been prepared. Single crystals are *dia*magnetic and black with metallic luster. The structure was determined and it shows short Nb-Nb distances [429].

Green crystals of Nb_3O_8 was prepared and their properties investigated [531]. The relation between Nb_3Cl_8 and other discrete *tri*nuclear niobium and tantalum clusters have been discussed [508].

Dark green single crystals of $Mg_3Nb_6O_{11}$ (with Nb of mean oxidation state 2.667) were prepared by heating a pellet containing MgO, Nb, Nb_2O_5 (15:14:8) at 1550 °C in a Nb-container. The X-ray structure was solved and found to contain clusters of Nb_6 octahedra, arranged in combination with other atoms to form cubic close-packed layers [532]. A similar structure was found for $Mn_3Nb_6O_{11}$ crystals, prepared in a somewhat different way [532].

Cluster compounds $Na_3Al_2Nb_{34}O_{64}$ and $Na(Si,Nb)Nb_{10}O_{19}$ with niobium in different oxidation states (+5, +4, +2.5 and +5, +4, +2.67, respectively) have been made and their crystal structures obtained by X-ray diffraction [533]. In both compounds, characteristic building units of Nb_6O_{12} and Nb_2O_{10} groups as well as isolated NbO_6 octahedra are found

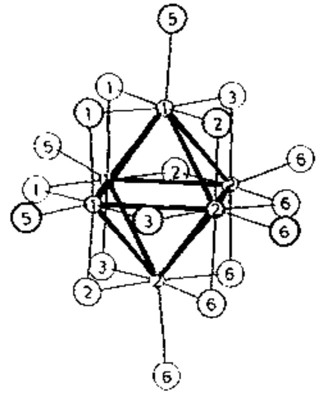


Figure 72. Structure of octahedral $Nb_6O_{12}O_6$ clusters found in Na(Si,Nb)$Nb_{10}O_{19}$. Large and small circles denote oxygen and niobium atoms. Reproduced with permission from [533], J. Köhler and A. Simon, *Z. Anorg. Allgem. Chem.* **553** (1987) 106.

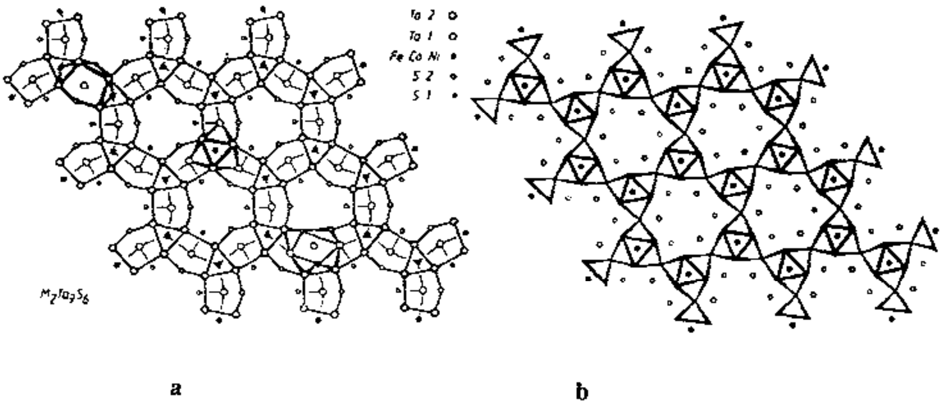


Figure 73. Projection of the $M_2Ta_9S_6$ structure with M = Fe, Co, Ni down the c-axis, with emphasis on (a): the coordination polyhedra and (b): the condensed tantalum clusters, centered on the 3d metal. Reproduced with permission from [535], B. Harbrecht and H. F. Franzen, *J. Less-Comm. Met.* **113** (1985) 349.

in layers. The Nb_6 units are close-packed and surrounded by oxygen, forming a $Nb_6O_{12}O_6$ unit (see Figure 72), closely analogous with the $Nb_6Cl_{12}Cl_6$ unit known from *e.g.* $K_4Nb_6Cl_{12}Cl_6$. The stability of the compounds are discussed [533].

New metal-rich sulphides Ta_2S, Ta_6S, $M_xTa_{6-x}S$ (M = V, Cr; x = *ca.* 1), $Fe_2Ta_9S_6$, $Ni_2Ta_9S_6$ and $Co_2Ta_9S_6$ have been prepared through high-temperature techniques [534-537]. The hexagonal crystal $M_2Ta_9S_6$ (M = Fe, Ni, Co) structures determined from X-ray data exhibit condensed tetrakaidecahedral tantalum clusters, accomodating the transition metal, surrounded by sulphur and having a channel structure, see Figure 73. Metal-metal interactions and the presence of S-lined channels in the $M_2Ta_9S_6$ (M = Fe, Ni, Co) structures were studied in connection with extended Hückel electron structure calculations [537]. The Ta_6S and $M_xTa_{6-x}S$ crystals contain pentagonal *anti*prismatic tantalum columns surrounded by sulphur, see Figure 74 [536-536A].

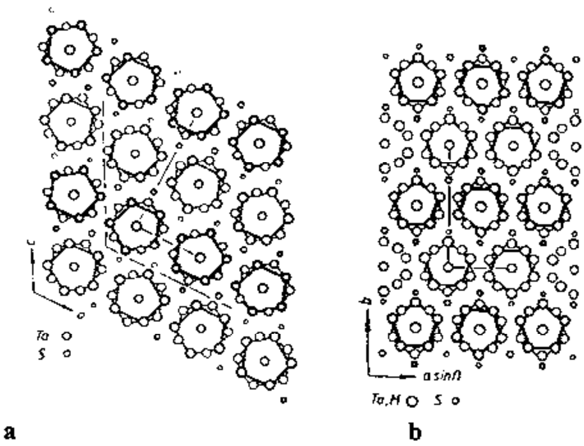


Figure 74. Projection of (a) Ta_6S (high temperature modification) and (b) $M_xTa_{6-x}S$ (M = V, Cr; $x \doteq$ *ca.* 1) structures, viewed with emphasis on the pentagonal *anti*prismatic metal columns (Ta, M, large circles). Reproduced with permission from [536], B. Harbrecht and H. F. Franzen, *Z. Anorg .Allgem. Chem.* **551** (1987) 74.

The technique of heating mixtures of metal sulphides or selenides in a tungsten Knudsen cell has been used for preparing new metal-rich transition metal sulphides and selenides. The following compounds have been made and their structures have been examined: $Nb_{14}S_5$, $Nb_{21}S_8$, Nb_2Se, Ta_2Se [536B], Ta_6S [536A], Ta_2S, $Fe_2Nb_9S_6$ and $M'_2Ta_9S_6$ and $M'_2Ta_{11}Se_8$ [563C] (M'= Fe, Co, Ni), as well as $Ta_{6-x}M_xS$. The structures can be thought of as modified metals with extended metal-metal bonding [538], and the oxidation state is not always known.

8. Nb(II) and Ta(II) complexes (d^3)

Thermodynamic data for gaseous tantalum(II) halides, TaF_2, $TaCl_2$, $TaBr_2$, TaI_2 and TaO were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20].

The thermodynamic properties of crystalline $TaCl_2$ were studied, and the composition of the vapour phase in equilibrium with it determined. The vapour contained $TaCl_5$, $TaCl_4$, $TaCl_3$, $TaCl_2$, TaCl, Ta, Cl and Cl_2. The heats, free energies and entropies of sublimation were determined [493].

Niobium and tantalum in K_2NbF_7 and K_2TaF_7 are reduced partly to oxidation state II after being bombarded by a 4 keV Ar^+ ion beam [412].

The He-I photoelectron spectra and first ionization energies of NbO and TaO molecules in the vapour phase have been obtained and assigned with the aid of Hartree-Fock-Slater calculations [539]. The optical spectrum of the gaseous free radical molecule NbO have been examined [540], and unusual intensity features have been found in its magnetic hyperfine structure [541]. By use of mass spectrometry and a Knudsen cell, the gaseous molecule NbO has been characterized thermodynamically with respect to dissociation stability [424]. Also, the NbO molecule was studied in argon and krypton matrix-isolation experiments (absorption and magnetic circular dichroism) at low temperatures [168]. Solid NbO, having a much discussed vacant NaCl type of structure [542], was shown to disportionate into NbO_2 and Nb at high temperatures and pressures [543].

The formation of vacancies in niobium oxide Nb_3O_3 has been studied theoretically [492].

The formation of chemical bonds in the hexagonal close-packed niobium carbide Nb_2C was studied by MO LCAO cluster calculations, and the results compared with the X-ray emission spectra [544].

The Nb(II) cyclo*penta*dienyl compound, $[(Cp)_4Nb_2(S)_2]$ has been studied [545].

9. Nb(I) and Ta(I) complexes (d^4)

Thermodynamic data for gaseous tantalum(I) halides, TaF, TaCl, TaBr, and TaI were reviewed and data given also for a large number of liquid and solid tantalum halide and oxyhalide compounds [20].

Nb(I) or Ta(I) complexes can be made from hexacarbonyl metalates of niobium(-I) or tantalum(-I), Na[M(CO)$_6$] or Na[M(CO)$_6$]$\cdot x$THF with M = Nb or Ta, x = *ca.* 0.5 to 5 and THF = tetrahydrofuran, by exclusively a two-electron transfer process using suitable agents such as CuCl, FeCl$_3$, or *bis*(acetylacetonato)nickel(II) [546]. The metallate(I)complexes were Na[$M_2(\mu\text{-}X)_3$(CO)$_8$] with X = Cl, Br, I, the 1,2-*bis*(*di*phenylphosphino)ethane complexes [M(acac)(CO)$_3$(Ph$_2$P-CH$_2$CH$_2$-PPh$_2$)], the *cyclo*hexyl*iso*cyanide complexes [M(acac)(CO)$_3$(CyNC)$_2$], and [M(acac)(CO)$_4$(THF)] [546]. The latter tantalum compound was studied by X-ray structure determination; tantalum(I) was *hepta*-coordinated, being surrounded by the *bi*dentate acetylacetonato ligand, by four carbon monoxide groups and by the oxygen atom of the tetrahydrofuran ligand, see Figure 75. The THF ligand can easily be substituted together with one of the carbonyl groups [546].

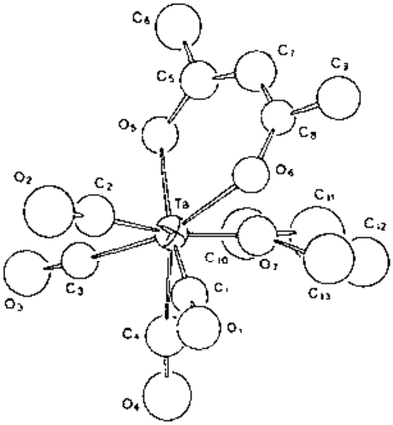


Figure 75. The [Ta(acac)(CO)$_4$(THF)] crystal structure. The tantalum(I) was found to be *hepta*coordinated, being surrounded by the *bi*dentate acetylacetonato ligand, the *mono*dentate tetrahydrofuran ligand and the four CO molecules. Reproduced with permission from [546], F. Calderazzo, G. Pampaloni and P. F. Zanazzi, *Chem. Ber.* **119** (1986) 2796.

The reaction between the Nb(I) cyclo*penta*dienyl carbonyl derivate (η^5-C$_5$Me$_5$)Nb(CO)$_4$ and sulphur in tetrahydrofuran solution under irradiation has been studied [388]. In this way, a new mixed valence (Nb(III) and Nb(IV)) compound of unknown structure, (C$_5$Me$_5$)$_3$Nb$_3$S$_7$), has been obtained and some of its properties have been determined [388].

The structures of niobocene carbonyl chloride, π-(C$_5$H$_5$)$_2$Nb(CO)Cl, and niobocene carbonyl hydride, π-(C$_5$H$_5$)$_2$Nb(CO)H, were reported [547-548]. Both compounds have a wedged sandwich geometry with four-coordinate Nb(I) and with an eclipsed conformation of the cyclo*penta*dienyl (Cp) rings, see Figure 76.

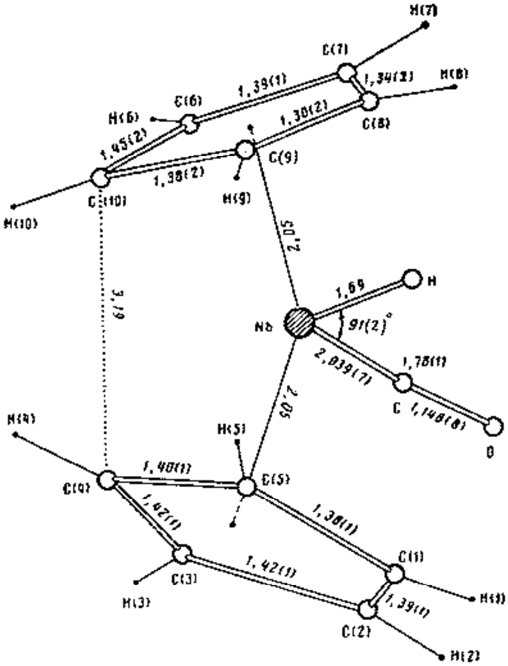


Figure 76. Structure view of the niobocene carbonyl hydride π-$(C_5H_5)_2Nb(CO)H$ molecule. Niobocene carbonyl chloride π-$(C_5H_5)_2Nb(CO)Cl$ has a closely similar structure. Reproduced with permission from [547], A. S. Antsyshkina, L. M. Dikareva, M. A. Porai-Koshits, V. N. Ostrikova, Yu. V. Skripkin, A. A. Pasynskii, O. G. Volkov and V. T. Kalinnikov, *Russ. J. Coord. Chem.* **10** (1984) 872, *Engl. Transl.* of *Koord. Khim.* **10** (1984) 1560.

Gas phase reactions of Nb^+ and Ta^+ with alkanes and alkenes in a mass spectrometer have been reported. A long list of reaction products were identified, including the first *mono*nuclear niobocene $Nb(Cp)_2^+$ structure (Cp = cyclo*penta*dienyl [549].

