



Vanadium 1996

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1. Introduction

This annual review attempts to summarise recent developments made within the coordination chemistry of vanadium and published during 1996. It was compiled with the help of the on-line searching facilities of the University of Bath (Bids).

The material is arranged, as is customary, in order of decreasing oxidation state and a final section details some of the recent solid-state chemistry of vanadium. Within each of the sections the information is organised roughly according to structural type of the vanadium complex described. This review deals only with the coordination chemistry of vanadium. The organometallic chemistry of the element is described in a separate review [1].

2. Reviews

The coordination chemistry of vanadium published during 1995 has been reviewed in this journal [2]. A comprehensive and systematic review of the syntheses, structures and reactivities of thiolate complexes of the Group 5 transition elements has been published. It includes a discussion on mono- and polymetallic species as well as recent advances in heterodimetallic derivatives [3].

A review has been made of the structure and bonding in transition metal tetrahydroborate complexes, including certain five and six-coordinate V complexes, for example $(\text{dmpe})_2\text{V}(\eta\text{-BH}_4)_2$ complexes with cyclopentadienyl rings, and bridging V_2 complexes [4].

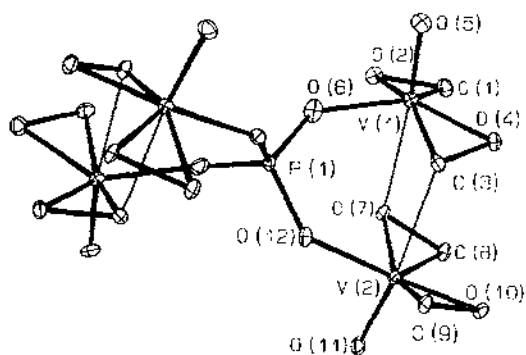
Structural data, nomenclature, synthetic routes and spectral properties of known aza-analogues of phthalocyanine complexes, including those of VO, have been summarised [5].

3. Vanadium(V)

3.1. Complexes having V–O units

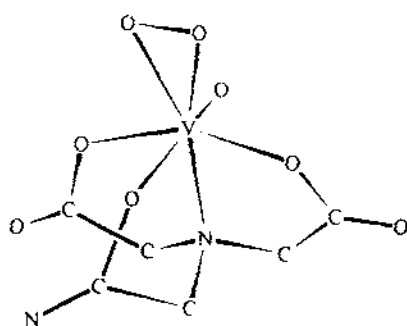
Synthesis of the first tetranuclear vanadium(V) peroxo complex, $\text{K}_7[\text{V}_4\text{O}_4(\text{O}_2)_8(\text{PO}_4)] \cdot 9\text{H}_2\text{O}$, has been reported and its structure determined. The peroxo complex was obtained from the $\text{KVO}_3\text{-KH}_2\text{PO}_4\text{-KOH-H}_2\text{O}_2\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ system. The structure (**1**) was found to consist of two dinuclear $[\text{V}_2\text{O}_2(\text{O}_2)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-O}_2)_2]$ units connected by a $\mu_4\text{-PO}_4$ group. The two bridging $(\mu\text{-}\eta^1\text{:}\eta^2\text{-O}_2)$ units show a similar geometry to those in the related $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{PO}_4)]^{5-}$ reported last year [6].

The synthesis, properties and crystal structure of the vanadium(V) monoperoxo-ada complex, $\text{K}[\text{VO}(\text{O}_2)\text{ada}] \cdot 4\text{H}_2\text{O}$, have been reported. The complex is thought to be the first known structure with a coordinated dianion of the biological buffer *N*-(carbamoylmethyl)iminodiacetic acid (ada). In the structure (**2**), the vanadium atom is seven-coordinate, being ligated by oxo, η^2 -peroxo and tetradentate ada^{2-}



(1)

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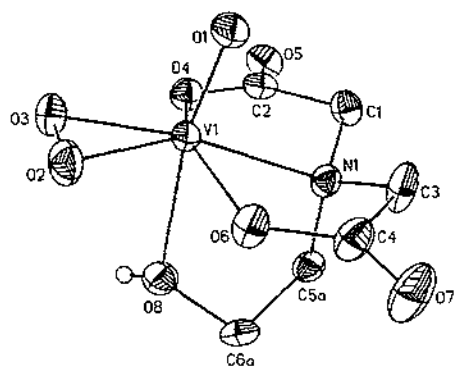


(2)

-N , O^1 , O^2 and O^3 ligands. The oxygen of the carbamoyl group is in the apical position *trans* to the $\text{V}=\text{O}$ group. The complexes $\text{Cs}[\text{VO}(\text{O}_2)\text{ada}]\cdot\text{H}_2\text{O}$ and $\text{Ba}[\text{VO}(\text{O}_2)\text{ada}]\cdot 3\text{H}_2\text{O}$ were also isolated from aqueous solution [7].

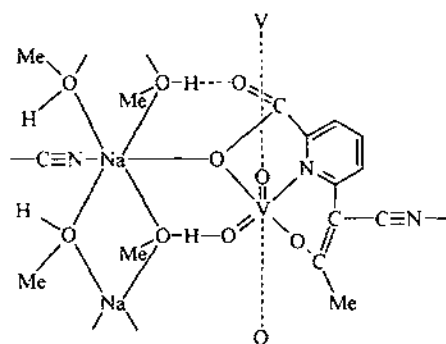
A series of oxoperoxovanadium(V) complexes with the ligands H_3nta , H_3heida (*N*-(2-hydroxyethyl)iminodiacetic acid), H_2ada (*N*-(2-amidomethyl)iminodiacetic acid), Hbpg (*N,N*-bis(2-pyridylmethyl)glycine) and tpa (*N,N,N*-tris(2-pyridylmethyl)amine) have been characterised as functional models for the vanadium haloperoxidase enzymes. The crystal structures of the $\text{K}[\text{VO}(\text{O}_2)\text{Hheida}]$ (3), $\text{K}[\text{VO}(\text{O}_2)\text{ada}]$, $[\text{VO}(\text{O}_2)\text{bpg}]$ and $\text{H}[\text{VO}(\text{O}_2)\text{bpg}]_2(\text{ClO}_4)$ complexes were determined and were all found to possess a distorted pentagonal bipyramidal coordination sphere containing a side-on bound peroxide. The kinetics of halide oxidation reactions were studied, in which the complexes act as catalysts [8].

A two-dimensional network (4) consisting of interlinked cationic $\text{Na}(\mu\text{-MeOH})_2$ and anionic $(\mu\text{-O})=\text{VL}(\text{O})\dots$ chains is formed by the reaction between VO^{2+} and



(3)

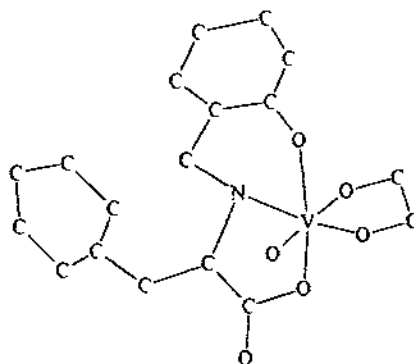
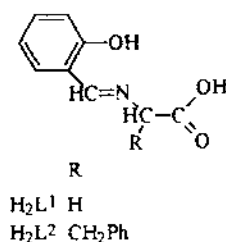
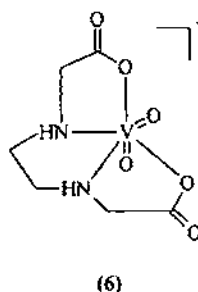
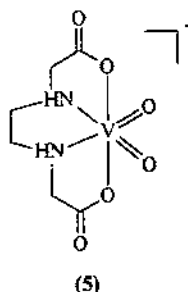
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(4)

Na^+ in methanol in the presence of the compound 6-(1-cyano-2-hydroxyprop-1-enyl)pyridine-2-carboxylic acid (H_2L) [9].

The solution properties of two isomeric forms of the V-EDDA (H_2EDDA = ethylenediamine- N,N' -diacetic acid) complex (**5**) have been studied using multinuclear NMR spectroscopy. The results were consistent with the interpretation that solvation is the major contributor to isomer stability. The solid-state structure of the β -*cis* isomer of $\text{NH}_4[\text{VO}_2(\text{EDDA})]$ (**6**) confirmed this finding [10].



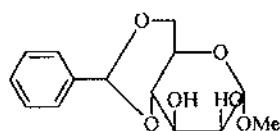
(7)

Mononuclear oxovanadium(V) alkoxides of the type $[\text{VO}(\text{L})(\text{Hed})]$ (H_2L^1 = *N*-salicylidene-glycine, H_2L^2 = *N*-salicylidene-*L*-phenylalanine) have been obtained by oxidation of the V(IV) complexes $[\text{VO}(\text{L})(\text{H}_2\text{O})]$ with ethane-1,2-diol (H_2ed) in methanol in the presence of air. To prevent alkoxide bridging, with the resultant formation of dimeric complexes, all but two of the coordination positions on the V(IV) were blocked, leaving just two positions for possible diol ligation. The crystal structure of $[\text{VO}(\text{L}^2)(\text{Hed})]$ (**7**) showed it to possess tridentate $[\text{L}^2]^{2-}$ and didentate Hed^- with the alkoxide and alcoholic oxygen atoms lying *trans* to the azomethine nitrogen and oxo oxygen respectively [11].

3.2. Complexes containing the vanadate(V) ion

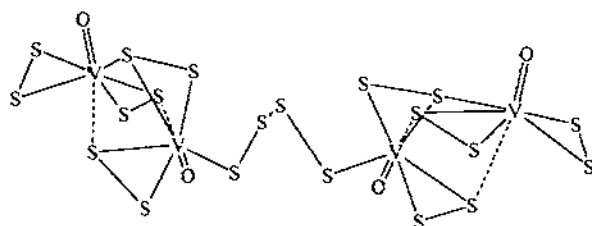
The structures of the reaction products obtained from vanadate or chlorovanadate reactions with 1,2- or 1,3-diols have been found to be very highly sensitive to the geometry and substituent groups of these diols. Ab initio and electrostatic potential distribution calculations have been conducted on both experimental and optimised geometries of the four- and five-coordinate oxovanadium(V) alkoxides with ethylene glycol and pinacol. Ab initio calculations showed that the five-coordinate species were favoured for all ligands at all levels of theory investigated [12].

In an attempt to understand the relationship between the mode of vanadate esterification and the number and configurations of free hydroxyl groups in carbohydrate residues in biological molecules, certain hydroxyl groups of some monosaccharides were blocked and their esterification reactions with vanadates studied in an acetonitrile medium. The reaction between $[\text{N}^n\text{Bu}_4][\text{H}_2\text{VO}_4]$ and methyl *O*-4,6-benzylidene- α -D-mannopyranoside (H_2L^1) (8) yielded $[\text{N}^n\text{Bu}_4]_2[(\text{VO}_2\text{L}_1)_2]$. The anion was found to consist of a dinuclear $\text{V}_2(\mu\text{-O})_2$ centre and two deprotonated H_2L^1 molecules. Each vanadium atom is bound to the deprotonated vicinal *cis*-diol of one mannopyranoside ring resulting in a five-membered ring complex. The geometry of the two vanadium atoms was found to be intermediate between square pyramidal and trigonal bipyramidal [13].



