

12 Vanadium, niobium and tantalum

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1 Introduction

This review covers the literature for 1996. One area of research too large to include here, however, is the biological chemistry of vanadium. Unfortunately, there appeared only one review in this area.¹ Production and applications for pure niobium and tantalum metals and their oxides have been reviewed.² Other review articles are noted within the appropriate sections.

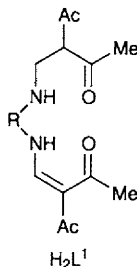
2 Co-ordination chemistry

Vanadium

The reactivity for some mono- and di-peroxovanadium(v) species has been correlated with ¹⁷O NMR, electronic and vibrational spectroscopic data.³ Peroxovanadium(v) complexes as *in situ* oxidants (with H₂O₂) for aliphatic and aromatic hydrocarbons, alkenes, alcohols, ketones and for sulfur, phosphorus and nitrogen derivatives have been reviewed.⁴

The oxovanadium halides, [VOCl₂(py)_n] (*n* = 2 or 3) and [VOCl₂(py)₂], were obtained from reaction of VCl₄ and VOCl₃ respectively with [(Ph₂SiOM)₂O] (M = Li or Na).⁵ Hydrothermal reaction of [PPh₄][VO₂Cl₂] with H₂C₂O₄ gives [PPh₄]₂[V₂O₂(H₂O)₂(C₂O₄)₃]-4H₂O and [PPh₄][VOCl(C₂O₄)] at 150 and 125 °C respectively.⁶ Macrocyclic thioether complexes of vanadium(-II), -(III) and -(IV) have been prepared and the structure of [VCl₃([9]aneS₃)] determined.⁷ Oxovanadium(IV) complexes with Jaeger-type ligands (H₂L¹) [VO(L¹)] (R = C₂H₄, *o*-phenylene or 4-methyl-*o*-phenylene)⁸ and some water-soluble mixed ligand oxovanadium(IV) complexes of acetylacetone and aldimine ligands⁹ have been reported.

The first oxovanadium(IV) complexes with dipeptides, [NH₄][VO(mpg)(phen)] and [V(O)L(phen)] (H₂L = glycylglycine or glycylalanine), were prepared from [VOCl₂(NMe)₂].¹⁰ Monodentate N-bonding of Him, Hpz and thiazole to tetra-valent VO species in solution yields complexes with 1:1, 1:2, 1:3 and 1:4 metal-to-ligand ratios.¹¹ For [{(VO₂SO₄)(H₂O)₂}L] and [(VO)₃L'(μ-SO₄)] (L, L' = phthalazine hydrazone ligands), each vanadium(IV) is five-co-ordinate with each hydrazone ligand bound to two metals.¹²



Vanadium-(iii), -(iv) and -(v) complexes containing the pentafluorophenyl-substituted triamidoamine ligand, $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ have been reported.¹³ The novel oxo-bridged vanadium(iv) complex, $[\{V(\mu-O)[N(SiMe_3)_2]_2\}_2]$, was prepared from reaction of $VOCl_3$ with $LiN(SiMe_3)_2$ ¹⁴ while VO_2^+ reacts with sal, asn and py to form $[VO(sal-D,L-asn)(py)(H_2O)]$ or coumarine-3-carboxamide upon ageing with O_2 .¹⁵ The redox chemistry associated with complexation of vanadium(v) by *meso*-octaethylporphyrinogen has been studied.¹⁶

The bidentate UV-stabiliser Tinuvin P (HL) displaces Hacac from $[VO(acac)_2]$ to give $[\{VO(acac)\}_2(\mu-L)_2]$.¹⁷ For the fluoride amino acid complexes, $A[VOF_2L(H_2O)]$ ($A = Na$ or NH_4 ; $L =$ cysteinate) and $A[VOF_3L(H_2O)]$ ($A = NH_4$, $L =$ alanine; $A = Na$, NH_4 or K , $L =$ serine),¹⁸ the fluorides act as stabilising ligands which facilitate solid-state isolation. The compound $VOCl_3$ reacts with $P(SiMe_3)_3$ to give $[VOCl_2\{P(SiMe_3)_3\}_2]$.¹⁹ Herberhold *et al.*²⁰ have reported several new vanadium complexes with phosphorus ligands and the layered vanadium(v) methylphosphonates, $M(VO_2)_3(PO_3CH_3)_2$ ($M = NH_4$, K , Rb or Tl), have also been reported.²¹