10. Nb(0) and Ta(0) complexes and alloys (d^5)

Small clusters of niobium Nb_x (x = *ca.* 5 - 10) were made and studied with a time-of-flight mass spectrometer [550]. Spectroscopic (photodetachment) data were given for Nb_2^+ and Nb_4^- [550].

The photoelectron spectrum (Al-Kα, HeI) of Nb was studied in an attempt to find the relation between the energy of the niobium core levels and the oxidation number [42].

Niobium and tantalum in K_2NbF_7 and K_2TaF_7 are partly reduced to oxidation state 0 after being bombarded by a 4 keV Ar^+ ion beam [412].

The formation of chemical bonds in the hexagonal close-packed niobium carbide Nb_2C and nitride Nb_2N was studied by MO LCAO cluster calculations, and the results compared with the X-ray emission spectra [544].

Enthalpies of formation and atomization for intermetallic compounds in the Al-Ta system (*e.g.* for $TaAl_3$, Ta_2Al_3, Ta_2Al and Ta_4Al) have been determined and compared with similar sulphur compounds [551].

Vapour phase reductions of $NbCl_5$ and $GeCl_4$ mixtures by hydrogen were studied at high temperatures. Under certain conditions the deposited products formed were super-conducting Nb_3Ge alloys [552].

In $NbTe_4$ and $TaTe_4$, the metals are in a square *anti*prism of Te atoms [16]. In the compounds $NbTe_2$ and $TaTe_2$ the metals occupy octahedral positions [16].

The Nb-Cr phase diagram was reviewed [553]. The intermediate compound Cr_2Nb has high and low temperature phases, whose structures and thermodynamics are given [553]. It was shown by self-consistent orbital calculations that the unknown compounds NbCe and NbLa should not be stable at ordinary pressure [554].

Crystal structure and magnetic properties of the *para*magnetic compounds NbCoSn, NbNiSn, TaCoSn and TaNiSn have been obtained [555]. Finally, $NbNiTe_5$ contains Nb in a *bi*capped trigonal prism of Te atoms [16].

11. Niobium and Tantalum in oxidation states below 0

Hexacarbonylmetallates of niobium(-I) or tantalum(-I), $Na[M(CO)_6]$ and $Na[M(CO)_6]\cdot x THF$ with M = Nb or Ta, x = *ca.* 0.5 to 5 and THF = tetrahydrofuran, have been prepared [556]. These compounds can be oxidized by suitable agents, exclusively by a two-electron transfer process to Nb(I) or Ta(I) complexes [546].

A new, safer synthetic procedure to carbonylate $NbCl_5$ forming the $[Nb(CO)_6]^-$ anion has been found [557]. Dry pyridine was used as the solvent, and magnesium/zink as the reducing agent at room temperature and at atmospheric pressure of carbon monoxide. The hexa-carbonyl niobium(V) complex ion was isolated as the yellow-orange, tetrahydrofuran-stabilized sodium salt $[Na(C_4H_8O)][Nb(CO)_6]$. Other salts, such as the brick-red nickel-phenanthroline salt, $[Ni(phen)_3][Nb(CO)_6]$, and the yellow μ-nitrido-*bis*(*tri*phenyl-phosphorous[1+]) salt, $[(PPh_3)_2N][Nb(CO)_6]$ have been prepared. According to X-ray diffraction methods applied on the latter salt, the $[Nb(CO)_6]^-$ ion has an almost perfect octahedral geometry [557].

The ^{93}NMR spectrum of the $[Nb(CO)_6]^-$ ion has been reported and the dependence upon *iso*topic replacement of $^{12}C^{16}O$ ligands by $^{13}C^{16}O$ and $^{12}C^{18}O$ studied. Also, IR and Raman spectra of the hexacarconyl anion were reported for the solid $(Et_4N)[Nb(CO)_6]$ [558]. Furthermore, the ^{181}Ta NMR spectrum of the $[Ta(CO)_6]^-$ ion in solution was obtained and interpreted in terms of a perfect octahedral symmertry: Tantalum has a large quadrupolar moment and without the cubic environment the NMR band would be much broader than found [44].

The *penta*carbonylniobate(-III) and the corresponding tantalate *tri*anion form the lowest known oxidation states of Nb and Ta. The synthesis and chemistry of some $[M(CO)_5]^{3-}$ complexes, M = Nb and Ta, have been described in a dissertation [559].

12. Compounds of unknown oxidation state

Some compounds have already been referred which have uncertain oxidation states. Additional information is given here.

By use of mass spectrometry and a Knudsen cell, gaseous molecules $EuNbO_3$, $EuNbO_2$, $EuNb_2O_6$ have been characterized thermodynamically and shown to have a relatively high stability [424].

Quasi-one-dimensional conductors have been of much interest to physicists, because of their interesting properties in relation to charge density wave-type instabilities [560]. Some of the papers do certainly not contain coordination chemical information and are not referred.

In NbS_3 the structural unit is the *bi*capped trigonal prism [561]. When heated, NbS_3 looses one sulphur atom for every S_2 pair, leading to formation of a non-stoichiometric NbS_2 structural type [561]. A monoclinic NbS_3 phase can be obtained at high pressures and temperatures [562]. Stacking disoder in NbS_3 was studied by diffuse X-ray scattering [563]. Electronic, vibrational and resonance Raman spectra were obtained of the layered semiconducting NbS_3 compound [564].

The $NbSe_3$ structure contains selenium in tetrahedral and octahedral cavities; the octahedral cavities are large enough to contain also lithium atoms without significant deformation of the lattice. Such lithium intercalated phases have been prepared by treating NbX_3 (X = S or Se) with *n*-butyl-lithium in hexane. Li_xNbS_3 and Li_xNbSe_3 phases with $x = 1 - 3$ were characterized by chemical analysis, X-ray powder diffraction and differential thermal analysis [562-565]; they might have a potential application as cathode material in lithium secondary batteries [514]. Optical investigations have been performed on the one-dimensional chain compounds $NbSe_3$ [566-567].

Thermal conductivity of whiskers of *ortho*rhombic NbS_3 and TaS_3 was studied versus temperature in the range 10 - 250 K, without any sharp anomaly being detected [568]. Monoclinic NbS_3 was prepared under high pressure, and it can be intercalated with lithium to form Li_xNbS_3 ($x = 2 - 3$) in batteries [569].

Charge density waves were studied in *ortho*rhombic [567,570-571] and monoclinic [572] phases of TaS_3. Unstoichiometric $Ta_3S_{1.8}$ has been prepared and its structure studied [573].

A comparative study was done on the layered MX_3 *tri*chalcogenides, $TaSe_3$, TaS_3 and $NbSe_3$ [574]. Broken X-X bonds of equilateral-like MX_3 chains and short intra- and interlayer $X \cdots X$ contacts were found to be crucial for the semi-metallic properties of $TaSe_3$ and for the charge density wave phenomena of $NbSe_3$ and TaS_3, and qualitative agreement was obtained between experimental observations and band electronic structure calculations [574].

The main representative, $(NbSe_4)_3I$, of an unusual series of one-dimensional compounds, - the $(MX_4)_nY$ type phases with M = Nb, Ta; X = S, Se; Y = halogen, - has had its structure thoroughly characterized by single crystal X-ray work [575]. Formally, the compond can be written as $2Nb^{4+}Nb^{5+}6Se_2^{2-}I^-$. The $(NbSe_4)_3I$ structure consists of essentially one-dimensional $NbSe_4$-chains separated by iodine ions (Nb-Nb inter-chain separation is < 6.7 Å). The coordination of the eight selenium(-I) ions is *anti*-prismatic as well for the Nb(V) as for the Nb(IV) ions, see Figure 77.

Optical investigations have been performed on the one-dimensional chain compound $(TaSe_4)_2I$ [566-567]. The low temperature IR spectrum and other properties were recorded [576-579]. Magnetic susceptibility and other properties of quasi-one-dimensional $(NbSe_4)_2I$ and $(TaSe_4)_2I$ were reported [580-581]. Thermal properites of the one dimensional $(NbSe_4)_3I$ were studied near its structural phase transition at 247 K [582]. Raman scattering spectra from $(NbSe_4)_{10/3}I$ and $(NbSe_4)_3I$ were recorded as a function of temperature in an effort to understand the nature of the phase transitions [583]. Also, ultrasonic properties [584], far-IR reflectance spectra [585] and the X-ray crystal structure of $(NbSe_4)_3I$ at 30 K [585] were determined, shedding light on the Nb-Nb chain interaction. ^{93}Nb NMR results on $(NbSe_4)_3I$ was discussed in terms of a charge density wave transition at 274 K [586]. At room temperature, Raman spectra of $(NbSe_4)_3I$ and $(TaSe_4)_3I$ single crystals are now known [587]. Other properties of $(NbSe_4)_3I$ and $(TaSe_4)_3I$ are reported in [588-589]. $(NbSe_4)_3I$ can be intercalated with lithium to form $Li_{7.5}(NbSe_4)_3I$ [420]. By passing through a second order displacive phase transition at 274 K, the Nb-Nb in-chain separations in $(NbSe_4)_3I$ changed from *tri*plets of two-long-one-short to one-long-one-mean-one-short (ranging from 3.31 to 3.06 Å) [575].

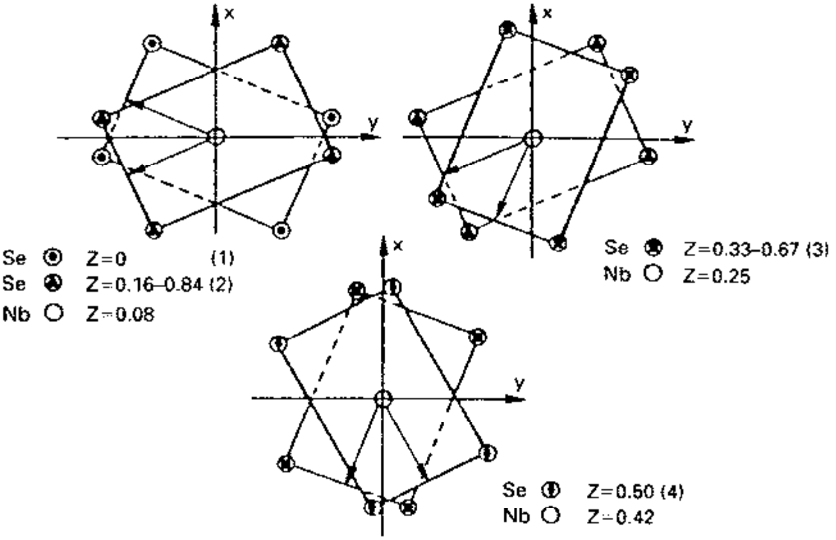


Figure 77. Three rectangular [$NbSe_8$] *anti*-prisms encountered in the mixed valence $(NbSe_4)_3I$ structure. Reproduced with permission from [575], P. Gressier, L. Guémas, A. Meerschaut, *Mater. Res. Bull.* **20** (1985) 539.

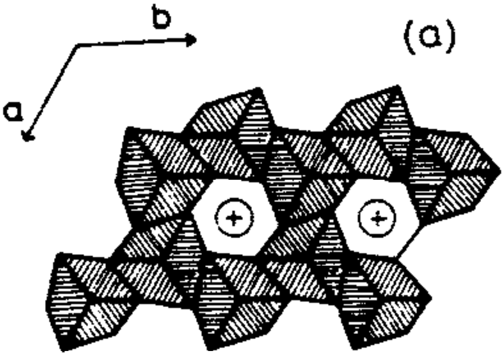


Figure 78. The structure of Nb_3Se_4, projection along the hexagonal *c*-axis. Empty channels between the edge and face-sharing $NbSe_6$ octahedra can easily take up *e.g.*alkali metals. After [591],T. Ohtani and S Onoue, *J. Solid State Chem.* **59** (1985) 324 and references there.

New $A_xNb_6Se_8$ phases with the Nb_3Te_4 structure have been prepared by molten salt ion exchange (A = Na, K, Rb, Cu, Ag, Zn, Cd, Pb and $0 \leq x \leq 1$) [590]. The A ions enter topotactically into the empty channels of the three-dimensional network structure of Nb_3Se_4, with little effect on the density, see Figure 78.

The charge-density-wave phase transition at 110 K in the hexagonal one-dimensional conductor Nb_3Te_4 was studied by X-ray diffraction and other methods [592].

The magnetic properties of $NbUS_3$ and $TaUS_3$ near the Curie points were investigated [593-594]. Also, the space groups and cell constants of $NbUS_3$ and $TaUS_3$ structures were given [594].

Needle crystals of $Nb_4Se_{16}Br_2$ and $Ta_4Se_{16}Br_2$ have been prepared from the elements contained in an evacuated sealed pyrex tube placed in a 500-460 °C gradient [560]. The crystal structures have been solved. The structures are based partly on the presence of waved [MSe$_4$] chains. Along the chains, four niobium or tantalum atoms in a near eight-coordinated *anti*-prismatic environment are found, forming groups of M_4Se_{16} with short (*ca.* 3.1 Å) bonds [560]. Also, chains were found in the solved structure of $Nb_6Se_{20}Br_6$ [595].

Crystals of $M'Nb_3Se_{10}$, with $M' =$ *e.g.* Fe, have been the subject for numerous studies on charge density wave phenomena. Part of the selenium can be substituted with sulphur, and also some of the niobium can be exchanged, *e.g.* with iron [596]. The compounds are structurally characterized by the presence of two distinct chains, (*1*) a trigonal prismatic [$NbSe_3$] chain similar to that exhibiting the shortest Se-Se pairing in $NbSe_3$, and (*2*) a double chain of edge-shared [(Fe,Nb)Se_6] octahedra. Structure determinations, and magnetic and ESR measurements are reported of some of the non-stoichiometric compounds [596].

$Nb_2Pd_{0.71}Se_5$ single crystal fibers have been obtained by the method of long-time heating of the elements in a closed quartz cell, placed in a temperature gradient and with bromine as transporting agent [347]. The structure was solved based on X-ray diffraction data. It was found to be related to the basic $Nb_2Pd_3Se_8$ channel type structure, see Figure 37. The $Nb_2Pd_{0.71}Se_5$ structure is laminar and contains slabs of [Nb_4PdSe_{10}]. Nb atoms are six and seven coordinated by Se in edge-sharing trigonal prisms and *mono*capped trigonal-prismatic sites. $Nb_2Pd_{0.71}Se_5$ is a metallic conductor along the needle axis, consistent with the non-stoichiometric composition and the non-integral formal oxidation state of the Nb atoms [347].