H_2L^1

(8)

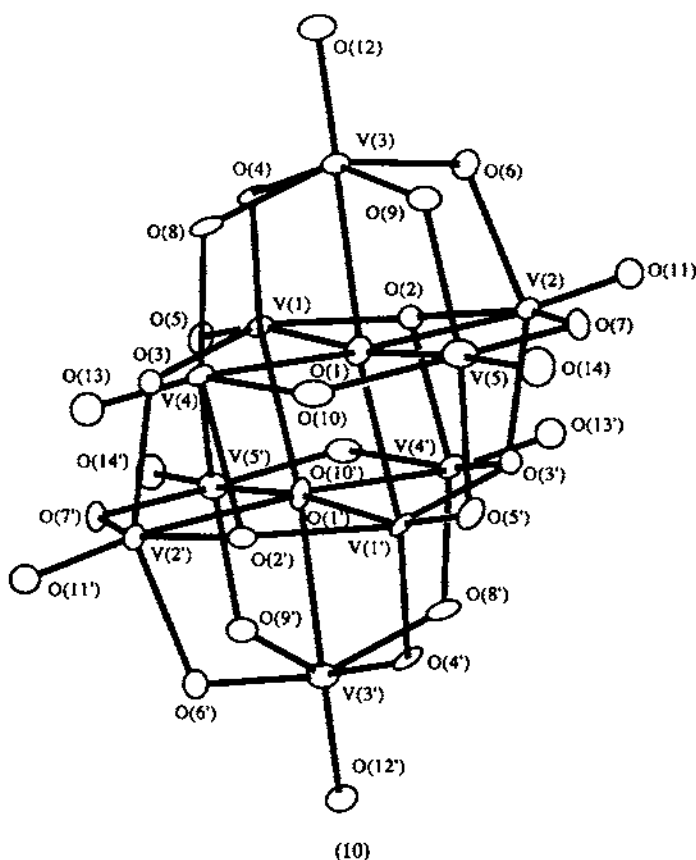


(9)

The preparation and characterisation of a sulfur rich tetranuclear complex which contains the anion $[\text{V}_4\text{S}_{20}\text{O}_4]^{6-}$ has been reported. The complex, whose structure can be written more meaningfully as $[\text{NH}_4]_6[\{\text{V}(\text{O})(\text{S}_2)_2\}_2(\mu^2\text{-S}_4)\{\text{V}(\text{O})(\text{S}_2)_2\}_2] \cdot 5\text{bpy} \cdot 7\text{H}_2\text{O}$ (9), was obtained from the reaction between solid $\text{NH}_4[\text{VO}_3]$ with an aqueous solution of ammonium polysulfides in the presence of bpy. The structure can be seen to consist of a chain of two $[\text{V}_2\text{S}_8\text{O}_2]^{2-}$ subunits connected to each

other by a zigzag S_4^{2-} tetrasulfide bridge. Each subunit contains two vanadium(V) ions in an approximately pentagonal bipyramidal environment [14].

Addition of a small amount of acetic acid to tetrabutylammonium vanadate, $(n\text{-C}_4\text{H}_9)_4\text{NVO}_3$, initiated self-condensation with the formation of the decavanadate species $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{H}_4\text{V}_{10}\text{O}_{28}]$ (10), whose structure was determined and shown to contain discrete $\text{H}_4\text{V}_{10}\text{O}_{28}^{2-}$ polyanions each of which contain 10 VO_6 distorted octahedra-sharing edges [15].

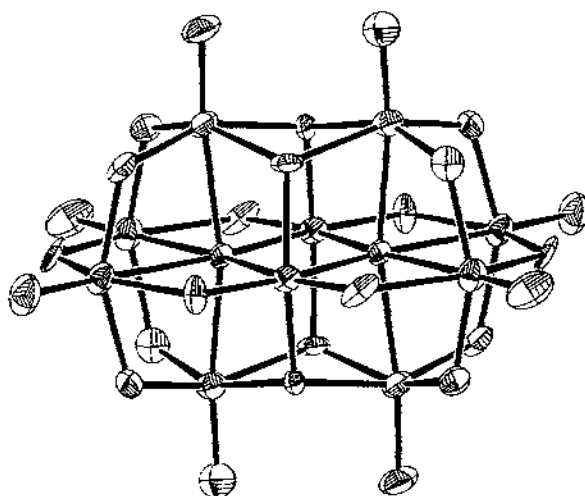


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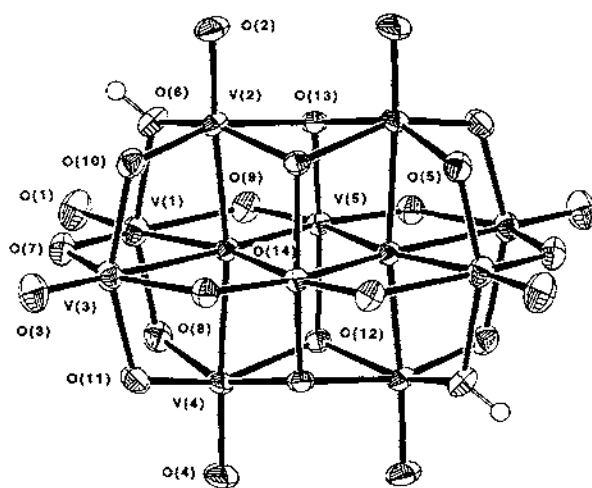
Two tert-butylammonium decavanadates, $[(\text{CH}_3)_3\text{CNH}_3]_6[\text{V}_{10}\text{O}_{28}] \cdot 8\text{H}_2\text{O}$ (11) and $[(\text{CH}_3)_3\text{CNH}_3]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ (12), have been synthesised to investigate the influence of protonation on both their crystal structures and thermal behaviour. The crystal structure of (11) was found to be stabilised by electrostatic forces and an extensive network of hydrogen contacts involving anions, cations and water molecules. The anions and cations are arranged in layers perpendicular to the $[010]$ axis. In (12) each dihydrogen decavanadate anion is joined to three adjacent polyanions

by means of O(6)–H...O(4) hydrogen contacts forming layers parallel to the (101) plane. The hydrophobic groups of the cations are arranged in layers parallel to the anionic sheets. Decomposition of (12) starts to occur around 200 °C whereas (11) loses water of crystallisation at 70 °C [16].

The equilibria depicted in Eq. (1) have been investigated. Linear tri- and tetravana-



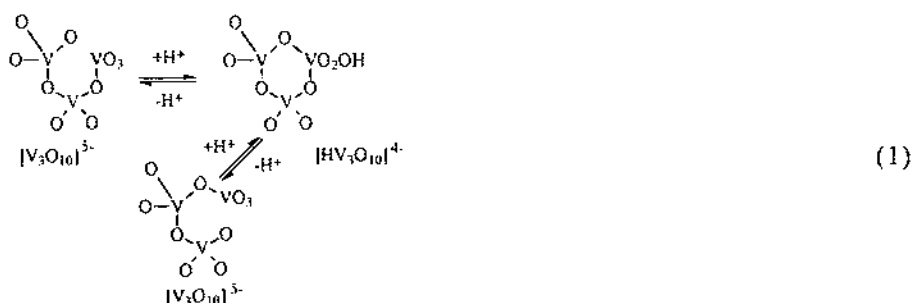
(11)



(12)

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date anions in aqueous solution have been shown to undergo an intramolecular exchange process involving a long-lived intermediate [17].



A series of aqueous tungstovanadates has been studied quantitatively under equilibrium conditions by a combination of potentiometry and ^{51}V , ^{183}W and ^{17}O NMR spectroscopy. Equilibrium constants were obtained and 11 species identified including $[\text{WV}_9\text{O}_{28}]^{5-}$, $[\text{H}_2\text{W}_{11}\text{VO}_{40}]^{7-}$ and *trans*- $[\text{W}_4\text{V}_2\text{O}_{19}]^{4-}$ [18].

β -Isomers of A-type vanadium-trisubstituted nonatungstophosphate anion salts were synthesised by a condensation reaction of NaVO_3 and $\text{A-Na}_9[\text{PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ in an aqueous HCl and 1,4-dioxane mixed solution. Their geometries were characterised by IR, ^{31}P , ^{51}V and ^{183}W NMR spectroscopies. The kinetics of the isomerisation of $\beta\text{-(N}^t\text{Bu}_4)_4\text{H}_2[\text{PV}_3\text{W}_9\text{O}_{40}]$ to the corresponding α -isomer both in the solid state and in solution was followed by FT-IR and ^{31}P NMR spectroscopies [19].

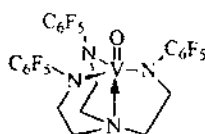
Solutions of $[\text{HVO}_4]^{2-}$ and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ were shown by ^{51}V and ^{17}O NMR spectroscopy to combine to form the anions $[\text{H}_2\text{VSiO}_7]^{3-}$ and $[\text{H}_3\text{VSiO}_7]^{2-}$ and various related monovanadooligosilicate species. Approximate equilibrium constants were derived for the reactions [20].

The interactions of vanadate and its complexes of uridine, 5,6-dihydrouridine and methyl- β -D-ribofuranoside with bovine pancreatic ribonuclease A (RNase A) have been studied by ^{51}V NMR and enzyme kinetics. From kinetics it was established that neither inorganic vanadate nor the methyl- β -D-ribofuranoside complex significantly inhibited the RNase A catalysed hydrolysis of uridine 2',3'-cyclicmonophosphate [21].

3.3. Oxovanadium(V) Schiff base complexes

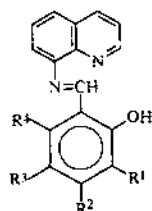
The dinuclear vanadium(V) complex $[\text{V}_2\text{O}_3(\text{sal-L-val})_2(\text{H}_2\text{O})]$ (sal-L-val = *N*-salicylidene-L-valinate) has been prepared and characterised and its crystal structure determined. The complex was found to have a double bridge in which the two VO groups make an angle of almost 90° . The V atoms are in distorted octahedral geometries and there are two similar but independent molecules in the asymmetric unit. The spectroscopic properties (ESR, UV and CD) of related complexes $[\text{VO}(\text{sal-L-aa})(\text{H}_2\text{O})]$ and $[\text{VO}(\text{sal-L-aa})(\text{bpy})]$ (sal-L-aa = *N*-salicylidene-L-amino acidate) were studied [22].

The complex $[N_3N]V=O$ ($[N_3N]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) (13) has been prepared by treatment of $VOCl_3$ with $H_3[N_3N]$ in CH_2Cl_2 in the presence of Et_3N . Related non-oxo arylimido complexes $[N_3N]V=NAr$ ($Ar = p\text{-MeC}_6\text{H}_4$, $p\text{-CF}_3\text{C}_6\text{H}_4$ or $p\text{-FC}_6\text{H}_4$) were prepared from the known $V(NAr)Cl_3(thf)$ complexes or from $[N_3N]V=O$ by treatment with an aryl isocyanate. Reactions between $VCl_3(thf)_3$ and $H_3[N_3N]$ in the presence of triethylamine gave $[HNEt_3]\{[N_3N]VCl\}$ in ether and $[N_3N]V(CH_3CN)$ in acetonitrile [23].



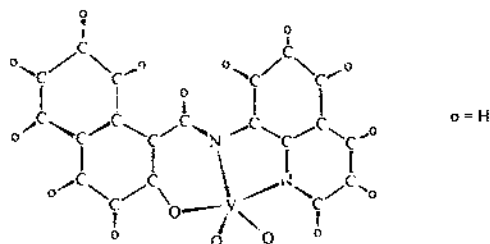
(13)

Several Schiff base complexes having the VO^{3+} unit have been synthesised and characterised by X-ray crystallography. A series of five mononuclear *cis*-dioxovanadium(V) complexes of tridentate Schiff bases derived from salicylaldehyde and its derivatives and 8-aminoquinoline (HL^1 – HL^5) have been prepared and characterised. The structures of the complexes $[VO_2L^1]$ and $[VO_2L^2]$ [L^1 and L^2 are the Schiff base anions (14) and (15)] were shown to contain *cis*-oxo groups in the equatorial plane and to possess trigonal bipyramidal geometry about the V atom. It was proposed that the rigidity and tridentate nature of the ligand favour a trigonal bipyramidal arrangement and intermolecular hydrogen bonding reduces the possibility of dimerization [24]. When the reactions with the above Schiff bases were carried out in the presence of a dibasic didentate ligand such as catechol, *p*-tertbutylcatechol or pyrogallol, six-coordinate complexes with a VN_2O_4 core were obtained. The stability of the complexes and conversion to pentacoordinated VO_2^+ species with the loss of catecholate ligand in DMSO was demonstrated by UV absorption, ^{51}V NMR and electrochemical studies [25].