Structural investigations for $LnVO_4$ ($Ln = Sm$, Eu , Gd or Dy)²² indicate that the orthovanadate group is a distorted tetrahedron while the Ln atoms are each co-ordinated to eight oxygen atoms with two unique $Ln-O$ bond lengths. Several $V^{IV}O-Ln^{III}$ ($Ln = La$, Eu or Gd) complexes of *N,N'*-bis(3-hydroxysalicylidene)ethylenediamine have also been prepared.²³ Crystal structures have been reported for $[V_2O_3(sal-L-val)_2(H_2O)_2]$,²⁴ $[NH_4]_2[(VO)_2(acac)_2(O_3PCH_2PO_3)]$,²⁵ $[PPH_4][(VO_2)_4(O_2CMe)_4Cl]$,²⁶ and β -*cis*- $NH_4[VO_2(edda)]$,²⁷ and structural anomalies for the alkali-metal vanadium β -alums, $MV(SO_4)_2 \cdot 12H_2O$ ($M = K$, Rb or Cs) have been investigated.²⁸

Niobium and tantalum

The compound $TaCl_4$ is isostructural with $NbCl_4$ ²⁹ and the structure has also been reported for tantalum orthoborate, $TaBO_4$.³⁰ In bis[phenyl(2-propenyl)ammonium] pentachloro(phenylamido)niobium(iv), $[NC_9H_{12}]_2[NbCl_5(NC_6H_5)]$, prepared from $NbCl_5$ and *N*-allylphenylamine,³¹ the co-ordinated secondary amine loses its allyl group in forming an imino-metal bond while the unreacted *N*-allylphenylamine behaves as a proton acceptor and counter ion. Niobium(v) bromide reacts with Me_3SiNPh_2 to give the trigonal-bipyramidal complex, $[Nb(NPh_2)_3Br_2]$.³² Arimondo *et al.*³³ have prepared the dialkylcarbamato species $[M(O_2CNR_2)_n]$ ($M = Nb$ or Ta , $R = Et$, $n = 5$; $M = Nb$, $R = Et$, Pr^i , $n = 4$).

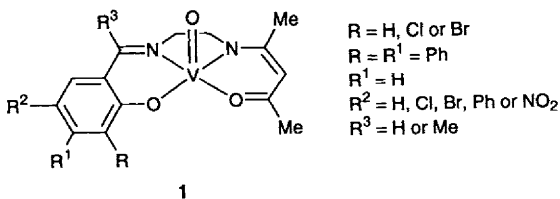
The bimetallics, $[\text{Cp}_2\text{Nb}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{M}(\text{CO})_3(\text{PMe}_2\text{H})]$ ($\text{M} = \text{Cr}$ or W), prepared by UV irradiation of the dinuclear monobridged species, $[\text{Cp}_2\text{Nb}(\text{PMe}_2\text{H})(\mu\text{-PPh}_2)\text{M}(\text{CO})_5]$ or, alternatively, from the reaction of $[\text{Nb}(\text{PPh}_2)(\text{PMe}_2\text{H})\text{Cp}_2]$ with $[\text{Cr}(\text{CO})_4(\text{nbd})]$ or $[\text{W}(\text{CO})_4(\text{pip})_2]$, show transmetalation of the PMe_2H ligand.³⁴ Tantalum(v) chloride is reduced in the presence of py to give $[\text{TaCl}_3(\text{py})_3]$ ³⁵ and undergoes reductive carbonylation in the presence of dppe to form $[\text{TaCl}(\text{CO})_2(\text{dppe})_2]_{2x}$ ($2x \geq 4$) and $[\text{TaCl}(\text{CO})_2(\text{dppe})_2]$ which can be further carbonylated to $[\text{TaCl}(\text{CO})_4(\text{dppe})]$.³⁶