REFERENCES

1 D. A. Rice, *Coord. Chem. Rev.* **37** (1981) 77.
2 R. J. Hobson, *Coord. Chem. Rev.* **45** (1982) 87.
3 R. J. Hobson, *Coord. Chem. Rev.* **57** (1984) 279.
4 J. E. Newbery, Chapter 8, *Annu. Rep. Prog. Chem. Sect. A* **80** (1984) 171.

5 J. E. Newbery, Chapter 8, *Annu. Rep. Prog. Chem. Sect. A* **81** (1985) 185.

6 J. E. Newbery, Chapter 8, *Annu. Rep. Prog. Chem. Sect. A* **82** (1986) 195.

7 L. G. Hubert-Pfalzgraf, M. Postel and J. G. Riess, *Comprehensive Coordination Chemistry*, edited by Sir G. Wilkinson, R. G. Gillard and J. A. McCleverty, 3, chpt. 34, (1987) 585.

8 C. E. Holloway and M. Melnik, *Rev. Inorg. Chem.* **7** (1985) 1 or *J. Organomet. Chem.* **303** (1986) 1.

9 C. E. Holloway and M. Melnik, *Rev. Inorg. Chem.* **7** (1985) 161 or *J. Organomet. Chem.* **303** (1986) 39.

10 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, J. Wiley & Sons, Chpt. 19B, (1988) 787.

11 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Chpt. 22 (1986) 1138.

12 N. Sato, M. Nanjo and K. Mimura, *Tohoku Daigaku Senko Seiren Kenkyusho Iho (Bulletin of Research Inst. of Mineral Dressing and Metallurgy)* **44** (1988) 222.

13 N. Sato and M. Nanjo, *Tohoku Daigaku Senko Seiren Kenkyusho Iho (Bulletin of Research Inst. of Mineral Dressing and Metallurgy)* **42** (1986) 204.

14 N. Sato, K. Mimura and M. Nanjo, *Tohoku Daigaku Senko Seiren Kenkyusho Iho (Bulletin of Research Inst. of Mineral Dressing and Metallurgy)* **43** (1987) 252.

15 N. Sato and M. Nanjo, *Tohoku Daigaku Senko Seiren Kenkyusho Iho (Bulletin of Research Inst. of Mineral Dressing and Metallurgy)* **44** (1988) 123.

16 S. S. Shunshine, D. A. Keszler and J. A. Ibers, *Acc. Chem. Res.* **20** (1987) 395.

17 V. N. Petrova, G. V. Girichev, V. M. Petrov and V. K. Goncharuk, *J. Struct. Chem. USSR.* **26** (1985) 192, *Engl. Transl.* of *Zh. Strukt. Khim.* **26** (1985) 56.

18 M. E. Ignatov, B. V. Levin, Z. G. Rumyantseva and E. G. Il'in, *Russ. J. Inorg. Chem.* **31** (1986) 373, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 654.

19 G. K. Semin, A. M. Raevsky and S. I. Gushin, *Chem. Phys. Letters* **121** (1985) 214.

20 G. Dittmer and U. Niemann, *Philips J. Res.* **40** (1985) 55.

21 A. Ya. Borshchevskii, E. B. Rudnyi, K. Yu. Evdokimov and L. N. Sidorov, *Khim. Fiz.* **3** (1984) 1679.

22 G. L. Gutsev and A. I. Boldyrev, *Sov. J. Coord. Chem.* **10** (1984) 810, *Engl. Transl.* of *Koord. Khim.* **10** (1984) 1455.

23 T. Nakajima, K. Okahara, D. K. Padma and N. Watanabe, *Chem. Letters* **1987** (1987) 1255.

24 E. E. Shawki, S. N. Flengas and D. R. Sadoway, *Can. J. Chem.* **67** (1989) 1193.

25 L. M. Bazhanova, A. S. Izmailovich and V. I. Tsirel'nikov, *Russ. J. Inorg. Chem.* **31** (1986) 1832, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 3189.

26 V. V. Bardin, A. A. Avramenko, V. A. Petrov, V. A. Krasil'nikov, A. I. Karelin, P. P. Tushin, G. G. Furin and G. G. Yakobson, *J. Organ. Chem. USSR* **23** (1987) 536, *Engl. Transl.* of *Zh. Organ. Khim.* **23** (1987) 593.

27 R. Silva and H. L. de C. Barroa, *Quim. Nova* 7 (1984) 185.

28 G. A. Berezovskii, L. M. Bazhanova, I. E. Paukov and V. I. Tsirel'nikov, *Russ. J. Phys. Chem.* **61** (1987) 727, *Engl. Transl.* of *Zh. Fiz. Khim.* **61** (1987) 1397.

29 S. Nunziante-Cesaro, M. Maltese, M. Spoliti and B. Janis, *Spectrochim. Acta* **40A** (1984) 579.

30 S. Elbel, A. Blanck and H. Walther, *J. Chem. Soc. Faraday Trans. 2* **81** (1985) 869.

31 H. Schäfer and W. Pölert, *Z. Anorg. Allgem. Chem.* **522** (1985) 117.

32 D. V. Drobot and E. A. Pisarev, *Russ. J. Inorg. Chem.* 29 (1984) 1561, *Engl. Transl.* of *Zh. Neorg. Khim.* **29** (1984) 2723.

33 H. Schäfer and W. Pölert, *Z. Anorg. Allgem. Chem.* **522** (1985) 117.

34 H. Schäfer, R. Gerken and L. Zylka, *Z. Anorg. Allgem. Chem.* **534** (1986) 209.

35 R. J. French, *Diss. Abstr. Int. B* **47** (1987) 3783.

36 E. M. Nour, *Spectrochim. Acta* **42A** (1986) 1411.

37 D. V. Drobot and E. A. Pisarev, *Russ. J. Inorg. Chem.* 29 (1984) 1461, *Engl. Transl.* of *Zh. Neorg. Khim.* **29** (1984) 2558.

38 N. Okubo and Y. Abe, *Phys. Letters*, **106** A (1984) 435.

39 C. J. du Toit, J. A. K. du Plessis and G. Lachmann, *S. Afr. J. Chem.* **38** (1985) 188.

40 J. A. K. Du Plessis, P. Smulders and C. J. Du Toit, *J. Molec. Catal.* **42** (1987) 105.

41 W. Loose, B. Monheim and H. Schäfer, *Z. Anorg. Allgem. Chem.* **522** (1985) 108.

42 J. Geyer-Lippmann, A. Simon and F. Stollmaier, *Z. Anorg. Allgem. Chem.* **516** (1984) 55.

43 P. K. Ummat, H. Zaleski and W. R. Datars, *J. Mater. Res.* **2** (1987) 317.

44 D. Rehder and W. Basler, *J. Magn. Reson.* **68** (1986) 157.

45 D. V. Tsikaeva, S. D. Nikitina, A. I. Agulyanskii and V. T. Kalinnikov, *J. Generel Chem. USSR* **57** (1987) 866, *Engl. Transl.* of *Zh. Obshch. Khim.* **57** (1987) 974.

46 A. G. Babkin, A. I. Nikolaev and E. V. Shevyreva, *Russ. J. Inorg. Chem.* **31** (1986) 1412, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 2444.

47 A. I. Agulyanskii, V. Ya. Kuznetsov, L.A. Agulyanskaya and V. T. Kalinnikov, *Koord. Khim.* **10** (1984) 1512.

48 V. Ya. Kuznetsov, D. L. Rogachev, A. I. Agulyanskii and V. T. Kalinnikov *J. Struct. Chem. USSR.* **26** (1985) 565, *Engl. Transl.* of *Zh. Strukt. Khim.* **26** (1985) 85.

49 S. P. Gabuda, S. G. Kozlova, Yu. G. Kriger and V. K. Goncharuk, *Russ. J. Struct. Chem.* **27** (1986) 221, *Engl. Transl.* of *Zh. Strukt. Khim.* **27** (1986) 53.

50 B. G. Müller, *Angew. Chem.* **99** (1987) 685.

51 W. R. Datars, P. K. Ummat and R. J. Gillespie, *Mater. Res. Bull.* **20** (1985) 865.

52 F. W. Poulsen, N. H. Andersen, K. N. Clausen, D. R. Sadoway and L. H. Øgendal, *Solid State Ionics* **28-30** (1988) 271.

53 N. Sato and M. Nanjo, *Proc. Electrochem. Soc.* **87-7** (1987) 267.

54 Ch. Papadimitriou, J. M. Tsangaris and A. Padadimitriou, *J. Less-Common Met.* **108** (1985) 217.

55 J. R. Kirk, D. Page, M. Prazak and V. Katovic, *Inorg. Chem.* **27** (1988) 1956.

56 I-Wen Sun, E. H. Ward and C. L. Hussey, *Inorg. Chem.* **26** (1987) 4309.

57 B. Krebs, H. Janssen, N. J. Bjerrum, R. W. Berg and G. N. Papatheodorou, *Inorg. Chem.* **23** (1984) 164.

58 J. Shamir, S. Luski, A. Bino, S. Cohen and D. Gibson, *Inorg. Chim. Acta* **104** (1985) 91.

59 J. Hanich and K. Dehnicke, *Z. Naturforsch.* **39b** (1984) 1467.

60 A. N. Baimakov, S.A.Kuznetsov, E.G.Polyakov, and P. T. Stangrit, *Soviet Electrochem.* **21** (1985) 541, translated from *Élektrokhimiya* **21** (1985) 592.

61 C. C Torardi, L. H. Brixner and G. Blasse, *J. Solid State Chem.* **67** (1987) 21.

62 G. Blasse and L. H. Brixner, *J. Luminescene* **35** (1986) 179.

63 P. Taxil and Z. Y. Qiao, *Proc. - Electrochem. Soc.* **86-1 (Molten Salts)** (1986) 485.

64 D. V. Tsikaeva, S. D. Nikitina, A. I. Agulyanskii and V. T. Kalinnikov, *Koord. Khim.* **12** (1986) 929.

65 D. Gantar and A. Rahten, *Thermochim. Acta* **117** (1987) 227.

66 S. S. P. Parkin and J. V. Acrivos, *Proceedings of Intnl. Conf. on Synthetic Metals, Japan*, **1986** (1986).

67 J. V. Acrivos, H. P. Hughes and S. S. P. Parkin, *J. Chem. Phys.* **86** (1987) 1780.

68 I. D. Brown, R. J. Gillespie, K. R. Morgan, J. F. Sawyer, K. J. Smidt, Z. Tun, P. K. Ummat and J. E. Vekris, *Inorg. Chem.* **26** (1987) 689.

69 H.-G. Nieder-Vahrenholz and H. Schäfer, *Z. Anorg. Allgem. Chem.* **544** (1987) 122.

70 P. P. Man, H. Theveneau and P. Papon, *J. Magn. Reson.* **64** (1985) 271.

71 B. Langenbach-Kuttert, R. Ross and R. Gruehn, *Monatsh. f. Chemie* **116** (1985) 1275.

72 R. Stomberg, *Acta Chem. Scand.* **A38** (1984) 603.

72A R. Stomberg, *Acta Chem. Scand.* **A37** (1983) 453.

73 E. G. Il'in, A. N. Zozulin and Yu. A. Buslaev, *Doklady Phys. Chem. Proc. Acad. Sci. USSR* **296** (1987) 956, *Engl. Transl.* of *Dokaldy Akad. Nauk SSSR* **296** (1987) 907.

74 A. K. Chulkevich, E. V. Smolina, I. P. Lavrent'ev and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.* **8** (1986) 1896.

75 A. I. Agulyanskii, E. L. Tikhomirova, V. Ya. Kuznetsov and V. T. Kalinnikov, *Russ. J. Inorg. Chem.* **33** (1988) 47, *Engl. Transl.* of *Zh. Neorg. Khim.* **33** (1988) 85.

76 L. De-Yu, M. Lundberg, P.-E. Werner and M. Westdahl, *Acta Chem. Scand.* **A38**(1984) 813.

77 J. K. Ghosh and G. Ghosh, *J. Fluorine Chem.* **38** (1988) 183.

78 A. I. Agulyanskii, E. L. Tikhomirova and V.T. Kalinnikov, *Russ. J. Inorg. Chem.* **32** (1987) 1221, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 2079.

79 A. I. Agulyanskii and V. T. Kalinnikov, *Russ. J.* Inorg. Chem. **31** (1986) 35, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 63.

80 V. T. Kalinnikov and A. I. Agulyansky, *Japan J. Appl. Phys. Supplement 24-2, Proc. Int. Meet. on Ferro-electricity* **24** (1985) 628.

81 S. Yu. Stefanovich, B. A. Strukov, A. P. Leonov, A. I. Agulyansky and V. T. Kalinnikov, *Japan J. Appl. Phys. Supplement 24-2, Proc. Int. Meet. on Ferro-electricity*, **24** (1985) 630.

82 A. I. Agulyanskii, V. A. Bessonova, V. Ya. Kuznetsov and V. T. Kalinnikov, *Russ. J. Inorg. Chem.* **31** (1986) 1547, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 2683.

83 A. I. Agulyanskii, D. V. Tsikaeva, N. F. Sklokina, R. A. Popova and V. T. Kalinnikov, *Russ. J. Inorg. Chem.* **29** (1984) 1646, *Engl. Transl.* of *Zh. Neorg. Khim.* **29** (1984) 2877.

84 A. I. Agulyanskii and D. V. Tsikaeva, *Russ. J. Inorg. Chem.* **31** (1986) 1743, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 3030.

85 P. N. Wa Llunga, *Acta Chem. Scand.* **A38** (1984) 641.

86 Ö. Sävborg, *J. Solid State Chem.* **57** (1985) 143.

87 Ö. Sävborg and M. Lundberg, *J. Solid State Chem.* **57** (1985) 135.

88 Ö. Sävborg, *J. Solid State Chem.* **57** (1985) 148.