	R ¹	R ²	R ³	R ⁴
HL ¹	H	H	H	H
HL ²	H	H	C ₆ H ₄	
HL ³	OMe	H	H	H
HL ⁴	H	H	Br	H
HL ⁵	H	H	OH	H

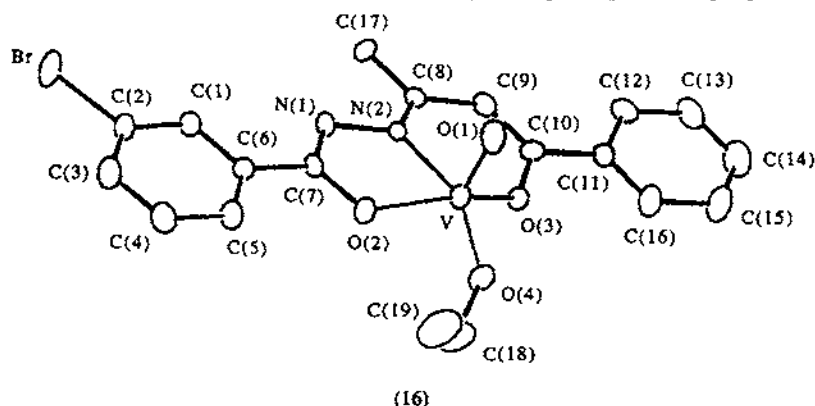
(14)



(15)

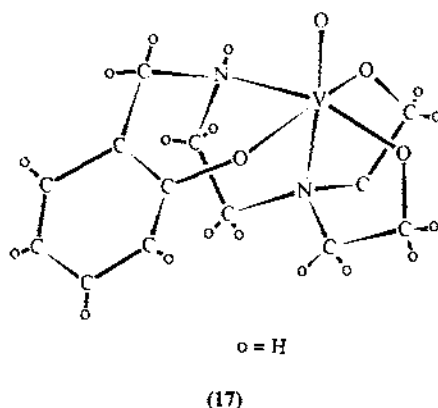
The more usual square pyramidal geometry was found in the dinuclear *cis*-dioxo vanadium(V) Schiff base complex, $[Et_4N]_2[(VO_2)_2SAL-OD]$ (SAL = salicylaldehyde; OD = oxalhydrazide) prepared by reaction of Et_4NVO_3 and $SAL-OD$. The *cis*-dioxo groups and ON groups of the ligand form the basal plane with the second

ligating O atom at the apex of the pyramid [26]. The same group have prepared $[\text{VO}(\text{L})(\text{OCH}_2\text{CH}_3)]$ (16) from the tridentate Schiff base ligand H_2L ($\text{H}_2\text{L} = N$ -benzoylacetone-*m*-bromobenzoylhydrazone) and $(n\text{-C}_4\text{H}_9)_4\text{NVO}_3$ in the presence of acetic acid. A similar square pyramidal environment was found for the V atom with the terminal oxo group occupying the apical position [27].



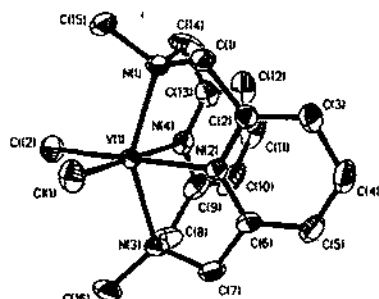
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A VO^{3+} complex with a pentadentate trivalent amine alcohol ligand (hebab) has been prepared and characterised (17). The ligand was obtained by reduction of the Schiff base precursor *N*-salicylidene-2-(bis(2-hydroxy-methyl)amino)ethylamine. The V(V) centre is in a distorted octahedral environment with the terminal oxo group in the *trans* position to the tertiary amine nitrogen. The behaviour of the complex upon methanolysis and hydrolysis was studied by ^{51}V NMR and the complex is considered as a possible model for vanadium dependent haloperoxidases [28].

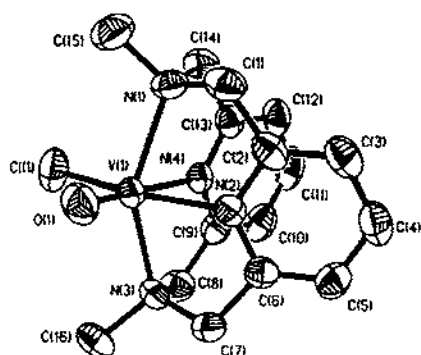


A series of three complexes containing V(III), (IV) and (V) has been prepared and each of the complexes structurally characterised. In all three complexes,

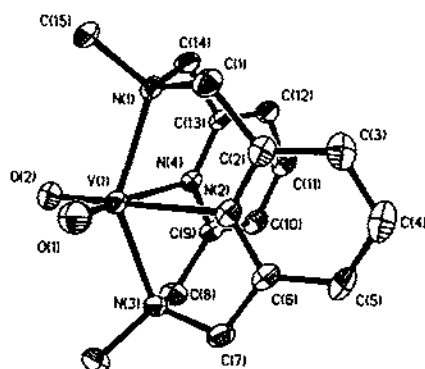
namely $[(L-N_4Me_2)V^{III}Cl_2](BPh_4)$ (**18**), $[(L-N_4Me_2)V^{IV}ClO](ClO_4)$ (**19**), and $[(L-N_4Me_2)V^{VO}_2](BPh_4)$ (**20**), the vanadium atom has a distorted *cis*-octahedral coordination geometry (L is the tetradentate ligand *N,N'*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane). The *cis*-coordination sites are occupied by either the terminal chloro or oxo ligands. Somewhat surprisingly, replacement of the Cl groups by O, with simultaneous increase in oxidation state through from III to V, does not result in a change in the coordination geometry about the vanadium atom [29].



(18)



(19)



(20)

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Vanadium bromoperoxidase isolated from marine algae has been shown to catalyse the oxidation of pseudohalide thiocyanate by hydrogen peroxide. Studies, followed by ^{13}C NMR spectroscopy, on the oxidation of $KS^{13}CN$ by H_2O_2 catalysed by V-BrPO show the formation of several oxidised thiocyanate species, as observed in natural product and biogenesis investigations [30].

3.4. Non-oxo vanadium(V) complexes

Photolysis of an octahedral monoazido complex $[LV^{III}(\text{acac})(N_3)]X$ in the solid state or in solution has been found to yield the corresponding six-coordinate nitrido complexes $[LV^V(\text{acac})(N)]X$ and one equivalent of dinitrogen (L represents the macrocycle 1,4,7-triazacyclononane) [31].

The molecules VF_5 , VMe_5 and VH_5 have been included in a study of the topology of the electron density and its Laplacian in an attempt to understand the structures of molecules which do not conform to the VSEPR model. Although VF_5 has the VSEPR predicted trigonal bipyramidal geometry, with longer axial than equatorial bonds, both VH_5 and VMe_5 have square pyramidal arrangements about the vanadium atom. This is found to be the norm for ligands which are predominantly covalently bonded. The paper attempts to rationalise the geometries of non-VSEPR species in terms of core distribution with non-spherical central atoms [32].

4. Mixed-valence vanadium(V) and vanadium(IV) complexes

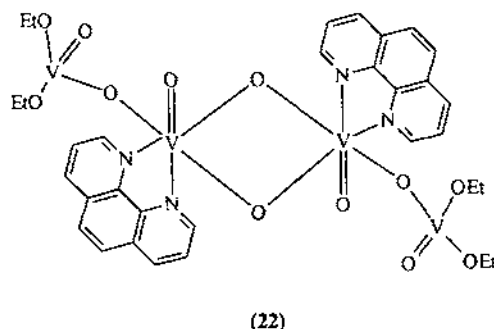
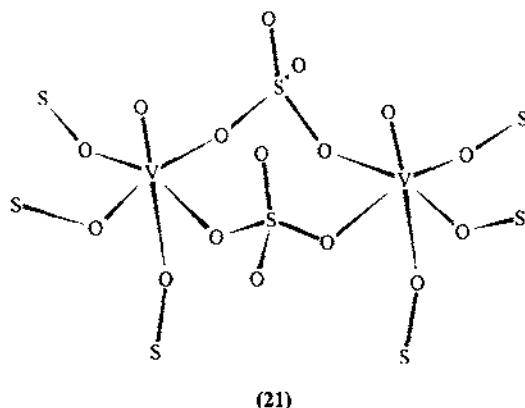
4.1. Redox chemistry

The ligand 1,2-dimethyl-3-hydroxy-4(1H)-pyridinone (HL) is able to displace oxo groups on both V^V and V^{IV} and has been shown to form a wide range of oxo, hydroxy and non-oxo complexes with V^V and V^{IV} in aqueous solution. The complex $[V^{IV}L_3]^+$ is stable towards hydrolysis in aqueous solution and its formation has been studied spectrophotometrically and was found to be favoured only in a narrow acidic pH range. The V^V complex $[V^V(OH)L_3]^+$ was formed by aerial oxidation of the oxovanadium(IV) complexes and is the first such species to be reported. The neutral bis complex $[V^V(O)(OH)L_2]$ is of physiological significance in the treatment of diabetes [33].

A study of the vanadium–maltol system (V–MaH) ($MaH = C_6H_6O_3$) has been carried out in 0.150 M NaCl using NMR, ESR and potentiometric techniques. A pH-, concentration- and time-dependent spontaneous reduction was found to occur from V^V to V^{IV} [34].

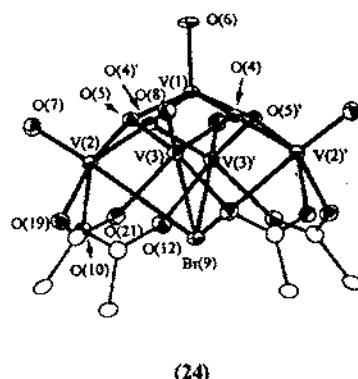
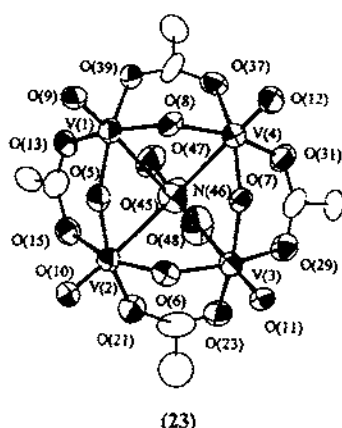
4.2. Structural chemistry

The catalytically important molten salt gas system $M_2S_2O_7$ – V_2O_5 / SO_2 – O_2 – SO_3 – N_2 ($M = Na, K$ or Cs) has yielded pleochroistic (dark green to colourless) crystals of a mixed-valence V^{IV} – V^V compound, $K_6(VO)_4(SO_4)_8$ (**21**). An X-ray investigation showed that the molecule consists of two similar V^{IV} – V^V pairs of distorted VO_6 octahedra. The bond lengths of the V^VO_6 octahedra were found to be significantly shorter than those of the $V^{IV}O_6$ octahedra. The compound is being considered as a possible cause of catalytic deactivation in the system used for the industrial production of sulfuric acid [35].



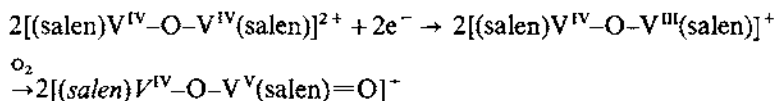
A mixed-valence tetranuclear $V^{IV,V}$ complex $[V_4O_4(\mu-OEt)_2-(\mu-O)_2(OEt)_4(phen)_2]$ (**22**) has been prepared by the reaction of $[VCl_3(thf)_3]$ with phen and NaSPh in thf/EtOH. The crystal structure of (**22**) showed it to consist of independent molecules each containing four mixed-valent vanadium ions in an approximately linear tetranuclear arrangement and bridged by μ -alkoxo and μ -oxo groups [36].