The compound $[\text{TaMe}_3\text{Cl}(\eta^5\text{-tmpr})]$ is the precursor to a series of Ta^{V} complexes $[\text{TaMe}_3\text{X}(\eta^5\text{-tmpr})]$ ($\text{X} = \text{SR}$, Me , pyrrolyl or indolyl).³⁷ The tantalum(iv) amido complexes, $[\text{TaCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$, $[\text{Ta}(\text{NPh}_2)_2(\text{NEt}_2)_2]$ and $[\text{Ta}\{\text{N}(\text{SiMe}_3)_2\text{Ph}_2\}]$ can be formed under the appropriate reduction conditions from the tantalum(v) precursors, $[\text{Ta}(\text{NR}_2)_2\text{Cl}_3]$ ($\text{R} = \text{SiMe}_3$ or Et).³⁸ Treatment of $[\text{Ta}(\text{silox})_3]$ with the aryl amines, $\text{H}_2\text{NC}_6\text{H}_4\text{X}$, leads to N-H addition giving $[\text{TaH}(\text{NHC}_6\text{H}_4\text{X})(\text{silox})_3]$ and/or C-N activation to give $[\text{Ta}(\text{NH}_2)(\text{C}_6\text{H}_4\text{X})(\text{silox})_3]$.³⁹ The compound, $[\{\text{TaCl}(\text{NCy}_2)_2\}_2]$ is the first example of a tantalum(III) dimer containing a Ta-Ta bond unsupported by bridging ligands.⁴⁰ Structures have also been reported for $[\text{Nb}(\text{pyca})_4] \cdot 2\text{EtOH}$,⁴¹ $[\text{H}_2\text{dafone}][\text{Nb}^{\text{V}}\text{OCl}_4(\text{H}_2\text{O})]\text{Cl}$,⁴² and $[\text{Te}_6(\text{NbOCl}_4)_2]$, formed from reaction of NbOCl_3 with Te-TeCl_4 .⁴³

Schiff-base ligands

Schmidt *et al.*⁴⁴ have prepared some VO^{2+} compounds in order to investigate their catalytic role in sulfide oxidation of dmsO and PhSMe . The vanadyl compound, $[\text{VO}(\text{L})(\text{dmsO})]$, was formed with L derived from dmn and sal .⁴⁵ The binuclear Schiff-base complex $[\text{NEt}_4]_2[(\text{VO}_2)_2(\mu\text{-salod})]$ has been reported.⁴⁶

Asgedom and co-workers have reported on a large variety of alkoxo bound oxovanadium(v) complexes of the type $[\{\text{VOL}\}_2]$, $[\{\text{VO}(\text{HL})\}_2]$, $[\text{VOL}(\text{Hhqn})]$, $\text{K}[\text{VO}_2(\text{HL})]$, $\text{K}[\text{VO}_2(\text{H}_2\text{L})]$ and $[\text{VO}_2\text{L}(\text{salampr})]$ ($\text{L} = \text{Schiff-base ligand}$),⁴⁷ dioxovanadium(v) complexes of tridentate Schiff bases derived from sal and its derivatives and 8-aminoquinoline,⁴⁸ and some mixed-ligand Schiff base $\text{HL-H}_2\text{cat}$ complexes, $[\text{VOL}(\text{cat})]$.⁴⁹ Vanadyl complexes containing unsymmetrical bis(Schiff base) ligands derived from sal , ethylenediamine and Hacac and a *cis*- N_2O_2 co-ordinate chromophore give complexes of structure **1**.⁵⁰ The structures of $[\text{VO}(\text{L})(\text{OCH}_2\text{CH}_3)]$ ($\text{H}_2\text{L} = N\text{-benzoylacetone-}m\text{-bromobenzoylhydrazine}$)⁵¹ and a series of complexes of formula $[\text{VOL}_2]$ ⁵² have been reported.