89 Ö. Sävborg, *J. Solid State Chem.* **57** (1985) 154.

90 Ö. Sävborg, *J. Solid State Chem.* **57** (1985) 160.

91 W. Hiller, J. Strähle, H. Prinz and K. Dehnicke, *Z. Naturforsch.* **39b** (1984) 107.

92 M. J. Collins, R. J. Gillespie, J. W. Kolis and J. F. Sawyer, *Acta Cryst. C* **43** (1987) 2033.

93 F. A. Cotton, S. A. Duraj and W. J. Roth, *Acta Cryst. C* **41** (1985) 881.

94 M. Hörner, K.-P. Frank and J. Strähle, *Z. Naturforsch.* **41 b** (1986) 423.

94A M. Hörner, W. Hiller, J. Strähle and G. M. Sheldrick, *Z. Naturforsch.* **43 b** (1988) 981.

95 J. H. von Barner, N. J. Bjerrum and R. W. Berg, *Proc. Electrochem. Soc.* **86-1, Molten Salts** (1986) 216.

96 J. F. Ackerman, *J. Solid State Chem.* **62** (1986) 92.

97 G. Blasse, M. J. J. Lammers, H. C. G. Verhaar, L. H. Brixner and C. C. Torardi, *J. Solid State Chem.* **60** (1985) 258.

98 L. H. Brixner, J. C. Calabrese and C. M. Foris, *Mater. Res. Bull.* **18** (1983) 1493.

99 J. W. Severin, M. J. J. Lammers, G. Blasse, L. H. Brixner and C. C. Torardi, *J. Solid State Chem.* **66** (1987) 318.

100 U. Schaffrath and R. Gruehn, *J. Less-Common Met.* **137** (1988) 61.

101 U. Schaffrath and R. Gruehn, *Naturwiss.* **74** (1987) 342.

102 R. Stomberg, *Acta Chem. Scand.* **A34** (1980) 193 and *Ibid.* **A35** (1981) 389.

103 E. M. Nour, A. B. El-Sayed and F. Abdel-Rehim, *Spectrochim. Acta* **41A** (1985) 865.

104 E. M. Nour, A. B. El-Sayed and F. Abdel-Rehim, *Indian J. Phys.* **59B** (1985) 467.

105 E. M. Nour, A. B. El-Sayed and F. Abdel-Rehim, *Pakistan J. Sci. Ind. Res.* **29** (1986) 9.

106 A. C. Dengel and W. P. Griffith, *Spectrochim. Acta* **43A** (1987) 1173.

107 S. M. Sinitsyna and N. A. Razorenova, *Koord. Khim.* **10** (1984) 1574.

108 J. K. Ghosh and G. V. Jere, *J. PhotoChem. Photobiol. A. Chem.* **40** (1987) 295.

109 J. K. Ghosh and G. V. Jere, *Thermochim. Acta* **114** (1987) 347.

110 Yu. V. Mironov, V. P. Fedin, P. P. Semyannikov and V. E. Fedorov, *Russ. J. Inorg. Chem.* **31** (1986) 617, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 1082.

111 U. Müller and P. Klingelhöfer *Z. Anorg. Allgem. Chem.* **510** (1984) 109.

112 J. L. Sella, J. C. Huffman and G. Christou, *Polyhedron* **8** (1989) 1797.

113 P. Klingelhöfer and U. Müller, *Z. Anorg. Allgem. Chem.* **516** (1984) 85.

114 K. M. Abraham, M. W. Rupich and J. E. Elliot, *Electrochim. Acta* **30** (1985) 1635.

115 I. H. Baba, *Sains Malays.* **13** (1984) 429.

115A B. Siewert, G. Koellner, K. Ruhlandt-Senge, F. Schmock and U. Müller, *Z. Anorg. Allgem. Chem.* in press (1990).

116 E. G. Il'in, É. Kharrmann, M. N. Shcherbakova and Yu. A. Buslaev, *Proc. Acad. Sci. USSR, Doklady Phys. Chem.* **296** (1987) 996, *Engl. Transl.* of *Dokl. Akad. Nauk SSSR* **296** (1987) 1153.

117 F. A. Cotton, M. P Diebold and W. J. Roth, *Inorg. Chem.* **27** (1988) 2347.

118 C. N. Geetha, I. Rani, H. B. Singh and R. K. Multani, *Indian J. Chem.* **24A** (1985) 236.

119 C. N. Geetha, I. Rani, H. B. Singh and R. K. Multani, *Current Science* **55** (1986) 310.

120 K. C. Malhotra, U. K. Banerjee, K. C. Mahajan and S. C. Chaudhry, *Acta Cienc. India, [Ser.] Chem.* **10** (1984) 26.

121 L. V. Kucheruk, I. E. Paleeva, E. P. Buchikhin, O. V. Braverman, I. P. Gol'dshtein and E. N. Gur'yanova, *J. Gen. Chem. USSR Engl. Transl.* **54** (1984) 1500.

122 S. M. Sinitsyna and N. A. Razorenova, *Koord. Khim.* **11** (1985) 617.

123 G. R. Clark, A. J. Nielson and C. E. F. Rickard, *Polyhedron* **6** (1987) 1765.

124 L. R. Chamberlain, I.P. Rothwell and J.C. Huffman, *Inorg. Chem.* **23** (1984) 2575.

125 S. C. Chaudhry, J. Gupta and S. Mehta, *Indian J. Chem.* **23 A** (1984) 1036.

126 S. C. Chaudhry, J. Gupta and S. Mehta, *Indian J. Chem.* **24A** (1985) 521.

127 S. Chomal, A. S. Aazim and G. Chandra, *Acta Chim. Hung.* **122** (1986) 127.

128 S. Gupta, B. Singh and R. N. Kapoor, *Synth. React. Inorg. Met.-org. Chem.* **15** (1985) 745.

129 R. Kapoor, R. Sharma and P. Kapoor, *Indian J. Chem.* **24A** (1985) 761.

130 M. T. El-Haty and F. A. Adam, *Bull. Soc. Chim. France* **1986** (1986) 351.

131 V. V. Grigor'eva and I. V. Golubeva, *Vestn. Kiev. Un-ta. Khimiya* **26** (1985) 59, ref. from *Zh. Khim.* **1985**, abstr. no. 20B86.

132 R. K. Sharma and G. C. Shivahare, *Monatsh. f. Chem.* **116** (1985) 297.

133 K. Behzadi, A. I. T. A. Ahwaz Iran and A. Thompson, *J. Less-Common Met.* **124** (1986) 135.

134 S. M. Sinitsyn and N.A. Razorenova, *Russ. J. Inorg. Chem.* **31** (1986) 1618, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 2811.

135 K.-P. Frank, J. Strähle and J. Weidlein, *Z. Naturforsch.* **35 b** (1980) 300.

136 L. Maya, *Inorg. Chem.* **26** (1987) 1459.

137 E. G. Il'in, M. N. Shcherbakova, M. E. Ignatov, V. P. Kukhar' and Yu. A. Buslaev, *Proc. Acad. Sci. USSR, Doklady Phys. Chem.* **283** (1985) 748, *Engl. Transl.* of *Dokl. Akad. Nauk SSSR* **283** (1985) 904.

138 G. Rajca and J. Weidlein, *Z. Anorg. Allgem. Chem.* **538** (1986) 36.

139 T. C. Jones, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc. Chem. Commun.* **1984** (1984) 205.

140 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron* **4** (1985) 1391.

141 A. J. Nielson, *Polyhedron* **7** (1988) 67.

142 K. Haug, W. Hiller und J. Strähle, *Z. Anorg. Allgem. Chem.* **533** (1986) 49.

143 N. A. Ovchinnikova and M. A. Glushkova, *Koord. Khim.* **12** (1986) 202.

144 P. J. H. Carnell and G. W. A. Fowles, *J. Chem. Soc.* **1959** (1959) 4113.

145 G. W. A. Fowles and C. M. Pleass, *J. Chem. Soc.* **1957** (1957) 2078.

146 B. Tamhina and A. G. Ivsic, *Solvent Extr. Ion Exch.* **5** (1987) 909.

147 N. S. Biradar, V. L. Roddabasanagoudar and T. M. Aminabhavi, *Indian J. Chem.* **24 A** (1985) 703.

148 S. Chomal and G. C. Shivahare, *Anales de Quimica A* **82** (1986) 214.

149 G. C. Shivahare and N. Pandey, *J. Indian Chem. Soc.* **63** (1986) 989.

150 S. Chomal and G. C. Shivahare, *Acta Chim. Hung.* **118** (1985) 31.

151 R. K. Sharma and G. C. Shivahare, *J. Indian Chem. Soc.* **62** (1985) 18.

152 J. A. M. Canich, F. A. Cotton, S. A. Duraj and W. J. Roth, *Polyhedron* **5** (1986) 895.

153 E. Hey, F. Weller and K. Dehnicke, *Z. Anorg. Allgem. Chem.* **514** (1984) 25.

154 F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 508.

155 J. Arnold and T. D. Tilley, *J. Am. Chem. Soc.* **107** (1985) 6409.

156 J. Arnold, T. D. Tilley and A. L. Rheingold, *J. Am. Chem. Soc.* **108** (1986) 5355.

157 J. Arnold, T. D. Tilley, A. L. Rheingold and S. J. Geib, *Inorg. Chem.* **26** (1987) 2556.

158 C. N. Geetha, I. Rani, H. B. Singh and R. K. Multani, *Synth. React. Inorg. Met.-Org. Chem.* **15** (1985) 873.

159 B. L. Gorsi and R. C. Mehrotra, *Indian J. Chem.* **23 A** (1984) 783.

160 C. N. Geetha, I. Rani, H. B. Singh and R. K. Multani, *Synt. React. Inorg. Met.-Org. Chem.* **17** (1987) 173.

161 G. Balducci, G. Gigli and M. Guido, *J. Chem. Phys.* **85** (1986) 5955.

162 O. F. Schilling, *J. Phys. Chem. Solids* **47** (1986) 595.

163 A. S. Fedyukov, S. I. Alyamovskii, L. D. Miroshnikova and Yu. G. Zainulin, *Russ. J. Inorg. Chem.* **32** (1987) 1223, *Engl. Transl. of Zh. Neorg. Khim.* **32** (1987) 2083.

164 M. Kikuchi, K. Kusaba, E. Bannai, K. Fukuoka, Y. Syono and K. Hiraga, *Jap. J. Appl. Phys.* **24** (1985) 1600.

165 N. Uyeda, Y. Fujiyoshi and K. Ishizuka, *Ultramicroscopy* **15** (1984) 139.

166 H. Schäfer, W. Jagusch, H. Wenderdel and U. Griesel, *Z. Anorg. Allgem. Chem.* **529** (1985) 189.

167 P. I. Tolmach K. S. Gavrichev, and V. E. Gorbunov, *Russ. J. Phys. Chem.* **61** (1987) 188, *Engl. Transl.* of *Zh. Fiz. Khim.* **61** (1987) 361.

168 M. Vala, R. D. Brittain and D. Powell, *Chem. Phys.* **93** (1985) 147.

169 I. S. Sukhushina and I. A. Vasil'eva, *Russ. J. Phys. Chem.* **59** (1985) 1446, *Engl. Transl.* of *Zh. Fiz. Khim.* **59** (1985) 2429.

170 D. Yu. Zhogin, P. P. Tolmach, E. A. Kosarukina and V. P. Kolesov, *Russ. J. Phys. Chem.* **59** (1985) 1436, *Engl. Transl.* of *Zh. Fiz. Khim.* **59** (1985) 2410.

171 A. L. Gubskii, A. P. Kovtun and S. D. Khanin, *Fiz. Tverd. Tela (Leningrad)* **29** (1987) 1067.

172 A. E. Solov'eva, K. K. Artemova and O. N. Vasil'eva, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 795.

173 S. F. Ho, S. Contarini and J. W. Rabalais, *Chem. Phys. Lett.* **133** (1987) 171.

174 N. Uyeda, Y. Fujiyoshi and K. Ishizuka, *Ultramicroscopy* **15** (1984) 139.

175 Yu. K. Voron'ko, A. B. Kudryavtsev, V. V. Osiko, A. A. Sobol and E. V. Sorokin, *Kratk. Soobshch. Fiz.* **1987** (1987) 34.

176 R. J. Esdaile, *J. Appl. Phys.* **58** (1985) 1070.

177 F. Abbattista, M. Vallino and D. Mazza, *Mater. Res. Bull.* **22** (1987) 1019.

178 R. Garavito, M. E. Villafuerte-Castrejon, R. Valenzuela and A. R. West, *Br. Ceram. Trans. J.* **84** (1985) 104.

179 B.-O. Marinder, *Chem. Scripta* **26** (1986) 547.

180 J.-O. Bovin, D. X. Li, L. Stenberg and H. Annehed, *Z. Kristallogr.* **168** (1984) 99.

181 H. Groh and R. Gruehn, *Z. Anorg. Allgem. Chem.* **529** (1985) 179.

182 D. X. Li and K. H. Kuo, *J. Solid State Chem.* **56** (1985) 236.

183 N. Kumada, N. Ozawa, N. Kinomura and F. Muto, *Mater. Res. Bull.* **20** (1985) 583.

184 C. L. Voss and R. Gruen, *Mater. Sci. Monogr.* **28A** (*React. Solids, Pt. A*) (1985) 619.

185 C. Raptis, *Phys. Rev. B* **38** (1988) 10007.

186 A. Kania, K. Roleder, G. E. Kugel and M. D. Fontana, *J. Phys. C: Solid State Phys.* **19** (1986) 9.

187 C. Yang, G. Feng, Y. Zhou and D. Tang, *Wuli Xuebao* **33** (1984) 1586; *Chem. Abstr.* **102** (1985) 37285x.

188 G. Feng, C. Yang, Y. Zhou and D. Tang, *Wuli Xuebao* **33** (1984) 1581; *Chem. Abstr.* **102** (1985) 70604y.

189 R. Sharma and M. Lundberg, *Acta Cryst. C* **41** (1985) 173.

190 C. E. Rice and R. J. Holmes, *J. Appl. Phys.* **60** (1986) 3836.

191 A. I. Agulyanskii, Yu. A. Serebryakov, M. N. Palatnikov, L. S. Korobeinikov, Yu. I. Balabanov, L. A. Agulyanskaya and V. T. Kalinnikov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 471.