A tetranuclear $V^{IV,V}$ complex, $[V_4O_8(NO_3)(tca)_4]^{2-}$ (**23**), containing a square V_4 unit has been prepared from the reaction between $(NEt_4)_2[VOC_4]$ with $AgNO_3$ and thiophene-2-carboxylate (tca) in MeCN. Structural parameters indicate four equivalent V centres suggesting an electronically delocalised system. Pentanuclear $V^{IV,V}$ carboxylate complexes, $[V_5O_9X(O_2CPh)_4]^{2-}$ ($X=Cl, Br$) (**24**), were obtained from $(NBzEt_3)_2[VOC_4]$ with NaO_2CPh and atmospheric H_2O/O_2 in MeCN. The anions of these complexes consist of a V_5 square pyramid with each vertical face bridged by a μ_3-O^{2-} ion, the basal face bridged by a μ_4-X^- ($X=Cl, Br$) ion and a terminal multiply bonded O^{2-} ion at each metal. The apical and basal metal ions have oxidation states of V and IV respectively and no delocalisation seems present in these complexes [37].



(Reproduced from ref. [37] with permission.)

Electroreduction of a vanadium dinuclear complex $[(\text{salen})\text{V}^{\text{IV}}-\text{O}-\text{V}^{\text{IV}}(\text{salen})]^{2+}$ in the presence of O_2 resulted in the eventual formation of a $[(\text{salen})\text{V}^{\text{IV}}-\text{O}-\text{V}^{\text{V}}(\text{salen})=\text{O}]^+$ complex according to Eq. (2) [38]. This reaction, and similar electroreductions, are discussed in more detail in Section 6.



5. Vanadium(IV)

5.1. Species having vanadium–halogen bonds

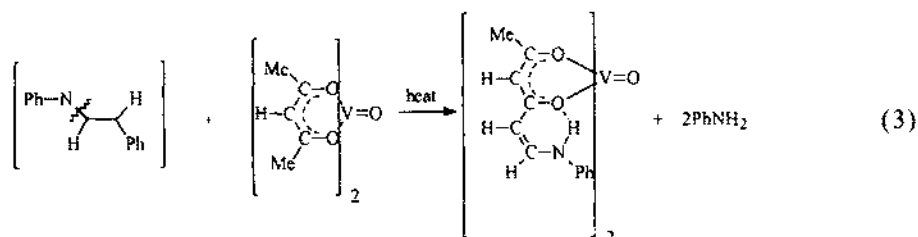
The existence of gaseous VOCl_2 has been demonstrated using Knudsen cell mass spectrometry by following the reaction of V_2O_3 with Cl_2 . The sublimation of VOCl_2 was measured at 550–620 K and the heat of sublimation defined [39]. The pyridine adducts of the oxovanadium chlorides, $\text{VOCl}_2 \cdot 2\text{py}$ and $\text{VOCl}_2 \cdot 3\text{py}$, have been obtained from an unusual route involving the reaction of $[(\text{Ph}_2\text{SiOLi})_2\text{O}]$ and VCl_4 . Reaction of VOCl_3 with $[(\text{Ph}_2\text{SiOM})_2\text{O}]$ ($\text{M}=\text{Li}/\text{Na}$) yielded the V(V) complex $\text{VO}_2\text{Cl} \cdot 2\text{py}$ along with $\text{VOCl}_2 \cdot 3\text{py}$. Further reaction of $\text{VOCl}_2 \cdot 2\text{py}$ with $[\text{O}(\text{SiPh}_2\text{OLi})_2 \cdot 2\text{thf}]$ gave the cyclosiloxoxovanadium(IV) complex $[\text{VO}\{\text{O}(\text{SiPh}_2\text{O})_2\}_2 \cdot \mu\text{-(Li(thf)}_2)_2]$. The X-ray crystal structures of $\text{VOCl}_2 \cdot 3\text{py}$ and $\text{VO}_2\text{Cl} \cdot 2\text{py}$ were determined [40].

The V^{IV} oxodichloro complex $[\text{VOCl}_2\{\text{P}(\text{SiMe}_3)_3\}_2]$ has been obtained by the reduction of VOCl_3 with $\text{P}(\text{SiMe}_3)_3$ and its structure determined. The VOCl_2 group

was found to be disordered, the V atom occupying a slightly distorted trigonal bipyramidal environment [41].

5.2. VO^{2+} complexes

The reaction between molten $VO(acac)_2$ and HDPhF (HDPhF = *N,N'*-diphenylformamidine) yielded the complex oxobis[6-(phenylamino)hexane-2,4-dionato-*O,O'*]vanadium(IV), $VO(Phad)_2$ (**25**) along with aniline according to Eq. (3). It can be seen from Eq. (3) that the new ligand arises from the cleavage of a C–N bond in the HDPhF molecule and the substitution of two hydrogen atoms from the methyl group of an acac ligand. The X-ray structure of (**25**) showed it to possess a five-coordinate vanadium atom surrounded by a terminal oxygen and two diketonate groups in the *trans* configuration [42].

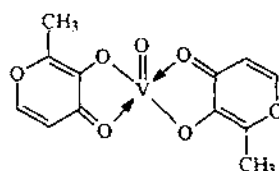
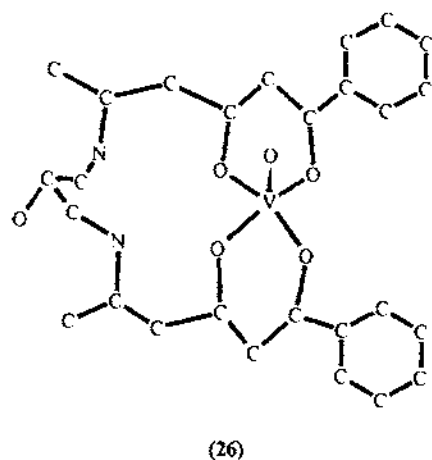
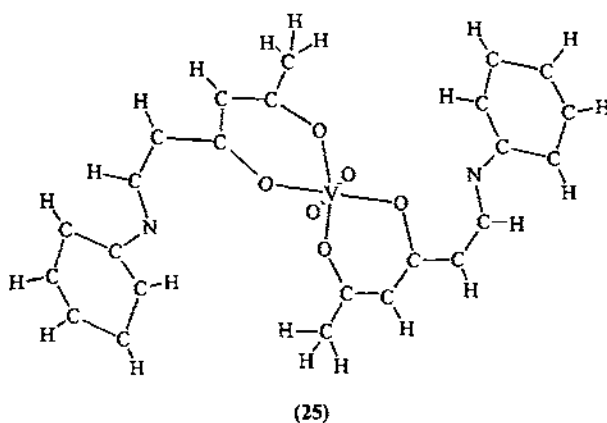


A synthetic attempt to prepare a dinuclear vanadyl complex of a triketone resulted in the formation of the mononuclear vanadium complex $[VO(C_{27}H_{28}N_2O_5)]$ (**26**). The complex was obtained from the reaction between $VO(acac)_2$ and the ligand 5,5'-(2-hydroxy-1,3-propandiyldiamino)bis(1-phenyl-1,3-hexanedione) in methanol. In the complex the vanadium atom is five-coordinate and equatorially bonded to four carbonyl oxygen atoms in a square planar arrangement and axially bonded to the terminal oxygen atom [43].

Three novel Mn^{II} – $V^{IV}O$ μ -oxalato complexes have been synthesised and characterised by IR, elemental analyses, conductivity measurements and EPR spectroscopy. The complexes $[MnVO(ox)_2(L)_2]$ (L = phen, bpy and Me_2bpy) were proposed to have extended oxalato-bridged structures consisting of vanadyl ions and manganese(II) ions in which the V atoms are in a distorted square pyramidal environment [44].

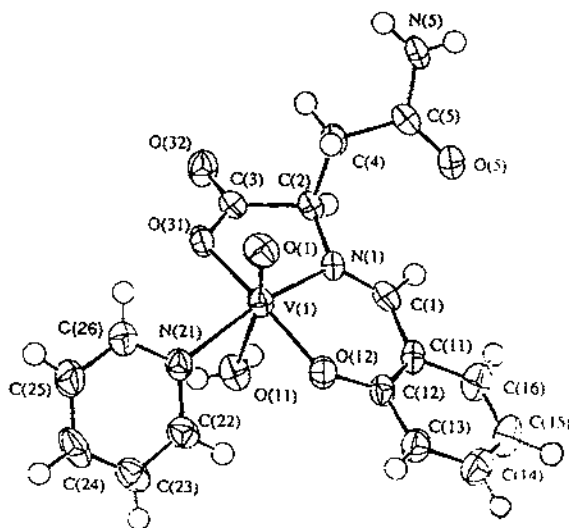
The complex bis(maltolato)oxovanadium(IV), $VO(MA)_2$ (**27**), which was first prepared electrochemically in 1978, has been characterised by EPR spectroscopy in CH_2Cl_2 , H_2O , MeOH and py at both room and low temperatures. Configurations for solvated vanadyl/maltol complexes $VO(ma)_2S$ in solution (S = solvent) were proposed on the basis of a comparison of their hyperfine coupling constants with those for related $V(IV)$ complexes in the literature [45].

There has been substantial interest in the complexation of metal ions with *N*-salicylideneamino acids which are thought to serve as model systems for pyridoxal potentiated enzymes. Reaction of $VOSO_4$ with salicylaldehyde, D,L-asparagine and pyridine in H_2O /MeOH yielded $[VO(\text{sal-D,L-Asn})(py)(H_2O)]$ (**28**) as red–orange

BMOV, VO(ma)₂

(27)

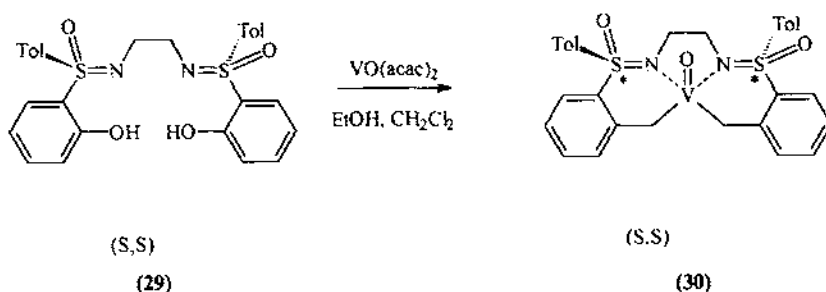
crystals. The complex was shown to exhibit octahedral geometry, the vanadium atom being coordinated by O,N,O atoms of the Schiff base and the pyridyl N in the equatorial plane [46].



(28)

(Reproduced from ref. [46] with permission.)

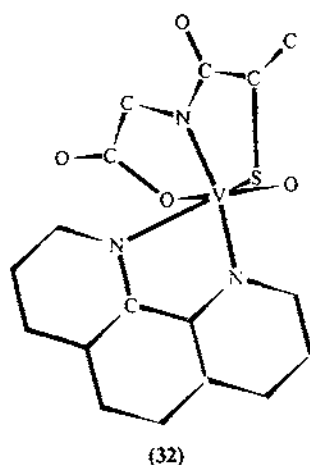
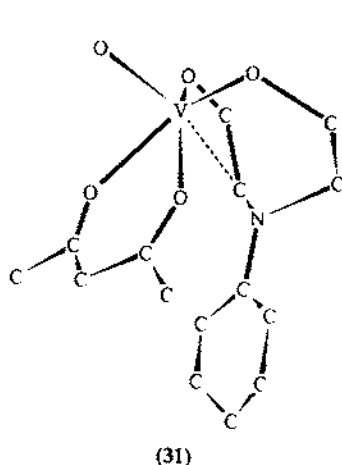
A series of salen-like C_2 -symmetric bisulfoximines has been synthesised and their ability to bind transition metals investigated. The reaction of (*S,S*)-(**29**) with $VO(acac)_2$ in EtOH/ CH_2Cl_2 resulted in the formation of crystals of the complex (*S,S*)-(**30**) whose structure was determined. The dianionic ligand was found to bind to the vanadium atom through the two phenolato oxygens and two sulfoximine nitrogens which results in an *anti*-orientation of the sulfoximine oxygens and the tolyl substituents at the sulfur. The ligating O and N atoms form the base of a square pyramidal plane above which the vanadyl oxygen is situated [47].