3 Organometallics

The inorganic/organometallic chemistry of Group 5 $\text{HB}(3,5\text{-Me}_2\text{pz})_3$ complexes has received much attention^{53–58} including a review article.⁵⁹ Arene complexes of vanadium and niobium have also been reviewed.⁶⁰

Vanadium

The thermal behaviour of vanadocene has been investigated⁶¹ and a separate variable-temperature crystallography study⁶² has elucidated the nature of the Cp ring disorder. Reaction of $[\text{LnI}_2(\text{dme})_3]$ (Ln = Eu or Sm) with KCp and $\text{K}[\text{V}(\text{C}_{10}\text{H}_8)\text{Cp}]$ in dme followed by treatment with thf yields the tetradecker bimetallic complexes $[\{\text{Cp}^{\text{V}}(\mu\text{-C}_{10}\text{H}_8)\}_2\text{Ln}(\text{thf})(\text{dme})]$ which, upon removal of dme solvent and addition of thf, gives the co-ordination polymers, $[\{\text{VCp}(\mu\text{-C}_{10}\text{H}_8)\text{LnCp}(\text{thf})\}_n]$.⁶³

A facile method for the general preparation of the ring-alkylated vanadocenes, $[\text{V}(\eta\text{-C}_5\text{H}_4\text{R})_2]$, and the related species, $[\text{VCl}_n(\eta\text{-C}_5\text{H}_4\text{R})_2]$ (R = Me, Prⁱ or Bu^t; $n = 1$ or 2),⁶⁴ and several new 1,1'-ring-substituted vanadocene dichlorides prepared from VCl_4 and $\text{LiC}_5\text{H}_4\text{R}$ (R = CMe₃, SiMe₃ or SiEt₃), have been reported along with crystal data for $[\text{VCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ and $[\text{VCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$.⁶⁵

1,2-*N,N*-Dimethylaminomethylferrocenyl has been used as a ligand towards tantalum(IV) and vanadium(V).⁶⁶ The first early-transition-metal complexes containing σ -bonded fluoromethyl ligands, $[\text{V}\{\text{C}_6\text{H}_2(\text{CF}_3)_3\text{-2,4,6}\}_2\text{Cl}(\text{thf})]$ and $[\text{V}\{\text{C}_6\text{H}_2(\text{CF}_3)_3\text{-2,4,6}\}_3\text{OLi}(\text{thf})_3]$, have been isolated from the reaction of $[\text{VCl}_3(\text{thf})_3]$ with $\text{Li}[\text{C}_6\text{H}_2(\text{CF}_3)_3\text{-2,3,6}]$.⁶⁷ The arylborane π complexes, $[\text{V}(\eta^6\text{-C}_6\text{H}_5\text{BR}_2)_2]$ (R = OPrⁱ or mes) were prepared by metal-atom-ligand-vapour cocondensation, as well as by lithiation and subsequent appropriate reactions.⁶⁸ The crystal structure for $[\text{VMe}(\text{thf})\{\text{N}(\text{SiMe}_3)_2\}_2]$ has been reported.⁶⁹