192 A. I. Agulyanskii, Yu. A. Serebryakov, M. N. Palatnikov, L. A. Agulyanskaya and Yu. I. Balabanov, *J. Generel Chem. USSR* **55** (1985) 1709, *Engl. Transl.* of *Zh. Obshch. Khim.* **55** (1985) 1923.

193 N. Kumada, N. Ozawa, N. Kinomura and F. Muto, *J. Mater. Sci.* **21** (1986) 4140.

194 M. T. Weller and P. G. Dickens, *J. Solid State Chem.* **60** (1985) 139.

195 J. Ph. Schnell and J. L. Fourquet, *Mater. Res. Bull.* **21** (1986) 1045.

196 P. Mouron and J. Choisnet, *J. Phys (Paris) C1 suppl. no.2* **47** (1986) C-491.

197 R. R. Neurgaonkar, W. K. Cory, J. R. Oliver and L. E. Cross, *Mater. Res. Bull.* **24** (1989) 1025.

198 G. D. Fallon, B. M. Gatehouse and L. Guddat, *J. Solid State Chem.* **61** (1986) 181.

199 M. Lundberg and M. Sundberg, *J. Solid State Chem.* **63** (1986) 216.

200 V. Bhat and J. Gopalakrishnan, *J. Solid State Chem.* **63** (1986) 278.

201 J. Gopalakrishnan, *Adv. Solid State Chem., Proc. INSA Golden Jubilee Symp. Solid State Chem.* **1985**, (1986) 48.

202 V. I. Popolitov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **23** (1987) 489.

203 V. I. Popolitov and G. F. Plakhov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **24** (1988) 100.

204 L. Jahnberg, *Acta Chem. Scand.* **A41** (1987) 527.

205 B. Langenbach-Kuttert, W. Mertin and R. Gruehn, *Z. Naturforsch.* **40b** (1985) 1651.

206 O. Yamaguchi, D. Tomihisa, N. Ogiso and K. Shimizu, *J. Am. Ceram. Soc.* **69** (1986) C-150.

207 R. Nedjar, M. M. Borel, A. Leclaire and B. Raveau, *Mater. Res. Bull.* **23** (1988) 497.

208 H. Müller-Buschbaum and R. Wichmann, *Z. Anorg. Allgem. Chem.* **536** (1986) 15.

209 P. Bordet, A. McHale, A. Santoro and R. S. Roth, *J. Solid State Chem.* **64** (1986) 30.

210 E. Tokizaki, Y. Sugitani and K. Nagashima, *Mater. Res. Bull.* **21** (1986) 231.

211 A. Aruga, E. Tokizaki, I. Nakai and Y. Sugitani, *Acta Cryst. C*, **41C** (1985) 663.

212 S. M. Eicher, J. E. Greedan and K. J. Lushington, *J. Solid State Chem.* **62** (1986) 220.

213 K. Kitayama, *J. Solid State Chem.* **64** (1986) 162.

214 K. K. Singh, G. N. Subbanna and P. Ganguly, *Rev. Chim. Minér.* **21** (1984) 632.

215 C. J. Chen, M. Greenblatt, K. Ravindran Nair and J. V. Waszczak, *J. Solid State Chem.* **64** (1986) 81.

216 N. M. Ghoneim and G. A. El-Shobaky, *Thermochim. Acta* **91** (1985) 213.

217 M. Waburg and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **542** (1986) 31.

218 L. Berzina, R. Svinka and V. Svinka, *Lavt. PSR Zinat. Akad. Vestis, Kim. Ser.* **1986** (1986) 404.

219 N. F. Feodorov, O.V. Mel'nikova, A. P. Pivovarova, N.V. Starkova and O. A. Bazhenova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **23** (1987) 692.

220 E. V. Murashova, V. K. Trunov and Yu. A. Velikodnyi, *Russ. J. Inorg. Chem.* **31** (1986) 951, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 1660.

221 F. Jasim and I. Jameel, *Thermochim. Acta* **115** (1987) 37.

222 R. S. Roth, L. D. Ettlinger and H. S. Parker, *J. Solid State Chem.* **68** (1987) 330.

223 V. K. Trunov, E. V. Murashova, Yu. V. Oboznenko, Yu. A. Velikodnyi and L. N. Kinzhibalo, *Russ. J. Inorg. Chem.* **30** (1985) 269, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 479.

224 V. B. Nalbandyan and A. V. Chinenova, *Russ. J. Inorg. Chem.* **30** (1985) 583, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 1036.

225 L. M. Rudkovskaya, O. N. Razumovskaya, V.G. Kryshtop, V. S. Filip'ev and T.B. Kuleshova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **21** (1985) 1374.

226 O. N. Razumovskaya, L. M. Rudkovskaya, T. B. Kuleshova and V. G. Kryshtop, *Term. Anal. Fazovye Ravnovesiya*, **1984** (1984) 29.

227 L. M. Rudkovskaya, T.B. Kuleshova, V.G. Kryshtop, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 1753.

228 D. Mezaoui, C. Michel, D. Groult and B. Raveau, *Mater. Res. Bull.* **21** (1986) 1039.

229 A. Grandin, M. M. Borel, M. Hervieu and B. Raveau, *J. Solid State Chem.* **68** (1987) 369.

230 E. L. Belokoneva, B. V. Mill'and A. V. Butashin, *Sov. Phys. Crystallogr.* **30** (1985) 167.

231 G. Blasse and G. J. Dirksen, *J. Solid State Chem.* **65** (1986) 283.

232 S. S. Lopatin, T. G. Lupeiko, I. B. Baranova and L. A. Derbaremdiker, *Russ. J. Inorg. Chem.* **31** (1986) 1431, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 2480.

233 S. S. Lopatin and I. N. Belyaev, *Russ. J. Inorg. Chem.* **29** (1984) 1506, *Engl. Transl.* of *Zh. Neorg. Khim.* 29 (1984) 2636.

234 A. Ya. Neiman, A. L. Podkorytov, I. E. Animitsa, A. S. Zhukovskaya and V. M Zhukovskii, *Russ. J. Inorg. Chem.* **32** (1987) 198, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 359.

235 B.-O. Marinder, P.-L. Wang and P.-E. Werner, *Acta Chem. Scand.* **A40** (1986) 467.

236 O. Yamaguchi, K. Matsui and K. Shimizu, *J. Am. Ceram. Soc.* **68** (1985) C-173.

237 G. Blase and L. H. Brixner, *Mater. Res. Bull.* **24** (1989) 363.

238 R. Gopalakrishnan, B. Viswanathan, V. Ramakrishnan and J. C. Kuriacose, *Mater. Chem. Phys.* **18** (1987) 171.

239 R. Wichmann and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **525** (1985) 135.

240 M. Gaitan, A. Jerez, C. Pico and M. L. Veiga, *Mater. Res. Bull.* **22** (1987) 477.

241 S. Martinez-Carrera, J. Sanz, C. Pico, M. Gaitan, A. Jerez and M. L. Veiga, *Mater. Res. Bull.* **22** (1987) 1405.

242 M. Waburg and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **522** (1985) 137.

243 M. Hervieu, B. Raveau, J. Lecomte and J.P. Loup, *Rev. Chim. Minérale* **22** (1985) 44.

244 J. A. Alonso, A. Castro, E. G. Puebla, M. A. Monge, I. Rasines and C. R. Valero, *J. Solid State Chem.* **69** (1987) 36.

245 G. V. Bazuev, O. V. Makarova and G. P. Shveikin, *Russ. J. Inorg. Chem.* **30** (1985) 1253, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 2204.

246 R. Sharma, *Mater. Res. Bull.* **20** (1985) 1373.

247 A. Jerez, S. Garcia-Martin, M. L. Veiga, M. Gaitan and C. Pico, *Thermochim. Acta* **120** (1987) 41.

248 G. V. Bazuev, G. P. Shveikin and O. V. Makarova, *Proc. Acad. Sci. USSR, Doklady Chem.* **286** (1986) 890, *Engl. Transl.* of *Dokl. Akad. Nauk SSSR* **288** (1986) 169.

249 K. Hayashi, H. Noguchi and I. Sato, *Mater. Res. Bull.* **21** (1986) 523.

250 G. Demazeau, E. Oh-Kim, J. Choy and P. Hagenmuller, *Mater. Res. Bull.* **22** (1987) 735.

251 K. Hayashi, H. Noguchi and S. Fujiwara, *Mater. Res. Bull.* **21** (1986) 289.

252 K. Hayashi, H. Noguchi and M. Ishii, *Mater. Res. Bull.* **21** (1986) 401.

253 W. Zhou, D. A. Jefferson and J. M. Thomas, *J. Solid State Chem.* **70** (1987) 129.

254 W. Zhou, D. A. Jefferson and J. M. Thomas, *Proc. Roy. Soc. London* **406A** (1986) 173.

255 D. A. Jefferson, *ACS Symposium Series, Solid State Chem. Catlysis* **279**, (1985) 183, Chapter 11.

256 A. V. Firsov, A. A. Bush, A. E. Mirkin and Yu. N. Venevtsev, *Sov. Phys. Crystallogr.* **30** (1985) 537, Engl. Transl. of *Kristallografiya* **30** (1985) 927.

257 B. Mössner and S. Kemmler-Sack, *J. Less-Common Met.* **105** (1985) 165.

258 N. F. Men'shenina, A. A. Evdokimov, V. B. Vyazovov, A. N. Klimenko and A. Ya. Neiman, *Neravnoves. Protsessy v Dielektr. Materialakh, M.* **1983** (1983) 3; *Chem. Abstr.* **102** (1985) 38494b.

259 B. Mössner and S. Kemmler-Sack, *J. Less-Common Met.* **120** (1986) 203.

260 B. Mössner and S. Kemmler-Sack, *J. Less-Common Met.* **120** (1986) 287.

261 B. Mössner and S. Kemmler-Sack, *J. Less-Common Met.* **120** (1986) 267.

262 J. M. Hayes, T. R. Gururaja, G. L. Geoffroy and L. E. Cross, *Mater. Letters* **5** (1987) 396.

263 S. S. Lopatin, T. G. Lupeiko and T. I. Ivleva, *Russ. J. Inorg. Chem.* **32** (1987) 483, *Engl. Transl.* of *Zh. Neorg. Khim.* **39** (1987) 865.

264 I. P. Raevskii, V. G. Smotrakov, A. A. Bokov, S. M. Zaitsev and V. P. Filippenko, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 807.

265 G. S. Knapp, M. V. Nevitt, A. T. Aldred and T. K. Klippert, *J. Phys. Chem. Solids* **46** (1985) 1321.

266 M. Yoshimura, Y. Yokogawa and S. Somiya, *J. Mater. Sci. Lett.* **5** (1986) 1022.

267 M. Yoshimura, Y. Yokogawa and S. Somiya, *Nippon Kagaku Kaishi* **1986** (1986) 1721.

268 M. Yoshimura, Y. Yokogawa and S. Somiya, *Yogyo Kyokaishi* **93** (1985) 593.

269 M. Gasperin, *J. Solid State Chem.* **67** (1987) 219.

270 M. Gasperin, *Acta Cryst. C* **43** (1987) 404.

271 C. Miyake, S. Ohana, S. Imoto and K. Taniguchi, *Inorg. Chem. Acta* **140** (1987) 133.

272 M. Dion, M. Ganne and M. Tournoux, *Rev. Chim. Minérale* **23** (1986) 61.

273 C. C. Torardi, L. H. Brixner and C. M. Foris, *J. Solid State Chem.* **58** (1985) 204.

274 B. Langenbach-Kuttert, J. Sturm and R. Gruehn, *Z. Anorg. Allgem. Chem.* **548** (1987) 33.

275 G. V. Bazuev, O. V. Makarova and G. P. Shveikin, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 434.

276 A. A. Kaminskii, B. V. Mill, E. L. Belokoneva, S. E. Sarkisov, T. Yu. Pastukhova and G. G. Khodzhabagyan, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **20** (1984) 2058.

277 G. A. Teterin, V. F. Zinchenko, V. E. Kuz'min, T. G. Babich and I. M. Minaev, *Soviet Progr. Chem.* **53** (1987) 8, *Engl. Transl.* of *Ukrain. Khim. Zh.* **53** (1987) 907.

278 V. P. Sirotinkin, V. A. Efremov and V. K. Trunov, *Russ. J. Inorg. Chem.* **30** (1985) 981, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 1727.

279 V. P. Sirotinkin, O. E. Averkova, A. M. Starikov and A. A. Evdokimov, *Russ. J. Inorg. Chem.* **32** (1987) 150, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 262.

280 V. A. Antonov, P. A. Arsen'ev, Kh. S. Bagdasarov, A. A. Evdokimov, E. K. Kopylova and Kh. G. Tadzhi-Aglaev, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 466.

281 M. Gasperin, *Acta Cryst. C* **42** (1986) 136.

282 L. Kihlborg, M. Sundberg and Ö. Sävborg, *Ultramicroscopy* **18** (1985) 191.

283 R. Brandt and H. Müller-Buschbaum, *Monatsh. f. Chemie* **117** (1986) 1239.

284 R. Brandt and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **542** (1986) 18.

285 R. Brandt and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **551** (1987) 13.

286 B. Jasper-Tönnies and H. Müller-Buschbaum, *Monatsh. f. Chemie* **115** (1984) 1151.

287 V. E. Dugin, M. L. Sholokhovich and A. A. Nesterov, *Russ. J. Inorg. Chem.* **30** (1985) 1036, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 1822.

288 M. M. Dobson and R. J. D. Tilley, *Chem. Scripta* **25** (1985) 137.

289 P. J. England and R. J. D. Tilley, *Chem. Scripta* **24** (1984) 130.

290 O. E. Averkova, A. A. Evdokimov, V. P. Sirotinkin and A. N. Pokrovskii, *Russ. J. Inorg. Chem.* **31** (1986) 1410, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 2442.