Three forms of the Schiff base oxo-vanadium(IV) complex $[\text{VO}\{\text{sal}-(RR)\text{-stien}\}] \cdot \text{MeOH}$ (green), $[\text{VO}\{\text{sal}-(RR)\text{-stien}\}] \cdot 2\text{CHCl}_3$ (green) and $[\text{VO}\{\text{sal}-(RR)\text{-stien}\}] \cdot \text{CH}_3\text{CN}$ (orange) ($\text{H}_2\{\text{sal}-(RR)\text{-stien}\} = N,N'$ -disalicylidene- (RR) -1,2-diphenyl-1,2-ethanediamine) have been prepared and their structures determined. The two green forms contain mononuclear square pyramidal molecules of the complex whereas the orange form consists of individual complexes stacked to give an infinite

linear polymeric type $\dots V=O\dots V=O\dots$ chain. Both forms were found to be interconvertible either by grinding or heating at 120 °C and the extent of conversion was investigated by EXAFS and IR spectroscopy [48]. A similar type of interconversion was observed between the Schiff base complexes $[VO\{3-Xsal-(R,R)-2,4-pentane\}]$ ($X=EtO, MeO, H$). Conversion between the orange polymeric crystals and the green monomeric ones could be promoted by heating to remove water of crystallisation [49].

The racemic Schiff base complex $[VO(L^1)]$ ($H_2L^1=N,N'$ -bis(3-methoxysalicylidene)cyclohexane-1,2-diamine) has been prepared by reaction of 3-methoxysalicylaldehyde and (*R,R*)-1,2-diaminocyclohexane with VO^{2+} as a template. Treatment of $[VO(L^1)]$ with $SOCl_2$ yielded *trans*- $[VCl_2(L^1)]$. The structures of both complexes were determined. The vanadyl complex was found to have typical tetragonal pyramidal geometry whereas the non-oxo complex exhibits a distorted octahedral geometry around the V atom. Reaction of $VO(acac)_2$ with $HN(CH_2CH_2OH)_2$ in the presence of oxygen resulted in the V(V) complex $[VO(acac)\{PhN(CH_2CH_2O)_2\}]$ (31), which was found to have a coordination geometry between tetragonal pyramidal and distorted octahedral, the sixth coordination site being filled by a weak vanadium to nitrogen bonding interaction. A further complex $[VO(L^2)]$ was obtained by aerial oxidation of $VO(acac)_2$ and the Schiff base H_2L^2 (H_2L^2 =Schiff base derived from *o*-hydroxynaphthaldehyde and $H_2NCH_2CH_2OH$) [50].

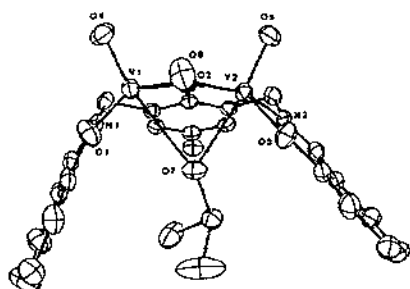


The synthesis, structural and physicochemical characterisation of the first oxovanadium(IV) dipeptide complex have been reported. Addition of 1,10-phen and a CH_3CN solution containing H_3mpg and triethylamine to a solution of $[VOCl_2(CH_3CN)_2]$ yields $Et_3NH[VO(mpg)(phen)]$ ($H_3mpg=N$ -(2-mercaptopropionyl)glycine). The reaction proceeds easily at $-15^\circ C$ in contrast to most other cases with aromatic amides where ionization of hydrogen in the presence of VO^{2+} requires reflux conditions and strong bases. The structure of the anion (32) shows it to possess a severely distorted octahedral geometry around the V

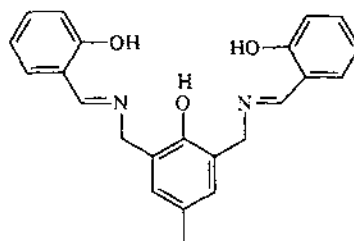
atom. Redox properties of (32) in CH_3CN were studied by cyclic voltammetric and polarographic techniques [51].

5.3. Dinuclear $\text{V}=\text{O}$ complexes

The dinuclear oxovanadium(IV) complex $[(\text{VO})_2(\text{L})(\text{CH}_3\text{O})(\text{dmsO})]$ (33) [$\text{H}_3\text{L} = 2,6\text{-bis}(\text{salicylideneaminomethyl})\text{-4-methylphenol}$ (34)] has been prepared and characterised by IR, electronic spectra and X-ray studies. Each V atom was found to have octahedral coordination and to be bridged by a phenoxo-oxygen, a methoxo ion and a dimethyl sulfoxide [52].



(33)



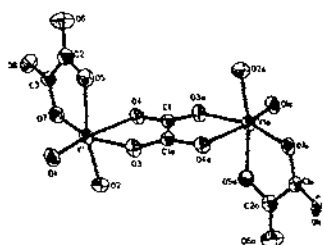
H_3L

(34)

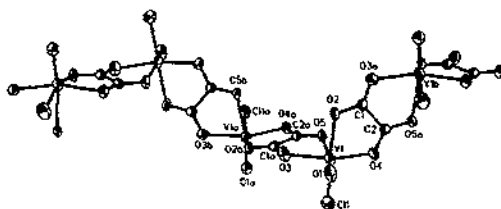
[(33) Reproduced from ref. [52] with permission.]

The possibility of designing ligand environments to introduce specific magnetic properties to dinuclear $d^1\text{--}d^1$ systems containing two V centres has been investigated. The possible configurations of a $\{\text{VO}(\mu_2\text{-OR})_2\text{VO}\}^{2+}$ core in complexes consisting of two edge-sharing octahedrally coordinated oxovanadium(IV) centres have been classified according to the orientation of the $\text{V}=\text{O}$ groups with respect to the plane defined by the two vanadium centres and the two bridging oxygen atoms (orthogonal, coplanar, twist) and the orientation of the two $\text{V}=\text{O}$ groups (*syn*, *anti*). The first examples of dimeric vanadium(IV) complexes with *anti*-coplanar (35) $[\{\text{VO}(\text{Hsabhea})\}_2]$ and a twist configuration (36) $[\{\text{VO}(\text{Hsabhea})\}\{\text{VO}(\text{acac})(\text{HOME})\}(\mu_2\text{-OMe})]$ have been synthesised by using the trivalent, pentadentate Schiff base ligand *N*-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine (H_3sabhea). The magnetochemistry of the two ferromagnetically coupled vanadium(IV) dimers has been studied [53].

The structure of the first dinuclear vanadium(IV) complex having two oxide bridges has been reported. The compound $\{(\mu\text{-O})_2\text{V}_2[\text{N}(\text{SiMe}_3)_2]_4\}$ (37) was obtained from the reaction between V(III)Cl_3 and $\text{LiN}(\text{SiMe}_3)_2$ in pentane. The molecular structure consists of two well-separated dimeric molecules of virtual D_{2h} symmetry in the asymmetric unit. The two V and two bridging O atoms are planar



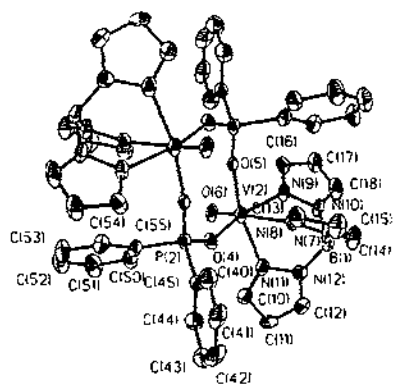
(38)



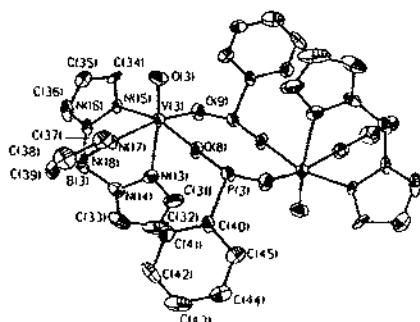
(39)

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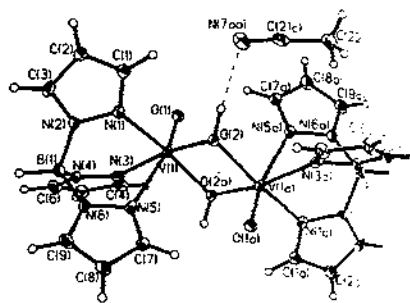
to be moderately antiferromagnetically coupled. A rationalisation for the magnetic behaviour of these and other complexes of this type was made based upon a direct overlap model modulated by the conformation of the eight-membered $V(\mu-OXO)_2V$ ring [56].



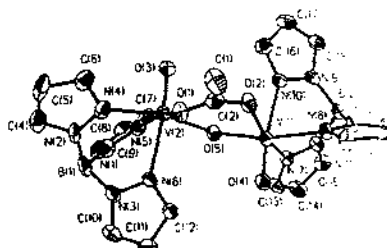
(40)



(41)



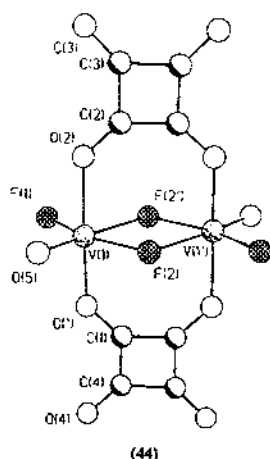
(42)



(43)

(Reproduced from ref. [56] with permission.)

Aqueous and methanolic solutions containing VOSO_4 and HF react with squaric acid to give the complexes containing the $[\text{V}_2\text{O}_2\text{F}_4(\text{C}_4\text{O}_4)_2]^{4-}$ and $[\text{V}_3\text{O}_3\text{F}_4(\text{C}_4\text{O}_4)_3]^{4-}$ ions. The $[\text{V}_2\text{O}_2\text{F}_4(\text{C}_4\text{O}_4)_2]^{4-}$ ion was found to consist of a planar $\text{V}_2\text{O}_2\text{F}_4$ core with the vanadium sites bridged by two μ -1,2-squarato ligands (**44**). The cone shaped $[\text{V}_3\text{O}_3\text{F}_4(\text{C}_4\text{O}_4)_3]^{4-}$ ion was found to contain a central defect and a severely distorted V_3F_4 cubane unit. Each V atom bears a terminal oxo ligand and pairs of V atoms are bridged by μ -1,2-squarato ligands [57].



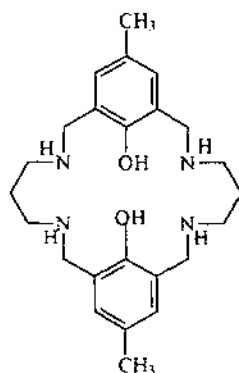
(Reproduced from ref. [57] with permission.)