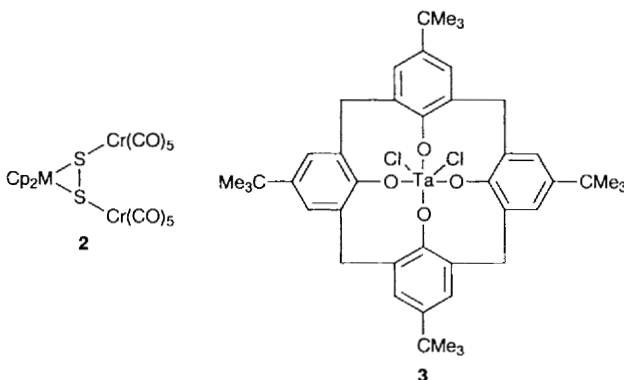
Niobium and tantalum

Visciglio *et al.*⁷⁰ have reported on the formation and reactivity of cyclohexa-1,3-diene aryloxide complexes of niobium and tantalum. The complex $[\text{NbH}_2(\text{BiPh}_2)\text{Cp}_2]$ is the first reported bismuthido-substituted niobocene.⁷¹ The complex $[\text{MCl}_4\text{Cp}^*]$ (M = Nb or Ta) reacts with LiCp^+ [$\text{Cp}^+ = \text{C}_5\text{H}_4(\text{SiMe}_3)$ or $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$] under reduction conditions to give the paramagnetic species $[\text{MCl}_2\text{Cp}^*\text{Cp}^+]$ which then react with PCl_5 to give $[\text{MCl}_3\text{Cp}^*\text{Cp}^+]$, with dry O_2 to give the diamagnetic species $[\{\text{TaCl}_2\text{Cp}^*\text{Cp}^*\}_2(\mu\text{-O})]$, with air to give the oxo derivatives $[\text{TaCl}(\text{O})\text{Cp}^*\text{Cp}^+]$, and with LiAlH_4 to give $[\text{MH}_3\text{Cp}^*\text{Cp}^+]$ which can go on to form $[\text{MH}(\text{L})\text{Cp}^*\text{Cp}^+]$ (L = CO, C_2H_4 or RNC).⁷² The complex $[\text{TaF}_4\text{Cp}^*]$ will react with AlMe_3 to give $[\text{TaMe}_4\text{Cp}^*]$ without further decomposition.⁷³ The complex $[\text{TaCl}_2\{\text{N}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\text{Cp}^*\}]$ reacts almost quantitatively with LiMe at -78°C to give $[\text{TaMe}_2(\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6})\text{Cp}^*]$ which reacts with CO and CNR to give various insertion products.⁷⁴

The compound $[\text{Ta}(\text{Me})(\text{PMe}_3)\text{Cp}_2]$ reacts with arylazides (RN_3) to give $[\text{Ta}(\text{Me})(\text{N}_3\text{R})\text{Cp}_2]$.⁷⁵ Reduction of $[\text{NbCl}_4(\eta\text{-C}_5\text{H}_4\text{R})]$ in the presence of phosphine ligands yields the 16-electron species $[\text{NbCl}_2\text{L}_2(\eta\text{-C}_5\text{H}_4\text{R})]$ (R = H or Me; $\text{L}_2 = 2\text{PEt}_3$ or dppe).⁷⁶ Some novel *ansa*-metallocene precursors containing metal-nitrogen triple bonds, $[\text{M}(\text{NR})(\text{NMe}_2)_3]$ (R = $\text{C}_6\text{H}_3\text{Pr}_1\text{-2,6}$; M = Nb or Ta),

have been prepared from reaction of $[M(NMe_2)_5]$ with RNH_2 .⁷⁷ The ansa-niobocene(IV) dichloride, $[NbCl_2\{\eta^5-C_5H_4SiMe_2\}]$, synthesised from $[NbCl_4(thf)_2]$ with $[Me_2Si(C_5H_4)_2]Ti_2$ in thf ,⁷⁸ can be reduced in the presence of alkyne to give $[NbCl(RCCR)\{\eta^5-C_5H_4SiMe_2\}]$ ($R = Me$ or Ph).