291 O. E. Averkova, A. E. Prozorovskii, V. P. Sirotinkin and A. A. Evdokimov, *Russ. J. Inorg. Chem.* **32** (1987) 357, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 639.

292 B. Langenbach-Kuttert, J. Sturm and R. Gruehn, *Z. Anorg. Allgem. Chem.* **543** (1986) 117.

293 G. V. Bazuev, L. D. Finkel'shtein, N. D. Samsonov, and G. P. Shveikin, *Russ. J. Inorg. Chem.* **32** (1987) 158, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1986) 3175.

294 G. V. Bazuev and G. P. Shveikin, *Russ. J. Inorg. Chem.* **30** (1985) 1497, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 2628.

295 K. Schückel and H. Müller-Buschbaum, *Rev. Chim. Minérale* **23** (1986) 154.

296 G. G. Khodzhabagyan and B. V. Mill, *Russ. J. Inorg. Chem.* **32** (1987) 246, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 444.

297 M. G. Zuev and A. A. Fotiev, *Russ. J. Inorg. Chem.* **31** (1986) 1398, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 2424.

298 M. G. Zuev and A. A. Fotiev, *Russ. J.* Inorg. Chem. **32** (1987) 299, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 535.

299 M. G. Zuev and A. A. Fotiev, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **23** (1987) 168.

300 H.-J. Lunk and S. Schönherr, *Z. f. Chem.* **27** (1987) 159.

301 E. Sh. Ganelina, A. I. Garkun and M. B. Krasnopol'skaya, *Russ. J. Inorg. Chem.* **30** (1985) 359, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 637.

302 V. P. Babaeva and V. Ya. Rosolovskii, *Russ. J. Inorg. Chem.* **29** (1984) 1566, *Engl. Transl.* of *Zh. Neorg. Khim.* **29** (1984) 2731.

303 V. P. Babaeva and V. Ya. Rosolovskii, *Russ. J. Inorg. Chem.* **31** (1986) 979, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 1710.

304 V. I. Kravtsov, V. I. Ivanenko and G. I. Kadyrova, *Soviet Electrochem.* **23** (1987) 30, *Engl. Transl.* of *Élektrokhimiya* **23** (1987) 36.

305 V. I. Ivanenko, V. I. Kravtsov, and G. I. Kadyrova, *Soviet Electrochem.* **23** (1987) 999, *Engl. Transl.* of *Élektrokhimiya* **23** (1987) 1056.

306 G. L. Kadyrova and E. A. Ivanova, *Pererab. Fiz.-Khim. Svoistva Soedin. Redk. Elem.* **1984** (1984) 52.

307 F. Borup, R. W. Berg and K. Nielsen, *Acta Chem. Scand.* **44** (1990) 328.

308 F. Borup and R. W. Berg, *unpublished*.

309 A. Leclaire, H. Chahboun, D. Groult and B. Raveau, *Z. Kristallog.* **177** (1986) 277.

310 H. Chahboun, D. Groult and B. Raveau, *C. R. Acad. Sci., Ser. 2* **304** (1987) 807.

311 S. Bruque, M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, B. Casal, E. Ruiz-Hitzky and J. Sanz, *Inorg. Chem.* **26** (1987) 847.

312 N. G. Chernorukov, T. S. Sharova, A. I. Kryukova and I. A. Korshunov, *Russ. J. Inorg. Chem.* **30** (1985) 665, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 1177.

313 V. P. Nikolaev, G. G. Sadikov, A. V. Lavrov and M. A. Porai-Koshits, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 1369.

314 A. El Jazouli, C. Parent, J. M. Dance and G. Le Flem, *C. R. Acad. Sci. Ser. 2,* **303** (1986) 1005.

315 V. P. Nikolaev, G. G. Sadikov, A. V. Lavrov and M. A. Porai-Koshits, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 1364.

316 A. El Jazouli, A. Serghini, R. Brochu, J.-M. Dance and G. Le Flem, *Compt. Rend. Acad. Sci. (Paris)*, Ser. II, **300** (1985) 493.

317 M. M. Borel, A. Grandin, A. Benabbas, A. Leclaire and B. Raveau, *Mater. Res. Bull.* **24** (1989) 1485.

318 S. Deniard-Courant, Y. Piffard and M. Tournoux, *Rev. Chim. Minérale* **24** (1987) 276.

319 M.-T. Averbuch-Pouchot, *Z. Anorg. Allgem. Chem.* **545** (1987) 118.

320 L. Ju and Y. Gu, *Fudan Xuebao, Ziran Kexueban* **24** (1985) 147, ref. from *Chem. Abstr.* **104** (1986) 60908c.

321 H. Chen and F. Gan, *Guisuanyan Xuebao* **12** (1984) 385.

322 Y. Qi and B. He, *Collect. Pap.-Int. Congr. Glass,* 14th, **1** (1986) 128.

323 K. Fukumi, S. Sakka and T. Kokubo, *J. Non-Crystalline Solids* **93** (1987) 190.

324 R. Nedjar, M. M. Borel and B. Raveau, *Z. Anorg. Allgem. Chem.* **540/541** (1986) 198.

325 R. Nedjar, M. M. Borel and B. Raveau, *J. Solid State Chem.* **71** (1987) 451.

326 A. Grandin, M. M. Borel and B. Raveau, *J. Solid State Chem.* **60** (1985) 366.

327 A. Grandin, M. M. Borel and B. Raveau, *Rev. Chim. Minérale* **24** (1987) 351.

328 A. J. Jacobson, J. W. Johnson and J. T. Lewandowski, *Mater. Res. Bull.* **22** (1987) 45.

329 J. Weber, M. Roch and A. F. Williams, *Chem. Phys. Letters* **123** (1986) 246.

330 M. Roch, J. Weber and A. F. Williams, *Inorg. Chem.* **23** (1984) 4571.

331 Yu. V. Mironov, V. P. Fedin and V. E. Fedorov, *Russ. J. Coord. Chem.* **32** (1987) 1339, *Engl. Transl. of Koord. Khim.* **32** (1987) 2290.

332 M. Latroche and J. A. Ibers, *Inorg. Chem.* **29** (1990) 1503.

333 K. Wacker and P. Buck, *Cryst. Res. Technol.* **20** (1985) 1025.

334 K. Cermák, *Cryst. Res. Technol.* **20** (1985) 619.

335 K. Cermák, *Sb. Ved. Pr., Vys. Sk. Chemickotechnol. Pardubice* **46** (1984) 23.

336 K. Cermák, *Sb. Ved. Pr., Vys. Sk. Chemickotechnol. Pardubice* **48** (1985) 11.

337 K. Zitter, J. Schmand and R. Schöllhorn, *Mater. Res. Bull.* **20** (1985) 787.

338 G. I. Makovetskii and E. I. Kasinskii, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 1797.

339 J. S. Swinnea, H. Steinfink, L. E. Rendón-Diaz Mirón and L. Banos-López, *J. Solid State Chem.* **56** (1985) 249.

340 F. J. Di Salvo, C. H. Chen, R. M. Fleming, J. V. Waszczak, R. G. Dunn, S. A. Sunshine and J. A. Ibers, *J. Less-Common Met.* **116** (1986) 51.

341 S. A. Sunshine and J. A. Ibers, *Inorg. Chem.* **24** (1985) 3611.

342 M. Saeki and M. Onoda, *Mater. Res. Bull.* **24** (1989) 1491.

343 S. A. Sunshine and J. A. Ibers, *Inorg. Chem.* **25** (1986) 4355.

344 E. Canadell and M.-H. Whangbo, *Inorg. Chem.* **26** (1987) 3974.

345 D. A. Keszler and J. A. Ibers, *J. Solid State Chem.* **52** (1984) 73.

346 P. J. Squattrito, S. A. Sunshine and J. A. Ibers, *J. Solid State Chem.* **64** (1986) 261.

347 D. A. Keszler, J. A. Ibers, S. Maoyu and L. Jiaxi, *J. Solid State Chem.* **57** (1985) 68.

348 D. A. Keszler, J. A. Ibers, M. Shang and J. Lu, *J. Solid State Chem.* **57** (1985) 68.

349 S. A. Sunshine and J. A. Ibers, *J. Solid State Chem.* **69** (1987) 219.

350 M. Evain, S. Lee, M. Queignec and R. Brec, *J. Solid State Chem.* **71** (1987) 139.

351 M. Evain, M. Queignec, R. Brec and J. Rouxel, *J. Solid State Chem.* **56** (1985) 148.

352 A. I. Yanovskii, E. P. Turevskaya, N. Ya. Turova and Yu. T. Struchkov, *Sov. J. Coord. Chem.* **11** (1985) 63, *Engl. Transl.* of *Koord. Khim.* **11** (1985) 110.

353 D. J. Eichorst, D. A. Payne, S. R. Wilson and K. E. Howard, *Inorg. Chem.* **29** (1990) 1458.

354 S. C. Goel, *Synth. React. Inorg. Met.-Org. Chem.* **15** (1985) 533.

355 E. P. Turevskaya, N. Ya. Turova and A. V. Novoselova, *Sov. J. Coord. Chem.* **10** (1984) 752, *Engl. Transl.* of *Koord. Khim.* **10** (1984) 1357.

356 S. K. Agarwal and R. C. Mehrotra, *Inorg. Chim. Acta* **112** (1986) 177.

357 R. Jain, A. K. Rai and R. C. Mehrotra, *Z. Naturforsch.* **40b** (1985) 1371.

358 R. K. Dubey, A. Singh and R. C. Mehrotra, *Transition Met. Chem.* **10** (1985) 473.

359 M. Aggrawal and R.C. Mehrotra, *Polyhedron* **4** (1985) 845.

360 R. Wang, K. Folting, J. C. Huffman, L. R. Chamberlain and I. P. Rothwell, *Inorg. Chim. Acta* **120** (1986) 81.

361 S. C. Goel, *Indian J. Chem.* **24A** (1985) 880.

362 K. C. Wallace, W. M. Davies and R. R. Schrock, *Inorg. Chem.* **29** (1990) 1104.

363 A. V. Saha and S. Sen, *J. Indian Chem. Soc.* **61** (1984) 704.

364 G. K. Nurtaeva and F. I. Lobanov, *Russ. J. Inorg. Chem.* **32** (1987) 825, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 1369.

365 J. Song, Y. Cao and Y. Hu, *Fenxi Huaxue* **13** (1985) 337.

366 M. G. B. Drew, D. A. Rice and D. M. Williams, *Inorg. Chim. Acta* **118** (1986) 165.

367 K. Tatsumi, Y. Sekiguchi, A. Nakamura, R. E. Cramer and J. J. Rupp, *Angew. Chem.* **98** (1986) 95.

368 M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc. Dalton Trans.* **1985** (1985) 1821.

368A B. Krebs and G. Henkel, in *Rings, Clusters and Polymers of Main Group and Transition Elements* Edited by H. W. Roesky, Elsevier (1987) 439.

369 A. Müller, J. Schimanski, M. Römer, H. Bögge, F.-W. Baumann, W. Eltzner, E. Krickemeyer and U. Billerbeck, *Chimia* **39** (1985) 25.

370 Y. Do and R. H. Holm, *Inorg. Chim. Acta* **104** (1985) 33.

371 Y. Do, E.D. Simhon and R. H. Holm, *Inorg. Chem.* **22** (1983) 3809.

372 J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White and E. N. Maslen, *J. Chem. Soc. Dalton Trans.* **1973** (1973) 2082.

373 E. J. Peterson, R. B. von Dreele and T. M. Brown, *Inorg. Chem.* **17** (1978) 1410.

374 R. R. Schrock, M. Wesolek, A. H. Liu, K. C. Wallace and J. C. Dewan, *Inorg. Chem.* **27** (1988) 2050.

375 R. Marchand, F. Pors and Y. Laurent, *Rev. Int. Hautes Temp. Refract.* **23** (1986) 11.

376 M. N. Mookerjee, R. V. Singh and J. P. Tandon, *Egypt. J. Chem.* **29** (1986) 39.

377 M. N. Mookerjee, R. V. Singh and J. P. Tandon, *Indian J. Chem.* **26 A** (1987) 521.

378 N. Pandey and G. C. Shivahare, *J. Inst. Chem. India* **57** (1985) 92.

379 A. K. Narula, B. Singh, S. Gupta and R. N. Kapoor, *Transition Met. Chem.* **9** (1984) 379.

380 S. Gupta, B. Singh, A. K. Narula and R. N. Kapoor, *Synth. React. Inorg. Met.-Org. Chem.* **15** (1985) 723.

381 J. Uttamchandani and R. N. Kapoor, *Indian J. Chem.* **24 A** (1985) 242.

382 J. Uttamchandani, S. K. Mehrotra, A.M. Bhandari and R. N. Kapoor, *Transition Met. Chem.* 1 (1976) 249.

383 S. Zhang, N. Xia, S. Gan and L. Zhang, *Fenxi Huaxue* **15** (1987) 604.

384 E. Yu. Rozhdestvenskii, *Sov. Progr. Chem.* **53** (1987) 18, *Engl. Transl.* of *Ukrainskii Khim. Zhurn.* **53** (1987) 242.

385 R. W. Chesnut, P. E. Fanwick and I. P. Rothwell, *Inorg. Chem.* **27** (1988) 752.

386 H.-G. von Schnering, J. Wolf, D. Weber, R. Ramirez and T. Meyer, *Angew. Chem.* **98** (1986) 372.

387 J. Pflüger, J. Fink and K. Schwarz, *Solid State Comm.* **55** (1985) 675.

388 H. Brunner, U. Klement, J. Wachter, M. Tsunoda, J.-C. Leblanc and C. Moise, *Inorg. Chem.* **29** (1990) 584.

389 N. Yu. Borovkov and A. S. Akopov, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **28** (1985) 34.

390 A. S. Akopov and N. Yu. Borovkov, *J. Generel Chem. USSR,* **56** (1986) 820, *Engl. Transl.* of *Zh. Obshch. Khim.* **56** (1986) 931.

390A F. Gingl and J Strähle, *Z. Naturforsch.* **44b** (1989) 110.

390B F. Gingl and J Strähle, *Z. Naturforsch.* **43b** (1988) 445.