A series of macrocyclic dimeric V(IV) and heterodinuclear V(IV)–Ni(II) complexes has been synthesised from the dinucleating tetraaminodiphenol macrocycle H_2L^1 (**45**). The crystal structure of $[(\text{VO}(\text{H}_2\text{L}^1))_2(\mu\text{-SO}_4)](\text{NO}_3)_2$ was determined and found to consist of two distorted octahedral vanadium centres, separated by 6.741 Å and bridged by sulfate. Solid-state magnetic measurements at reduced temperatures suggested very weak intra- or intermolecular exchange interactions. The complex was found to undergo stepwise oxidation to $\text{V}^{\text{IV}}\text{OV}^{\text{V}}\text{O}$ and $\text{V}^{\text{V}}\text{OV}^{\text{V}}\text{O}$ species. The heterodinuclear complexes $[(\text{VO})\text{L}^1\text{Ni}(\text{H}_2\text{O})_2(\text{SO}_4)] \cdot \text{H}_2\text{O}$ and $[(\text{VO})\text{L}^1\text{Ni}(\mu\text{-SO}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ prepared from $[\text{VO}(\text{H}_2\text{L}^1)(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ and $[\text{Ni}(\text{acac})_2]$ have identical composition but differ in their IR and UV–vis spectra and electrochemistry [58].

5.4. Non-oxo vanadium(IV) complexes

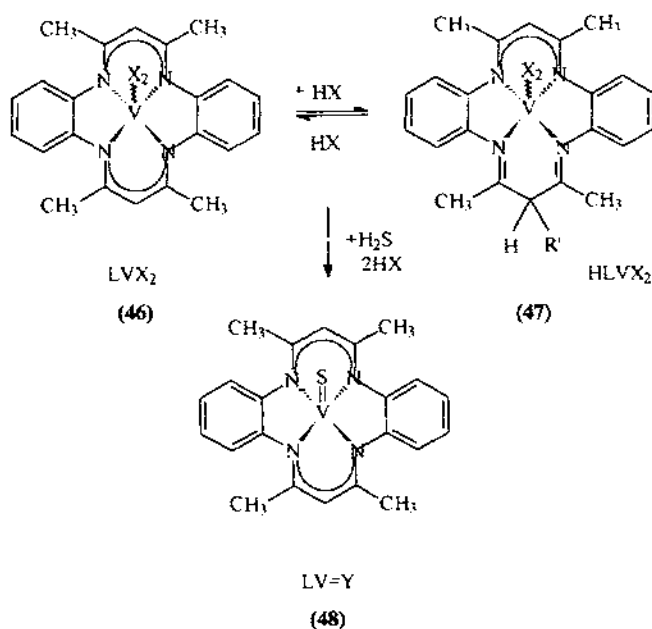
The tridentate diacidic ligand 4-[1-(*N'*-benzoylhydrazino)-1-phenyl-methylidene]-3-methyl-1-phenyl-pyrazol-5-one (H_2L), formed from 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one with benzoylhydrazine, undergoes reaction with V^{IV} ions to give complexes of the type VL_2 . The species were characterised by mass spectrometry and their electrochemical behaviour investigated [59].

The reactions of $(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{V}=\text{O}$ with different halogenating agents have been

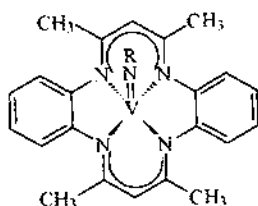
 H_2L

(45)

investigated and the products found to depend upon the halogenating agent used. Two equivalents of oxalyl or thionyl dihalide ($\text{X}=\text{Cl}, \text{Br}$) gave quantitative conversion to complexes LVX_2 (46). In the presence of HX ($\text{X}=\text{F}, \text{Cl}, \text{Br}$), ionic salts of the type $[(\text{HL})\text{VX}_2]\text{X}$ (47) were isolated. Complexes of the type $\text{LV}=\text{Y}$ could be obtained from reaction of LVX_2 with H_2S and $\text{H}_2\text{NC}_6\text{H}_5 \cdot \text{B}(\text{C}_2\text{H}_5)_3$ (48), $(\text{C}_2\text{H}_5)_3\text{Y}$ ($\text{Y}=\text{S}, \text{NC}_6\text{H}_5 \cdot \text{B}(\text{C}_2\text{H}_5)_3$), thus enabling the formation of new non-oxo vanadium compounds [60].



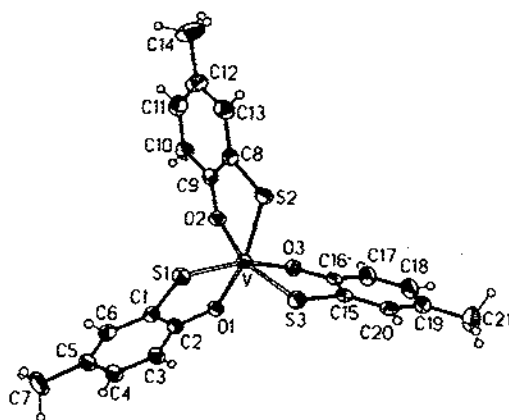
The synthesis, molecular structure and redox chemistry of new imidovanadium(IV)dibenzotetraazaannulene complexes of the type $(\text{TMTAA})\text{V}=\text{NR}$ (**49**) ($\text{R} = \text{CH}_3$, $t\text{-C}_4\text{H}_9$, C_6H_5 , C_6F_5 and $\text{N}(\text{CH}_3)_2$; $\text{TMTAA}^{2-} = 5,7,12,14\text{-tetramethyldibenzotetraazaannulene}$) have been reported. The complexes were characterised by EPR, IR, UV-vis spectroscopic and mass spectrometric techniques. Cyclic voltammetric measurements indicated a reversible one-electron oxidation to the corresponding diamagnetic $\text{V}(\text{V})$ cations $[(\text{TMTAA})\text{V}=\text{NR}]^+$ [61].



$(\text{TMTAA})\text{V}=\text{NR}$

(**49**)

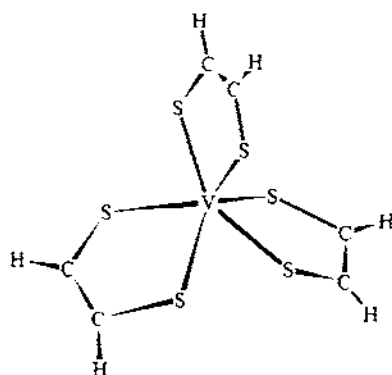
Displacement of the vanadyl oxygen atom during the reaction of $\text{VO}(\text{acac})_2$ with 2-mercaptophenol (mpH_2) in the presence of triethylamine leads to the mononuclear tris complex $(\text{Et}_3\text{NH})_2[\text{V}(\text{mp})_3]$. The analogous reaction with 2-mercapto-4-methylphenol (mmpH_2) yields $(\text{Et}_3\text{NH})(\text{PNP})[\text{V}(\text{mmp})_3]$ (**50**), which has been structurally characterised. In the complex the vanadium atom is coordinated by three didentate chelating mmp^{2-} ligands binding through three oxygen and three sulfur atoms. The coordination geometry around the vanadium atom is between octahedral and trigonal prismatic. Reaction of $\text{VO}(\text{acac})_2$ with the sodium salt of 2-mercaptophenol fails to promote oxygen abstraction and the vanadyl complex $\text{Na}(\text{Ph}_4\text{P})[\text{VO}(\text{mp})_2] \cdot \text{Et}_2\text{O}$ is formed [62].



(**50**)

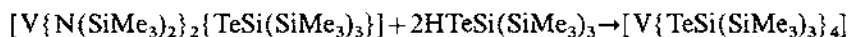
(Reproduced from ref. [62] with permission.)

The tris(dithiolene)vanadium(IV) complex $[V(S_2C_2H_2)_3]$ (**51**) has been obtained from the reaction between $VCl_3(thf)_3$ with sodium *cis*-ethenedithiolate in MeOH. The crystal structure of the complex showed it to have near perfect D_{3h} geometry and it is thought to be the first example of a V(IV) dithiolene complex with such symmetry [63].

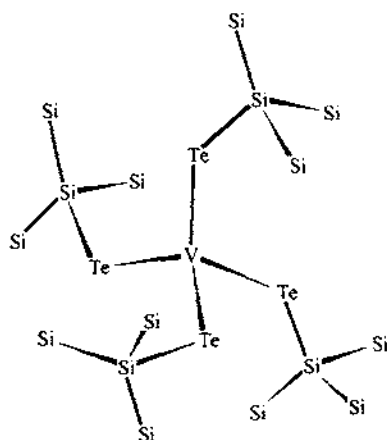


(51)

The crystal structures of homoleptic d^1 and d^2 transition metal tellurolates $[M\{TeSi(SiMe_3)_3\}_4]$ ($M=V, Mo$) have been determined and compared. The vanadium complex (**52**) was obtained according to Eq. (4). The geometry around the V atom is best described as a flattened tetrahedron. The V–Te bond order was estimated between 2 and 3 by comparison with the few other known V–Te bond distances [64].



(4)



(52)

The reactions of tetracyanoethene (TCNE) with $V(C_5R_5)_2Br$ ($R = H, Me$) yielded complexes formulated as $V^{IV}(C_5R_5)_2Br(TCNE^{-I})$ and $[V^{IV}(C_5R_5)_2Br]_2(TCNE^{-II})$ having markedly different electronic structures in terms of electrochemistry, IR and UV-vis spectra and magnetic susceptibility from the 16 valence electron precursors [65].

The 1,1'-ring-substituted vanadocene dichlorides $[V(\eta^5-C_5H_4R)_2Cl_2]$ ($R = CMe_3, SiMe_3, SiEt_3$) have been prepared from VCl_4 and the appropriate lithiated cyclopentadiene C_5H_4RLi in 1:2 ratio. The crystal structures of $[V(\eta^5-C_5H_4Me_3)_2Cl_2]$ and the parent compound $[V(\eta^5-C_5H_5)_2Cl_2]$ have been determined and were found to be in line with those of other closely related molecules [66].

5.5. Complexes containing the vanadate(IV) ion

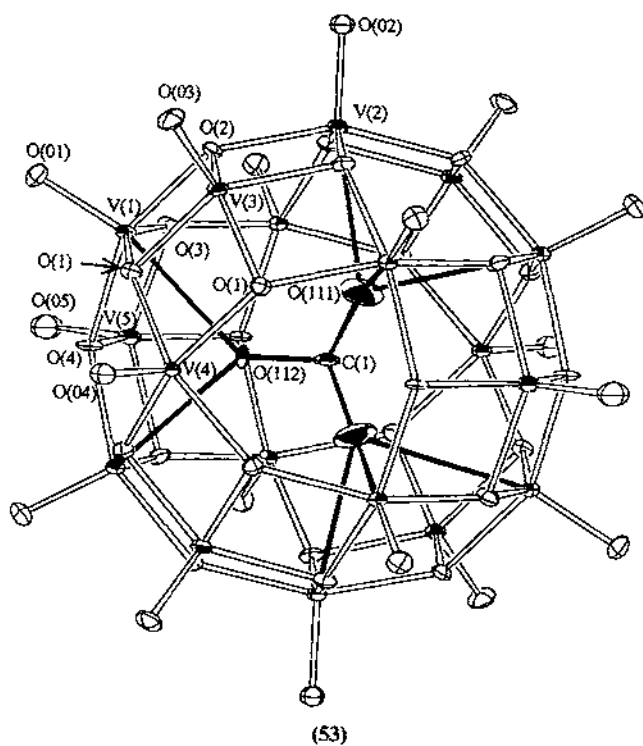
The spherical octadecavanadate complexes $K_{9.5}[H_{3.5}V_{18}O_{42}Cl] \cdot 11.5H_2O$ and $K_{10}[H_2V_{18}O_{42}(H_2O)] \cdot 16H_2O$ have been photochemically prepared from $[NH_3^+Bu]_4[V_4O_{12}]$ in pH specific solutions in water under ambient conditions. Structural studies showed both complexes to consist of $(VO)_{18}O_{24}$ shells encapsulating either Cl^- or H_2O at the centre. Each shell is composed of 18 edge-sharing $V^{IV}O_5$ square pyramids and has approximate D_{4d} symmetry [67].