Reaction between $[Cr(CO)_5(thf)]$ and $[MH(S_2)Cp_2]$ ($M = Nb$ or Ta) leads to complex **2**.⁷⁹ Reduction of $[NbClL(\eta^5-C_5H_4SiMe_3)_2]$ ($L = CO, PMe_3$ or $CNBU^t$), gives rise to the electron-rich niobium(II) radicals, $[NbL(\eta^5-C_5H_4SiMe_3)_2]$, which react with elemental mercury to give the heterometallic adducts, $[Hg\{NbL(\eta^5-C_5H_4SiMe_3)_2\}_2]$, as a convenient source for niobium(II) radicals.⁸⁰



Nitrile insertion reactions and C–H activation of a cationic niobium alkyldiene complex have been reported⁸¹ as has intramolecular activation of aromatic C–H bonds, *via* cyclometallation in tantalum alkylidene complexes.⁸² The complex $[NbCl_2(NOBU^t)Cp]$ is the first example of the terminal metal-alkoxyimide system, $M:NOR$.⁸³ Aoyagi *et al.*⁸⁴ have prepared $[TaX_2\{\eta^4-C_6H_4(NSiPr^i)_2-o\}Cp^*]$ ($X = Cl$ or Me). Entry into the organometallic chemistry of Ta bonded to the *p*-*tert*-butylcalix[4]arene skeleton **3** was achieved using $[TaCl_2\{\text{calix}[4]OMe\}]$.⁸⁵ Addition of $Li_3[N_3N^*]$ $\{[N_3N^*] = [N(CH_2CH_2NSiEt_3)_3]^{3-}\}$ to $TaCl_5$ leads to $[TaCl_2(N_3N^*)]$ which reacts with Li/Grignard reagents to give $[TaMe_2(N_3N^*)]$ or $[Ta:CHR(N_3N^*)]$ ($R = Et, Pr^i, CH_2CHMe_2, SiMe_3$ or Ph) which in turn, undergo some interesting thermolysis chemistry.⁸⁶

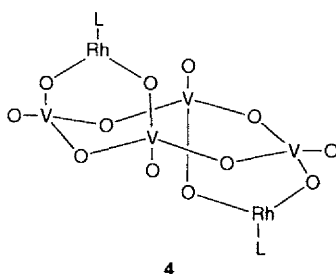
Crystal structures have been reported for $[Nb_2(\mu-1)_4(\eta^6-C_6H_3Me_3-1,3,5)_2]$,⁸⁷ the tribenzylidenemethane compound, $[TaMe_2\{\eta^4-C(C_6H_5)_3\}Cp]$,⁸⁸ zero-valent $[Nb(\eta^5-C_6H_5Me)_2]$,⁸⁹ $[Ta\{N(C_6H_4OCH_3-4)C(CH_3)=C(CH_3)N(C_6H_4OCH_3-4)\}Cl_2Cp^*]$,⁹⁰ the substituted niobocene formaldehyde complex, $[NbCl(\eta^2-CHO)(\eta^5-C_5H_4SiMe_3)_2]$,⁹¹ and the optically active diastereoisomers, $[Cp^tCpTa(CO)(\mu-PMe_2)W(CO)_4(pamp)]$ ($Cp^t = C_5H_2Bu^t-1-Me_2-3,4$).⁹²

4 Clusters and metalates

MO/LCAO calculations for bare niobium clusters (2–10 atoms) indicate a balance between s and d electrons with lowest total energies for highly co-ordinated structures

having a maximum of interatomic bonds. Investigation of CO adsorption shows a strong cluster site and size dependence with particularly low chemisorption energy for the Nb_{10} cluster.⁹³

The *closo*-nitride cubane, $[\{\text{V}(\mu_3\text{-N})\text{Cp}^*\}_4]$ has been reported.⁹⁴ Reckeweg and Meyer⁹⁵ have reported thiocyanate compounds of $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ from ASCN ($\text{A} = \text{K}$, Rb or NH_4) and $[\text{Nb}_6\text{Cl}_{12}]$ and the crystal structure for $\text{A}_4[\text{Nb}_6\text{Cl}_{12}(\text{NCS})]\cdot 4\text{H}_2\text{O}$. The metallocarbohedrene $[\text{Nb}_8\text{C}_2]^+$ reacts with water and alcohols to give $[\text{Nb}_8\text{C}_{12}(\text{OR})_4]^+$ ($\text{R} = \text{H}$, Me , Et or Bu^n) which reacts with NH_3 and CH_3X to give $[\text{NbC}_{12}(\text{NH}_3)_4]^+$ and $[\text{Nb}_8\text{C}_{12}\text{X}_n]^+$ ($n = 4$, $\text{X} = \text{Cl}$; $n = 5$, $\text{X} = \text{Br}$, I) respectively.⁹⁶