391 P. Richard and R. Guilard, *Nouveau J. Chemie* **9** (1985) 119.

392 G. W. Rayner-Canham, *Polyhedron* **3** (1984) 1029.

393 N. I. Kasikova, A. I. Nikolaev and V. G. Maiorov, *Russ. J. Inorg. Chem.* **32** (1987) 75, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 137.

394 V. Vojkovic and B. Tamhina, *Solvent Extr. Ion Exch.* **5** (1987) 245.

395 G. K. Nurtaeva and F. I. Lobanov, *Russ. J. Inorg. Chem.* **31** (1986) 423, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 742.

396 A. Hussain, B. Reitz and R. Gruehn, *Z. Anorg. Allgem. Chem.* **535** (1986) 186.

397 B. Reitz and R. Gruehn, *Z. Anorg. Allgem. Chem.* **540/541** (1986) 215.

398 B. Reitz and R. Gruehn, *Naturwiss.* **71** (1984) 474.

399 E. Wang, N. Kimura and M. Greenblatt, *J. Electrochem. Soc.* **132** (1985) 1505.

400 F. Dageförde, R. Ross and R. Gruehn, *Z. Anorg. Allgem. Chem.* **553** (1987) 64.

401 K. Schückel and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **528** (1985) 91.

402 K. Schückel and H. Müller-Buschbaum, *Z. Anorg. Allgem. Chem.* **523** (1985) 69.

403 M. L. Luetkens, Jr., *Diss. Abstr. Int. B* **45** (1985) 3813.

404 D. V. Drobot, A. I. L'vovskii and P. G. Detkov, *Russ. J. Inorg. Chem.* **31** (1986) 443, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 779.

405 H. Schäfer, W. Loose and B. Monheim, *Z. Anorg. Allgem. Chem.* **522** (1985) 99.

406 L. M. Bazhanova, A. S. Izmailovich and V. I. Tsirel'nikov, *Russ. J. Inorg. Chem.* **31** (1986) 1824, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 3175.

407 L. M. Bazhanova, M. E. Efimov, V. A. Medvedev and V. I. Tsirel'nikov, *Russ. J. Phys. Chem.* **60** (1986) 946, *Engl. Transl.* of *Zh. Fiz. Khim.* **60** (1986) 1573.

408 B. Monheim and H. Schäfer, *Z. Anorg. Allgem. Chem.* **520** (1985) 87.

409 M. B. de Bournonville, D. Bizot, J. Chassaing and M. Quarton, *J. Solid State Chem.* **62** (1986) 212.

410 A. D. Westland, *Thermochim. Acta* **87** (1985) 29.

411 D. Bizot, J. Chassaing, J. Pannetier, M. Leblanc, A. Le Bail and G. Ferey, *Solid State Comm.* **58** (1986) 71.

412 C. S. Sass and J. W. Rabalais, *J. Phys. Chem.* **92** (1988) 2072.

413 F. A. Cotton, E. Babaian-Kibala, L. R. Falvello and M. Shang, *Inorg. Chem.* **29** (1990) 2591.

414 V. Delobbe, J. Chassaing and D. Bizot, *Rev. Chim. Minérale* **22** (1985) 784.

415 F. A. Cotton, M. P Diebold and W. J. Roth, *Inorg. Chem.* **26** (1987) 3319.

416 F. A. Cotton, M. P. Diebold and W. J. Roth, *Polyhedron* **4** (1985) 1485.

417 H. G. v. Schnering and W. Beckmann, *Z. Anorg. Allgem. Chem.* **347** (1966) 230.

418 H. Schäfer and W. Beckmann, *Z. Anorg. Allgem. Chem.* **347** (1966) 225.

419 C. Sourisseau, P. Gard and M. Fouassier, *Chem. Phys.* **123** (1988) 405.

420 A. V. Mishchenko, V. E. Fedorov and Yu. I. Mironov, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987** (1987) 1931.

421 M. D. Curtis and J. Real, *Organometallics* **4** (1985) 940.

422 M. D. Curtis, *Polyhedron* **6** (1987) 759.

423 M. D. Curtis and J. Real, *Inorg. Chem.* **27** (1988) 3176.

424 G. Balducci, G. Gigli and M. Guido, *Ber. Bunsenges. Phys. Chem.* **91** (1987) 635.

425 H. Yoshino, K. Shimokoshi and E. Miyazaki, *J. Electron Spectrosc.* **36** (1985) 269.

426 J.-F. Marucco, B. Poumellec, J. Gautron and P. Lemasson, *J. Phys. Chem. Solids* **46** (1985) 709.

427 M. Kikuchi, K. Kusaba, K. Fukuoka and Y. Syono, *J. Solid State Chem.* **63** (1986) 386.

428 B. Poumellec, J. F. Marucco and B. Touzelin, *Phys. Stat. Sol.* **137** (1986) 519.

429 J. Köhler and A. Simon, *Angew. Chem.* **98** (1986) 1011.

430 H. Müller-Buschbaum and U. Werthmann, *Z. Anorg. Allgem. Chem.* **545** (1987) 134.

431 C. Michel, B. Raveau and D. Mezaoui, *Mater. Chem. and Phys.* **15** (1986) 559.

432 F. A. Cotton, M. P Diebold and W. J. Roth, *Inorg. Chem.* **26** (1987) 2889.

433 F. A. Cotton, M. P Diebold and W. J. Roth, *Inorg. Chem.* **27** (1988) 3596.

434 M. Nishio, N. Kuwata, H. Hinode, M. Wakihara and M. Taniguchi, *Thermochim. Acta* **88** (1985) 101.

435 O. S. Rajora and A. E. Curzon, *Phys. Stat. Sol.* **A99** (1987) 65.

436 S. I. Kondrat'ev, S. B. Nikishenko, G. V. Antoshin, A. A. Slinkin, E. A. Fodorovskaya and Kh. M. Minachev, *Kinet. Catal.* **26** (1985) 1009, *Engl. Transl.* of *Kinet. Katal.* **26** (1985) 1167.

437 S. K. Basu and M. Taniguchi, *J. Thermal Anal.* **32** (1987) 1105.

438 Y. Ohno, *Phys. Rev. B* **36** (1987) 7500.

439 R. V. Coleman, W. W. McNairy, C. G. Slough, P. K. Hansma and B. Drake, *Surf. Sci.* **181** (1987) 112.

440 M. Eibschütz, D. Salomon, S. Zahurak and D. W. Murphy, *Phys. Rev. B* **37** (1988) 3082.

441 G. Y. Guo and W. Y. Liang, *J. Phys. C: Solid State Phys.* **20** (1987) 4315.

442 S. M. Zahurak and D. W. Murphy, *J. Solid State Chem.* **70** (1987) 137.

443 D. Salomon, A. Lerf, W. Biberacher, T. Butz and S. Saibene, *Chem. Phys. Letters* **119** (1985) 238.

444 M. Kuwabara, H. Hashimoto and H. Endoh, *Japan. J. Appl. Phys.* **25** (1986) L1.

445 L. D. Chapman and R. Colella, *Phys. Rev. B* **32** (1985) 2233.

446 R. L. Withers and S. W. Steeds, *J. Phys. C: Solid State Phys.* **20** (1987) 4019.

447 R. L. Winthers *J. Phys. C: Solid State Phys.* **20** (1987) 5975.

448 M. Naito, H. Nishihara and S. Tanaka, *J. Phys. Soc. Japan* **55** (1986) 2410.

449 A. Furukawa, Y. Kimishima, Y. Oda, H. Nagano and Y. Onuki, *J. Phys. Soc. Japan* **54** (1985) 4300.

450 A. Suzuki, M. Koizuma and M. Doyama, *Solid State Comm.* **53** (1985) 201.

451 J. Van Landuyt, G. Van Tendeloo and S. Amelinckx, *Pure & Appl. Chem.* **57** (1985) 1373.

452 J. V. Acrivos, *J. Phys. C: Solid State Phys.* **20** (1987) 4377.

453 K. Hayashi, A. Kawamura and H. Nishihara, *Solid State Comm.* **58** (1986) 781.

454 K. Hayashi and A. Kawamura, *Mater. Res. Bull.* **21** (1986) 1405.

455 C. G. Slough, W. W. McNairy and R. V. Coleman, *Phys. Rev. B* **34** (1986) 994.

456 G. A. Wiegers, H. J. M. Bouwmeester and A. G. Gerards, *Solid State Ionics* **16** (1985) 155.

457 P. R. Sarode , *Phys. Stat. Sol.* **A98** (1986) 391.

458 D. C. Dahn, J. F. Caolan and R. R. Haering, *Phys. Rev.* **B33** (1986) 5214.

459 Y. Ohno, K. Kaneda and K. Hirama, *Phys. Rev. B* **30** (1984) 4648.

460 H. Hinode, M. Wakihara and M. Taniguchi, *J. Crystal Growth* **84** (1987) 413.

461 H. J. M. Bouwmeester, *Solid State Ionics* **16** (1985) 163.

462 J. Huster and H. F. Franzen, *J. Less-Common Met.* **113** (1985) 119.

463 E. Wein, W. Müller-Warmuth and R. Schöllhorn, *Ber. Bunsenges. Phys. Chem.* **90** (1986) 158.

464 M. J. Smith and C. A. Vincent, *J. Chem. Thermodynamics* **18** (1986) 1183.

465 L. M. Kulikov, A. A. Semenov-Kobzar, A. A. Yanaki, L. G. Aksel'rud and O. S. Koshel, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **23** (1987) 1968.

466 O. S. Rajora and A. E. Curzon, *Phys. Stat. Sol.* **97** (1986) 65.

467 D. J. St. Julian, *Diss. Abstr. Int. B* **47** (1987) 3374.

468 Cl. Ritter and R. Schöllhorn, *Solid State Comm.* **61** (1987) 117.

469 T. Butz and A. Lerf, *Ber. Bunsenges. Phys. Chem.* **90** (1986) 638.

470 Y.-W. Chao, P. A. Wexler and D. E. Wigley, *Inorg. Chem.* **28** (1989) 3860.

471 N. Kumada, S. Hosoda, F. Muto and N. Kinomura, *Inorg. Chem.* **28** (1989) 3592.

472 S. Schreiner, L. E. Aleandri, D. Kang and J. A. Ibers, *Inorg. Chem.* **28** (1989) 392.

473 K. Tatsumi, I. Matsubara, Y. Sekiguchi, A. Nakamura and C. Mealli, *Inorg. Chem.* **28** (1989) 773.

474 M. D. Fryzuk and D. H. McConville, *Inorg. Chem.* **28** (1989) 1613.

475 C. Ting and L. Messerle, *Inorg. Chem.* **28** (1989) 171.

476 A. M. Ghorayeb, W. Y. Liang and A. D. Yoffe, *J. Phys. C: Solid State Phys.* **19** (1986) 7323.

477 M. Saeki and M. Onada, *J. Less-Common Met.* **135** (1987) L1.

478 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron* **4** (1985) 1391.

479 H. J. M. Bouwmeester, G. A. Wiegers and C. F. van Bruggen, *J. Solid State Chem.* **70** (1987) 58.

480 B. G. Silbernagel, *Z. Phys. Chem. N.F.* **151** (1987) 85.

481 P. L. McDaniel, T. M. Barbara and J. Jonas, *J. Phys. Chem.* **92** (1988) 626.

482 J. F. Lomax, B. N. Diel and T. J. Marks, *Mol. Cryst. Liq. Cryst* **121** (1985) 145.

483 Y. Saito, M. Makino, N. Yamazoe and T. Seiyama, *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **52** (1984) 734.

484 Y. Kanzaki, N. Watanabe, K. Maeda and O. Matsumoto, *J. Phys. Chem.* **91** (1987) 2727.

485 S. A. Sunshine and J. A. Ibers, *Acta Cryst.* **C43** (1987) 1019.

486 P. J. Squattrito, P. E. Swepston and J. A. Ibers, *Inorg. Chem.* **26** (1987) 1187.

487 W. Abriel and R.-R. Kozik, *Mater. Res. Bull.* **22** (1987) 895.

488 P. J. Squattrito, S. A. Sunshine and J. A. Ibers, *Solid State Ionics* **22** (1986) 53.

489 E. W. Liimatta and J. A. Ibers, *J. Solid State Chem.* **71** (1987) 384.

490 M. Sheer, V. P. Fedin, V. E. Fedorov, M. A. Fedotov and P.P. Semyannikov, *Russ. J. Inorg. Chem.* **32** (1987) 1049, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 1769.

491 M. M. B. Holl, M. Kersting, B. D. Pendley and P. T. Wolczanski, *Inorg. Chem.* **29** (1990) 1518.

492 H. Erschbaumer, R. Podloucky and A. Neckel, *J. Phys. C: Solid State Phys.* **15** (1985) L279.

493 A. A. Tripolski, V. G. Kamburg, V. N. Kulyukin and N. I. Pusynina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1985** (1985) 13.

494 H. B. Yaich, J. C. Jegaden, M. Potel, M. Sergent, A. K. Rastogi and R. Tournier, *J. Less-Common Met.* **102** (1984) 9.

495 F. A. Cotton, M. P Diebold and W. J. Roth, *Inorg. Chem.* **26** (1987) 3323.

496 F. A. Cotton, M. P. Diebold, M. Matusz and W. J. Roth, *Inorg. Chim. Acta* **112** (1986) 147.

497 J. A. M. Canich and F. A. Cotton, *Inorg. Chem.* **26** (1987) 3473.

498 F. A. Cotton, S. A. Duraj and W. J. Roth, *Acta Cryst.* **C41** (1985) 878.

499 F. A. Cotton, M. P. Diebold, S. A. Duraj and W. J. Roth, *Polyhedron* **4** (1985) 1479.

500 A. Goursot, B. Le Motais, C.Daul, E. Penigault, and A. M. Koulkès-Pujo, *Chem. Phys. Letters* **138** (1987) 339.

501 A. M. Koulkès-Pujo, B. Le Motais, and L. G. Hubert- Pfalzgraf, *J. Chem. Soc. Dalton Trans.* **1986** (1986) 1741.

502 J. A. Canich and F. A. Cotton, *Inorg. Chem.* **26** (1987) 4236.

503 F. A. Cotton, M. P Diebold and W. J. Roth, *Inorg. Chem.* **26** (1987) 4130.

504 N. T. Denisov, N. I. Shuvalova and A. E. Shilov, *Kinet. Catal.* **26** (1985) 1286, *Engl. Transl.* of *Kinet. Katal.* **26** (1985) 1493.