The kinetics of the formation of carbonato-oxovanadate(IV) complexes have been reported and the crystal structure of the sodium salt of the polyvanadate(IV) ion containing the captured carbonate moiety, $[V_{18}O_{42}(CO_3)]^{14-}$ (53), has been determined. The chemistry has relevance to the sulfolin process in which V^V is used in weakly basic bicarbonate solution to remove H_2S from CO_2 gas streams by oxidation to molecular sulfur. The presence of ligands such as HCO_3^- can substantially alter the redox properties of the V centres [68].

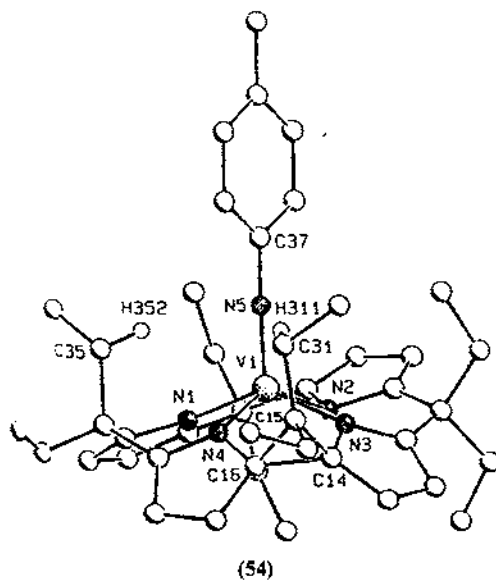
The reaction of $[p-MeC_6H_4N \dots VCl_3]$ with *meso*-octaethylporphyrinogen-lithium derivatives, $[Et_8N_4Li_4(thf)_4]$, yields oxidised forms of *meso*-octaethylporphyrinogen containing *mono* and *bis*(cyclopropane) units which can act as two-electron shuttles. The structure of the complex $[p-MeC_6H_4N \dots V\{Et_8N_4(D)\}]$ (54), which contains a vanadium(IV) nitrene fragment bound to the two-electron-oxidised form of the porphyrin having a cyclopropane unit, was determined [69]. The electrochemistry of two vanadium complexes of *o*-*N*-salicylidene-aminoethylphenol, $VO(HSalamp)_2$ and $[VO(Salamp)]_2O$, has been reported [70].

6. Mixed-valence vanadium(IV) and vanadium(III) complexes

Interest in the V catalysed O_2 oxidative polymerization of organosulfur compounds has led to an examination of the V mediated electrochemical reduction of O_2 . The controlled potential reduction of $[(salen)V^{IV}-O-V^{IV}(salen)]^{2+}$ to the mixed-valence species $[(salen)V^{IV}-O-V^{III}(salen)]^+$ has been reported [71]. The complex is also obtained from treatment of solutions of $[(salen)VOV(salen)][BF_4]_2$ in MeCN with excess $BuNi_3$. The crystal structure of the complex showed it to have a V–V distance

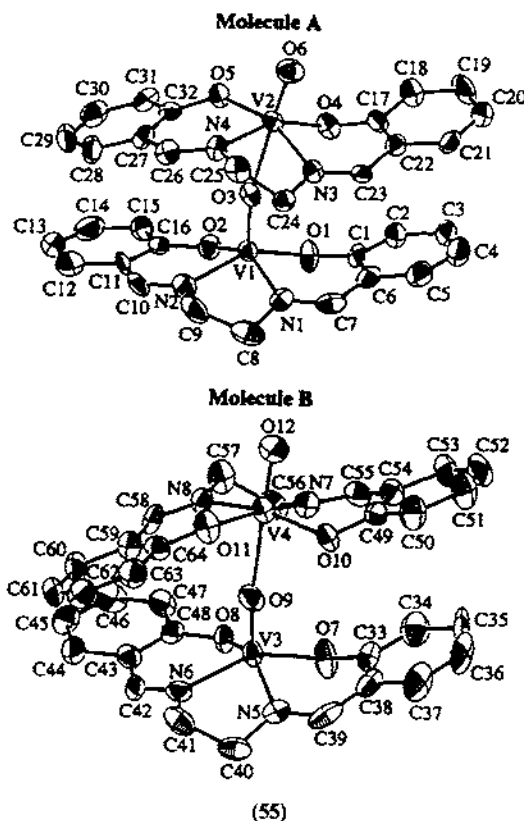


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of 3.569(4) Å, consistent with its formulation as a weakly coupled mixed-valence V^{III}/V^{IV} complex [72]. Oxidation of the cation with O_2 gas and crystallisation of the product after addition of Bu_4NI_3 resulted in the formation of a compound composed of $[(salen)VIVO(salen)]^+$ cations and $[I_3]^-$ anions, (55). The structure was found to consist of two crystallographically independent molecules, A and B, per unit cell. The geometries of the two molecules and various V–O bond lengths suggest the formation of a V^{IV}/V^V mixed-valent complex resulting from the reaction shown in Eq. (5):

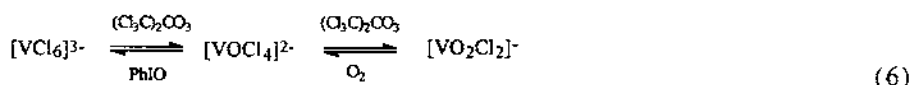


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A range of *N*-substituted mono- and dihydroxamic acids undergo oxygen abstraction on reaction with V(III) and V(IV) compounds to form V(V) hydroxamates together with the corresponding amides and diamides. Vanadyl hydroxamates form metal–oxygen clusters under FAB-MS conditions [73].

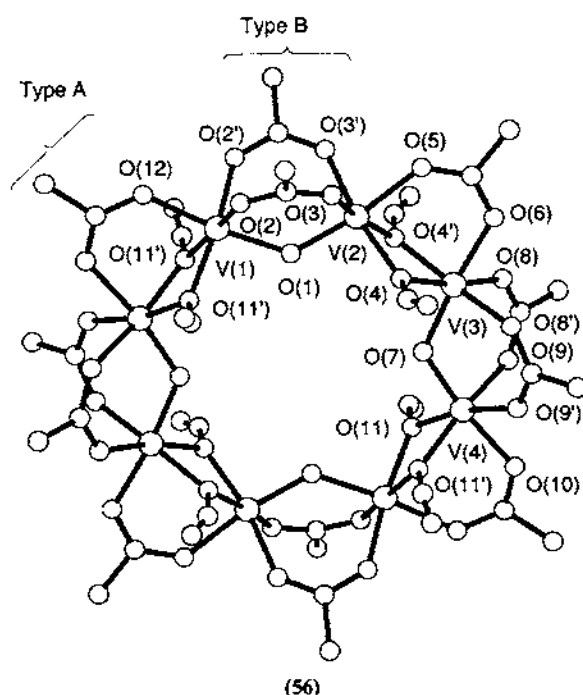
Bis(trichloromethyl) carbonate, $(Cl_3C)_2CO_3$, has been used as a phosgene substi-

tute in the investigation of the oxo exchange chemistry of a number of vanadium complexes dissolved in a room temperature ionic liquid [74]. Reactions were found to proceed according to Eq. (6).



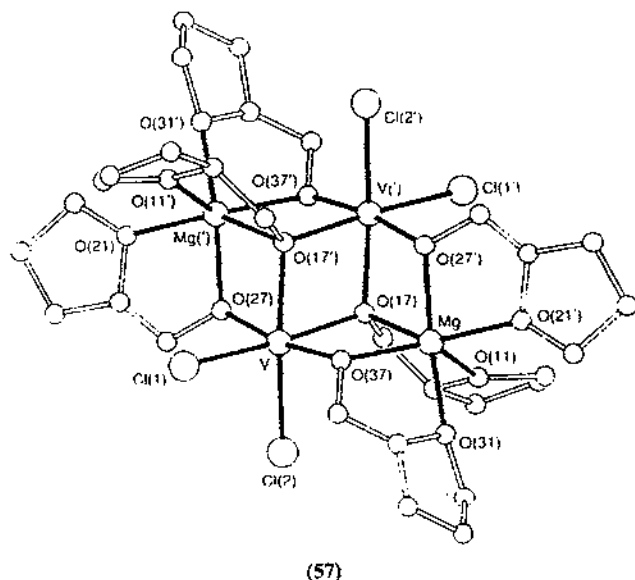
7. Vanadium(III)

A novel cyclic octanuclear vanadium(III) complex $[\text{V}_8(\mu\text{-OH})_4(\mu\text{-OEt})_8(\mu\text{-CH}_3\text{COO})_{12}]$ (**56**) has been synthesised and structurally characterised. The complex was obtained, along with the trinuclear vanadium complex $[\text{V}_3(\mu\text{-O})(\mu\text{-C}_6\text{H}_5\text{COO})_6(\text{EtOH})_3]^+$, from treatment of $\text{VCl}_3(\text{thf})_3$ with dipyrindylamine, sodium hydride and sodium acetate. The cyclic octanuclear complex contains V atoms in distorted octahedral environments alternately bridged by hydroxide, ethoxide and carboxylate ions. The molecule has near D_{4h} symmetry with a crystallographic C_2 axis passing through the centre of the cavity. The possible oxidation states of the metal atoms in the complex are considered [75].



(Reproduced from ref. [75] with permission.)

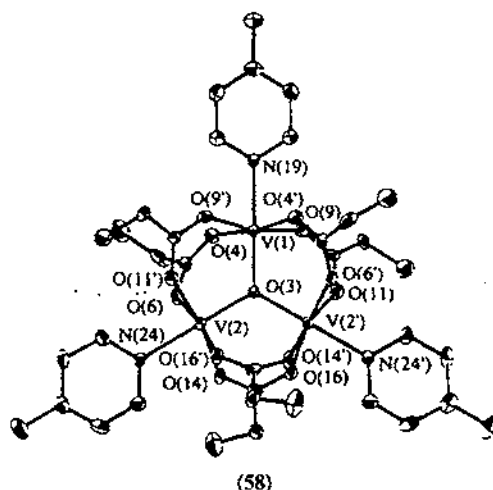
The tetranuclear vanadium(III)–magnesium(II) complex $[\text{V}_2\text{Mg}_2(\mu_3, \eta^2\text{-thfco})_2(\mu, \eta^2\text{-thfco})_4\text{Cl}_4] \cdot 2\text{CH}_2\text{Cl}_2$ (**57**) has been prepared by the reaction between $[\text{VCl}_3(\text{thf})_3]$ with $[\text{Mg}(\text{thfco})_2]$ (thfco = 2-tetrahydrofurfuroxide) in a 1:1.5 molar ratio. The crystal structure of (**57**) showed it to be composed of centrosymmetric tetranuclear molecules. The two Mg atoms and two V atoms form a near regular Mg_2V_2 rhombus. The four metal centres are bridged by two μ_3 -alkoxo oxygen atoms. The catalytic activity of the compound in ethene polymerization has been studied [76].



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A series of trinuclear vanadium(III) carboxylates, $[\text{V}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3](\text{ClO}_4)$ ($\text{R} = \text{Me, Et; L} = \text{py, pic, lut}$), has been prepared by treatment of $\text{VCl}_3(\text{thf})_3$ with NaO_2CR^1 ($\text{R} = \text{Me, Et}$) in $\text{R}^1\text{CO}_2\text{H/py, pic/MeCN}$ or CH_2Cl_2 solution followed by addition of $\text{N}^+\text{Bu}_4\text{ClO}_4$. A similar procedure for $\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{-}p\text{-OMe, C}_6\text{H}_3\text{-}m\text{-Me}_2, \text{C}_6\text{H}_4\text{-}p\text{-Cl}$, but omitting addition of NaO_2CR^1 , provides the corresponding benzoate or substituted benzoate derivatives. The X-ray structure of $[\text{V}_3\text{O}(\text{O}_2\text{CEt})_6(\text{pic})_3](\text{ClO}_4)$ (**58**) showed the anion to consist of a V_3O^{7+} triangular framework with a $\mu_3\text{-O}^{2-}$ ion in the V_3 plane. Each triangular edge is bridged by two EtCO_2^- groups and there is a terminal pic group on each V^{III} atom completing the distorted octahedral geometries at the metal atoms. Spectroscopic and magnetochemical measurements were made on the complexes [77].