The layered mixed-valence $\text{V}^{\text{IV}}\text{-V}^{\text{V}}$ oxides incorporating interlamellar organic cations, α -, β - $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3][\text{V}_4\text{O}_{10}]$ and α -, β - $[\text{H}_2\text{N}(\text{C}_2\text{H}_4)_2\text{NH}_2][\text{V}_4\text{O}_{10}]$, were prepared under hydrothermal conditions.⁹⁷ The vanadate-supported organorhodium complex, $[\{(\eta^4\text{-C}_6\text{H}_{10})\text{Rh}\}_2(\text{V}_4\text{O}_{12})]^{2-}$ **4** has been reported.⁹⁸ The polyoxometalates, $[\text{MW}_5\text{O}_{19}]^{n-}$ and $[(\text{MeO})\text{MW}_5\text{O}_{18}]^{(n-1)-}$ ($\text{M} = \text{V}$, Nb or Ta), have been prepared;⁹⁹ some three-co-ordinate vanadium(III,V) chalcogenates¹⁰⁰ and a new series of niobium oxychlorides, $\text{M}_2\text{ANb}_6\text{Cl}_{17}\text{O}$ (M = monovalent cation, A = rare-earth element)¹⁰¹ have been reported.

Crystal structures have been determined for the $\text{V}^{\text{IV}}\text{-V}^{\text{V}}$ mixed valence compound, $[\text{V}_4\text{O}_4(\mu\text{-OEt})_2(\mu\text{-O})_2(\text{OEt})_4(\text{phen})_2]$,¹⁰² $\text{A}_7[\text{MAS}_4]$ ($\text{A} = \text{K}$ or Rb ; $\text{M} = \text{Nb}$ or Ta),¹⁰³ $[\text{Al}(\text{NCMe})_6][\text{MCl}_6]_3\cdot 3\text{MeCN}$ ($\text{M} = \text{Nb}$ or Ta),¹⁰⁴ $\text{Na}_8\text{H}_{18}[\{\text{Er}_3\text{O}(\text{OH})_3(\text{H}_2\text{O})_3\}_2\text{Al}_2(\text{Nb}_6\text{O}_{19})_5]\cdot 40.5\text{H}_2\text{O}$,¹⁰⁵ $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{V}_4\text{O}_{10}]$,¹⁰⁶ $\text{A}_6[\text{Nb}_4\text{S}_{22}]$ ($\text{A} = \text{Rb}$ or Cs),¹⁰⁷ the octadecachlorohexaniobate clusters, $\text{Rb}_2\text{Cu}_2[\text{Nb}_6\text{Cl}_{18}]$,¹⁰⁸ isotypic with $\text{Tl}_2\text{Cu}_4[\text{Nb}_6\text{Cl}_{18}]$ and $\text{In}_2\text{Li}_2[\text{Nb}_6\text{Cl}_{18}]$, and $\text{Rb}_4[\text{Nb}_6\text{Cl}_{18}]$.¹⁰⁹

5 Catalysis

Heterogeneous

The preparation of vanadium phosphate (VPO) catalysts¹¹⁰ as well as V_2O_5 -based catalysts¹¹¹ prepared in flames has been reviewed. In reviewing the kinetics for the selective oxidation of ethane to ethylene and acetaldehyde over silica-supported V_2O_5 , Erdohelyi¹¹² found that selectivity and activity strongly depend upon the mode of preparation. Centi¹¹³ has reviewed the structure and properties of vanadium oxide supported on titania in relation to selective oxidation and ammoxidation of alkyl aromatics. The ideal structure, real structure and stability region for VPO catalysts

have been examined¹¹⁴ as have titania-supported¹¹⁵ and silica-supported¹¹⁶ VPO. Wachs *et al.*¹¹⁷ have reviewed the redox properties of niobium oxide catalysts.