505 L. G. Hubert-Pfalzgraf and G. Aharonian, *Inorg. Chim. Acta* **100** (1985) L21.

506 F. A. Cotton, S. A. Duraj and W. J. Roth, *J. Am. Chem. Soc.* **106** (1984) 4749.

507 M. L. Luetkens, Jr., M. D. Hopkins, A. J. Schultz, J. M. Williams, C. K. Fair, F. K. Ross, J. C Huffmann and A. P. Sattelberger, *Inorg. Chem.* **26** (1987) 2430.

508 F. A. Cotton, M. P Diebold, X. Feng and W. J. Roth, *Inorg. Chem.* **27** (1988) 3413.

509 P. F. Gilletti, V. G. Young and T. M. Brown, *Inorg. Chem.* **28** (1989) 4034.

510 C. J. du Toit, J. A. K. du Plessis and G. Lachmann, *S. Afr. J. Chem.* **38** (1985) 195.

511 F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 2619.

512 F. A. Cotton and M. Shang, *J. Am. Chem. Soc.* **112** (1990) 1584.

513 F. A. Cotton and M. Shang, *Inorg. Chem.* **29** (1990) 2614.

514 M. Koizumi and S. Kikkawa, *Kagaku Kogyo* **36** (1985) 206.

515 E. A. Pazyuk, E. N. Moskvitina and Yu. Ya. Kuzyakov, *Spectrosc. Letters* **19** (1986) 627.

516 E. A. Pazyuk, E. N. Moskvitina, P. I. Stepanov and Yu. Ya. Kuzyakov, *Moscow Univ. Chem. Bull.* **40** (1985) 98, *Engl. Transl.* of *Vestnik Moskovskogo Univ. Khimiya* **40** (1985) 418.

517 W. Lengauer and P. Ettmayer, *Monatsh. f. Chemie* **117** (1986) 275.

518 A. Callenås, L. I. Johansson, A. N. Christensen, K. Schwarz and P. Blaha, *Phys. Rev. B* **32** (1985) 575.

519 R. B. King, *U.S. Gov. Report* **TR-34** (1986), NTIS order no. AD-A1742201/4/-GAR (25 p.).

520 R. Eisenbraun and H. Schäfer, *Z. Anorg. Allgem. Chem.* **530** (1985) 222.

521 A. Marchaj and N. Brnicevic, *Proc. 11th Conf. Coord. Chem.* **1987** (1987) 211.

522 H. Schäfer, M. Wolter and C. Brendel, *Z. Anorg. Allgem. Chem.* **517** (1984) 185.

523 S. P. Christiano, *Diss. Abstr. Int. B* **45** (1985) 3810.

524 N. Brnicevic, S. Mesaric and H. Schäfer, *Croatica Chem. Acta* **57** (1984) 529.

525 S. Ihmaïne, C. Perrin and M. Sergent, *Acta Cryst. C* **43** (1987) 813.

526 F. Ueno and A. Simon, *Acta Cryst. C* **41** (1985) 308.

527 A. Simon, H.-G. von Schnering and H. Schäfer, *Z. Anorg. Allgem. Chem.* **361** (1968) 235.

528 S. Ihmaine, C. Perrin and M. Sergent, *C. R. Acad. Sci. Ser. 2*, **303** (1986) 1293.

529 N. Brnicevic, F. Mustovic and R. E. McCarley, *Inorg. Chem.* **27** (1988) 4532.

530 H. Imoto, S. Hayakawa, N. Morita and T. Saito, *Inorg. Chem.* **29** (1990) 2007.

531 H. Schäfer and H. Lesaar, *Z. Anorg. Allgem. Chem.* **523** (1985) 187.

532 R. Burnus, J. Köhler and A. Simon, *Z. Naturforsch.* **42b** (1987) 536.

533 J. Köhler and A. Simon, *Z. Anorg. Allgem. Chem.* **553** (1987) 106.

534 B. Harbrecht, *J. Less-Common Met.* **124** (1986) 125.

535 B. Harbrecht and H. F. Franzen, *J. Less-Common Met.* **113** (1985) 349
(and reprinted *J. Less-Common Met.* **115** (1986) 177).

536 B. Harbrecht and H. F. Franzen, *Z. Anorg. Allgem. Chem.* **551** (1987) 74.

536A B. Harbrecht, *J. Less-Common Met.* **138** (1988) 225.

536B B. Harbrecht, *Angew. Chemie* **28** (1989) 1660.

536C B. Harbrecht, *J. Less-Common Met.* **141** (1988) 59.

537 M. J. Calhorda and R. Hoffmann, *Inorg. Chem.* **27** (1988) 4679.

538 H. F. Franzen, *J. Solid State Chem.* **64** (1986) 283.

539 J. M. Dyke, A. M. Ellis, M. Fehèr, A. Morris, A. J. Paul and J. C. H. Stevens, *J. Chem. Soc. Faraday Trans. 2* **83** (1987) 1555.

540 V. Sassenberg, A. Merer, G. Cheval, J. L. Féménias and R. Stringat, *Proc. Seventeenth Internat. Symp. on Free Radicals, Snow Mountain Ranch, Aug. 18-23*, 1985, U.S. Natl. Bur. Stand. Special Publ., **716** (1986) 602.

541 A. J. Merer, U. Sassenberg, J.-L. Féménias and G. Cheval, *J. Chem. Phys.* **86** (1987) 1219.

542 J. K. Burdett and T. Hughbanks, *J. Am. Chem. Soc.* **106** (1984) 3101.

543 T. V. D'yachkova, S. I. Alyamovskii and Yu. G. Zainulin, *Russ. J. Inorg. Chem.* **31** (1986) 1082, *Engl. Transl.* of *Zh. Neorg. Khim.* **31** (1986) 1879.

544 A. L. Ivanovskii, V. A. Gubanov and E. Z. Kurmaev, *Russ. J. Inorg. Chem.* **30** (1985) 1691, *Engl. Transl.* of *Zh. Neorg. Khim.* **30** (1985) 2969.

545 Y. V. Skripkin, I. L. Eremenko, A. A. Pasynskii, Y.T. Struchkov and V.E. Shklover, *J. Organomet. Chem.* **267** (1984) 285.

546 F. Calderazzo, G. Pampaloni and P. F. Zanazzi, *Chem. Ber.* **119** (1986) 2796.

547 A. S. Antsyshkina, L. M. Dikareva, M. A. Porai-Koshits, V. N. Ostrikova, Yu. V. Skripkin, A. A. Pasynskii, O. G. Volkov and V. T. Kalinnikov, *Sov. J. Coord. Chem.* **10** (1984) 872, *Engl. Transl.* of *Koord. Khim.* **10** (1984) 1560.

548 A. S. Andisjkina, I. M. Dikareva, M. A. Porai-Kosjits, V. N. Ostrikova, Ju. V. Skripkin, A. A. Pasynskij, O. G. Volkov and V. T. Kalinnikov and A. I. Agulyansky, *Koord. Khim.* **10** (1984) 1564.

549 S. W. Buckner, T. J. MacMahon, G. D. Byrd and B. S. Freiser, *Inorg. Chem.* **28** (1989) 3511.

550 L.-S. Zheng, P. J. Brucat, C. L. Pettiette, S. Yang and R. E. Smalley, *J. Chem. Phys.* **83** (1985) 4273.

551 S. R. Schmidt and H. F. Franzen, *J. Less-Common Met.* **116** (1986) 73.

552 K. Fujiura, T. Watari and A. Kato, *J. Less-Common Met.* **113** (1985) 283.

553 M. Venkatraman and J. P. Neumann, *Bull. Alloy Phase Diagr.* **7** (1986) 462.

554 H. Rushan, Z. Xifeng, Lu Guo and Yin Dole, *Solid State Comm.* **57** (1986) 595.

555 R. V. Skolozdra, Yu. V. Stadnyk and E. E. Starodynova, *Ukr. Fiz. Zh.* (Russ.ed.) **31** (1986) 1258.

556 F. Calderazzo, U. Englert, G. Pampaloni G. Pelizzi, and R. Zamboni, *Inorg. Chem.* **22** (1983) 1865.

557 F. Calderazzo, G. Pampaloni and J.E.Ellis, *Inorg. Synth.* **23** (1985) 34.

558 C. J. Jameson, D. Rehder and Martin Hoch, *Inorg. Chem.* **27** (1988) 3490.

559 G. F. Warnock, *Diss. Abstr. Int. B* **46** (1986) 2303.

560 P. Grenouilleau, A. Meerschaut, L. Guemas and J. Rouxel, *J. Solid State Chem.* **66** (1987) 293.

561 M. Kurdi, A.-M. Marie and M. Danot, *Solid State Comm.* **64** (1987) 395.

562 T. Yamamoto, S. Kikkawa and M. Koizumi, *J. Electrochem. Soc.* **133** (1986) 1558.

563 T. Iwazumi, M. Izumi, K. Uchinokura, R. Yoshizaki and E. Matsuura, *Physica* **143B** (1986) 255.

564 C. Sourisseau, R. Cavagnat, M. Fouassier and P. Maraval, *J. Mol. Struct.* **219** (1990) 183.

565 A. V. Mishchenko, Yu. I. Mironov, V. E. Federov, Yu. G. Kriger and S. P. Gabuda, *Russ. J. Inorg. Chem.* **32** (1987) 951, *Engl. Transl.* of *Zh. Neorg. Khim.* **32** (1987) 1591.

566 H. P. Geserich, G. Scheiber, F. Levy, P. Gressier and P. Monceau, *Mol. Cryst. Liq. Cryst.* **121** (1985) 19.

567 J. Nakahara, T. Taguchi, T. Araki and M. Ido, *J. Phys. Soc. Japan* **54** (1985) 2741.

568 A. V. Inyushkin, A. N. Taldenkov and V. V. Florentiev, *Synthetic Metals* **19** (1987) 843.

569 T. Yamamoto, S. Kikkawa and M. Koizumi, *Kenkyu Hokoku Asahi Garasu Kogyo Gijutsu Shoreikai* **46** (1985) 217.

570 J. W. Brill, W. Roark and G. Minton, *Phys. Rev. B.* **33** (1986) 6831.

571 S. L. Herr, *Diss Abstr. Int. B.* **47** (1987) 4570.

572 S. Dai, X. Zhou, A. H. Morrish, and Z. Shan, *Phys. Rev. B.* **36** (1987) 1.

573 H. Wada and M. Onoda, *Mater. Res. Bull.* **24** (1989) 191.

574 E. Canadell, I. E.-I. Rachidi, J. P. Pouget, P. Gressier, A Meerschaut, J. Rouxel and D. Jung, *Inorg. Chem.* **29** (1990) 1401.

575 P. Gressier, L. Guémas, A. Meerschaut, *Mater. Res. Bull.* **20** (1985) 539.

576 G. Minton and J. W. Brill, *Phys. Rev. B* **36** (1987) 4254.

577 D. C. Johnston, J. P. Stokes and R. A. Klemm, *J. Magn. Magn. Mater.* **54-57** (1986) 1317.

578 K. Biljakovic, J. C. Lasjaunias, F. Zougmore, P. Monceau, F. Levy, L. Bernard and R. Currat, *Phys. Rev. Letters* **57** (1986) 1907.

579 K. Ohtake, E. Sato, S. Koshiba, R. Yamamoto, M. Doyama, K. Soda, T. Mori, S. Suga and K. Endo, *Physica* **143B** (1986) 192.

580 M. Sato and H. Nishihara, *J. Phys. C: Solid State Phys.* **18** (1985) 2145.

581 S. Sugai, S. Kurihara and M. Sato, *Physica* **143B** (1986) 195.

582 A. Smontara, K. Biljakovic and L. Forro, *Synthetic Metals* **19** (1987) 859.

583 T. Sekine, M. Izumi, and E. Matsuura, *Synthetic Metals* **19** (1987) 869.

584 M. Saint-Paul and P. Monceau, *Phys. Rev. B* **37** (1988) 1024.

585 M. Izumi, T. Iwazumi, T. Seino, T. Sekine, E. Matsuura, K. Uchinokura and R. Yoshizaki, *Synthetic Metals* **19** (1987) 863.

586 P. Butaud, P. Segransan, C. Berthier and A. Meerschaut, *Congr. AMPERE Magn. Reson. Relat. Phenom., Proc. 22nd* (Eds. K. A. Mueller et al.) **1984** (1984) 40.

587 T. Ikari and F. Lévy, *J. Phys. C: Solid State Phys.* **18** (1985) L1109.

588 A. Smontara, K. Biljakovic, L. Forro and F. Levy, *Physica* **143B** (1986) 264.

589 T. Iwazumi, M. Izumi, F. Sasaki, R. Yoshizaki and E. Matsuura, *Physica* **143B** (1986) 261.

590 G. Huan and M. Greenblatt, *Mater. Res. Bull.* **22** (1987) 505.

591 T. Ohtani and S Onoue, *J. Solid State Chem.* **59** (1985) 324.

592 T. Sekine, Y. Kiuchi, M. Izumi, K. Uchinokura, R. Yoshizaki and E. Matsuura, *Synthetic Metals* **19** (1987) 875.

593 P. V. Nutsubidze, V.I. Chechernikov, Z. B. Chachkhiani and V. K. Slovyanskikh, *Soobshch. Akad. Nauk Gruz. SSSR* **124** (1986) 85.

594 P. V. Nutsubidze, P. V. Chechernikov, N. T. Kuznetsov, V. K. Slovyanskikh and N. V. Gracheva, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **21** (1985) 492.

595 A. Meerschaut, P. Grenouilleau and J. Rouxel, *J. Solid State Chem.* **61** (1986) 90.

596 A. B. Salem, P. Molinie and A. Meerschaut, *J. Physique (Paris).* **48** (1987) 277.