The role of ammonium ions during toluene ammoxidation on α -[NH₄]₂-[(VO)₃(P₂O₇)₂] catalyst¹¹⁸ and the acid–base character of supported vanadium oxide catalysts for oxidative dehydrogenation of alkanes have also been investigated.¹¹⁹ Vanadium–alumino–phosphate (VAPO) and vanadium–silico–alumino–phosphate (VSAPO) catalysts are effective for oxidation and ammoxidation of toluene and benzyl alcohol.¹²⁰ Hydropyranone derivatives were formed from the polymer-anchored vanadium(V)-catalysed epoxycyclisation of hydroxymethylfurans with 70% *tert*-butyl hydroperoxide under ambient conditions.¹²¹ Barium based BaCO₃–Ba₃(VO)₂ catalysts for the oxidative coupling of methane have proved to be very active for production of ethane and ethylene.¹²²

A solid solution of niobium phosphate and vanadyl pyrophosphate reduced with benzyl alcohol (VNbPO catalysts) is highly active for the oxidation of butane to maleic anhydride.¹²³ The compound [Ta(CH₂CMe₃)₃(CHCMe₃)] treated with SiO₂ (dehydroxylated at 500 °C) and with H₂ (200 °C) leads to silica-supported tantalum(III) monohydride complexes effective in the formation of monoalkyls *via* C–H bond activation of the corresponding cycloalkanes (C₅–C₈).¹²⁴

Homogeneous

Vanadium oxidative polymerisation catalysts have been reviewed¹²⁵ and Bjar-nason¹²⁶ has reported on V⁺ as a catalyst effective for polymerisation of naphthalene halides in the gas phase *via* loss of V⁺ or VX from [V(C₁₀H₆)_n]⁺ or [V(C₁₀H₆)_nX]⁺. A mixture of [VCl₂(tmeda)₂] and O₂ was used to promote coupling of propiophenone to give 3,4-dimethyl-3,4-diphenylhexane.¹²⁷ The salt [V₂Cl₃(thf)₆]₂[Zn₂Cl₆] catalyses the formation of 1,4-diamino-2,3,5,6-tetrahydroxycyclohexane from L-serine methyl ester hydrochloride *via* homo-coupling of aminobutyldimethylsiloxypyranol.¹²⁸ The total synthesis of (+)-eurylene was effected using the double vanadium-catalysed oxidation reaction of different bis(homoallyl alcohol) systems.¹²⁹ Hydrazine is catalytically reduced to ammonia, acetylene to ethylene, and cyanide to ammonia/methane by single cubane-like clusters that contain a [VFe₃S₄]ⁿ⁺ core¹³⁰ which is relevant to the function of nitrogenase. Mono- and bis-Cp derivatives of vanadium are active for the polymerisation of 1,3-dienes.¹³¹

The hydrolysis of acetonitrile to ammonium ion in the presence of NbCl₅ has been examined as a catalysis *versus* Pinner synthesis mechanism.¹³² The Lewis acidity of Nb and Ta with respect to Diels–Alder reactions has been investigated.¹³³ Catalysis by niobic acid for the benzylation of toluene and anisole by benzyl alcohol is optimised by catalyst pretreatment with phosphoric acid¹³⁴ and/or heating at 573 K.¹³⁵ The novel homologation reaction for α -trialkylstannylmethyl- β -keto esters to give the corresponding γ -keto esters is mediated by NbCl₅, possibly *via* a cyclopropanol complex intermediate.¹³⁶ The *cis*-iso-specific ring-opening metathesis polymerisation of norbornenes using [Ta(CH₂Ph)₂(η^4 -C₄H₆)Cp*] whose crystal structure and benzyldiene derivative, [Ta(CHPh)(PMe₃)(η^4 -C₄H₆)Cp*] formed by thermolysis in the presence of PMe₃, are also reported.¹³⁷

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