Treatment of the dinuclear vanadium(III) thiolate complex $(\text{NEt}_4)_2[\text{V}_2(\text{edt})_4]$ ($\text{edtH}_2 = \text{ethane-1,2-dithiol}$) with $(\text{C}_{12}\text{H}_8\text{S}_2)\text{BF}_4$ resulted in the isolation of the mixed-valence $\text{V}^{\text{III}}/\text{V}^{\text{IV}}$ complex $(\text{NEt}_4)[\text{V}_2(\text{edt})_4]$ via a one-electron oxidation. The trinuclear complex $(\text{NEt}_4)_3[\text{V}_3\text{Cl}_6(\text{edt})_3]$ was obtained from

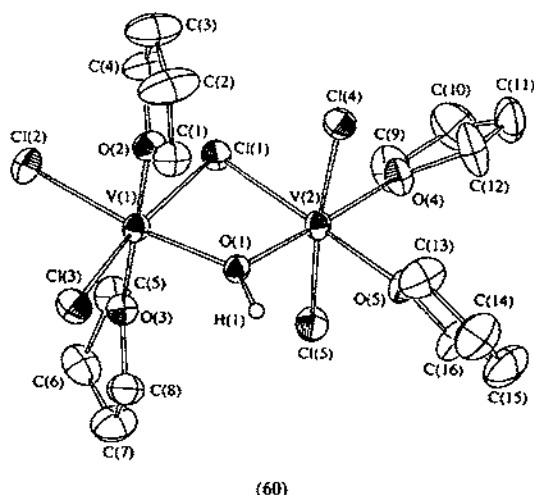
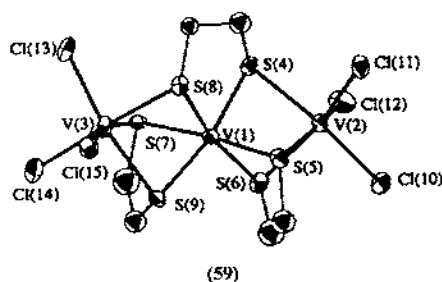


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(NEt_4)[$\text{V}_2(\text{edt})_4$] by reaction with $\text{VCl}_3(\text{thf})_3$ and NEt_4Cl . An alternative route to this compound is by reaction of $\text{VCl}_3(\text{thf})_3$, Na_2edt and NEt_4Cl in MeCN in a 1:1:1 molar ratio. The structure of the MeCN adduct of $(\text{NEt}_4)_3[\text{V}_3\text{Cl}_6(\text{edt})_3]$ (**59**) was determined and found to contain a near linear V_3 unit with a face-sharing trioctahedral structure. The $\text{V}\dots\text{V}$ distances do not suggest metal–metal bonding. Variable temperature solid-state magnetic susceptibility studies were performed on the complexes [78].

A dimeric V(III)/thf species has been obtained in this case from reaction of $[\text{VCl}_3(\text{thf})_3]$ and NaCPh_3 in thf solution. The complex $[\text{V}_2(\mu\text{-Cl})(\mu\text{-OH})\text{Cl}_4(\text{thf})_4] \cdot \text{thf}$ (**60**) was found to comprise two octahedral V(III) centres, one having two axial and two equatorial thf ligands and the other with two axial thf ligands and two equatorial Cl ligands. The two V centres are linked by Cl and OH bridges and have different configurations [79].

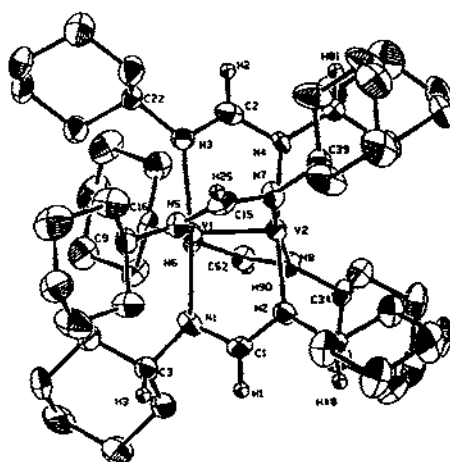
There is considerable interest in the existence and stability of multiple bonds between first row transition metals, and careful choice of ligand has permitted the formation of divanadium complexes with very short V–V bonds. There is uncertainty though as to the nature of these extremely short contacts as the ligands in question appear to enable the assembly of dimers with very short metal–metal contacts but no direct M–M bond. The reaction of $\text{VCl}_2(\text{TMEDA})_2$ and $\text{VCl}_3(\text{thf})_3$ with two equivalents of formamidinate lithium salts was found to yield $\{[\text{CyNC}(\text{H})\text{NCy}]_2\text{V}\}_2$ (**61**) and $\{[\text{CyNC}(\text{H})\text{NCy}]_2\text{VCl}\}_2$, both of which are dimeric. The formation of dimeric $\{[\text{CyNC}(\text{H})\text{NCy}]_2\text{V}_2\}$ was found to proceed via the intermediate $[\text{CyNC}(\text{H})\text{NCy}]_2\text{V}(\text{TMEDA})$ (**62**), which was shown to be monomeric. The V(II) dimer was found to possess a structure similar to those formed by the formamidinate anion with other transition metal ions. Each formamidinate ligand adopts the three-centre chelating geometry where each of the two donor atoms of one ligand binds to one of the metal centres forming a five-membered ring



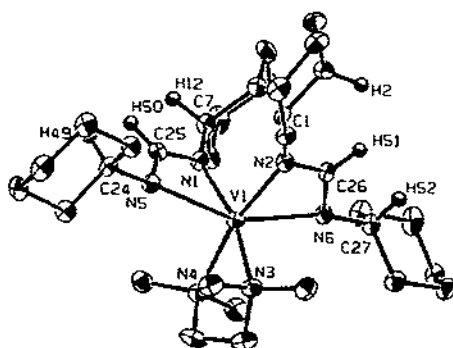
[(59) Reproduced from ref. [78] with permission; (60) reproduced from ref. [79] with permission.]

with the V_2 unit. The V–V distance of 1.968(2) Å is the shortest reported to date. The monomer (62) possesses V atoms in a distorted octahedral geometry with two chelating formamidine ligands almost coplanar with the metal. The TMEDA molecule provides the two remaining coordination sites. Similar reactions of $VCl_2(TMEDA)_2$ and $VCl_3(thf)_3$ with the acetamidinate ion resulted in monomeric $[CyNC(Me)NCy]_2V(thf)_2$ and $[CyNC(Me)NCy]_2VCl$ only. When the more bulky benzamidinate ligand was used similar monomeric complexes were obtained. Attempts to form dinuclear units by thf dissociation of $[Me_3SiNC(Ph)NSiMe_3]_2V(thf)_2$ or reduction of $[Me_3SiNC(Ph)NSiMe_3]_2VCl$ gave the novel dinitrogen compound $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2$ (63) [80].

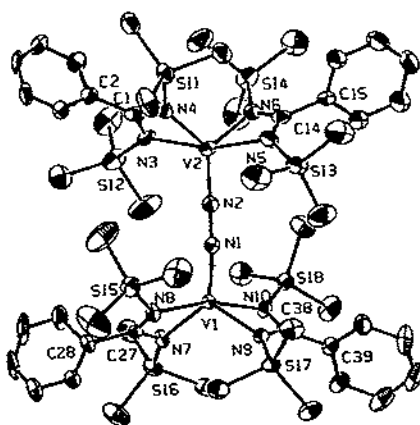
The same group has studied the reactions of $VCl_3(thf)_3$ with two equivalents of R_2NLi ($R = Cy, Me_3Si$) which yielded the complexes $(Cy_2N)_2V(\mu-Cl)_2Li(thf)_2$ (64) and $\{[Me_3Si]_2N\}_2VCl(thf)$ (65). Both complexes were found to decompose in hot toluene. $(Cy_2N)_2V(\mu-Cl)_2Li(thf)_2$ undergoes dimerization with the formation of $[(Cy_2N)_2V(\mu-Cl)]_2$. Reaction of (65) with $NaBH_4$ led to



(61)



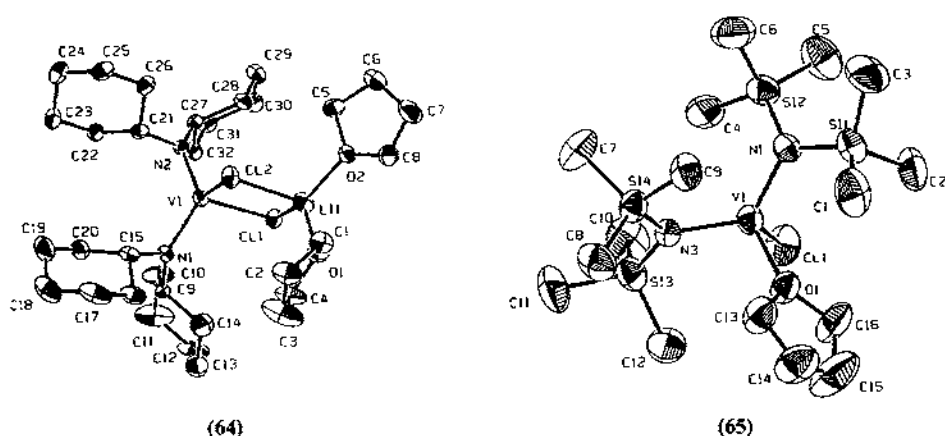
(62)



(63)

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$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}(\text{BH}_4)(\text{thf})$. The structures of all four complexes were determined crystallographically [81].

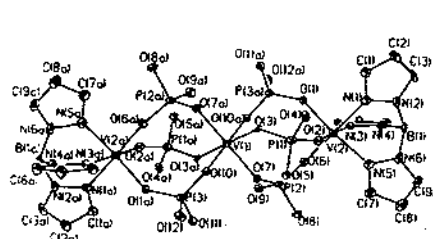


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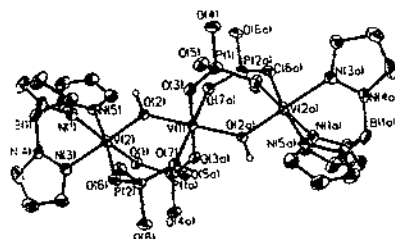
Interest in the physiological role of V(III) in tunicates has led to an investigation of the effect of sulfate ion on the coordination geometry of V(III) complexes. Surprisingly, tunicates preferentially employ sulfate as a counterion for V(III) species rather than the vastly more abundant chloride ion in sea water. Several V(III) complexes with a tetradentate *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bis-picen) or hexadentate *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen) ligand have been prepared and characterised by UV-vis and Raman spectroscopy. Two of the V(III) complexes having a didentate sulfate ion, namely $[\text{V}_2(\text{SO}_4)_3(\text{bis-picen})_2]$ and a complex containing the $[\text{V}(\text{SO}_4)(\text{tpen})]^+$ cation, were studied by X-ray crystallography. Both complexes were found to adopt a heptacoordinate pentagonal bipyramidal structure in which the SO_4^{2-} ion is situated in the pentagonal plane. In aqueous solution the bis-picen- SO_4^{2-} species is readily aquated to form a hexacoordinate oxo-bridged dinuclear species [82].

The X-ray structures of dimeric $[(\text{V}(\text{phen})_2\text{Cl})_2\text{O}]^{2+}$ and monomeric $[\text{VO}(\text{phen})_2\text{Cl}]^+$ have been determined and were found to be similar to those of the bipyridyl analogues. One remarkable feature of the dimer is the proximity of the phenanthroline groups coordinated to different metal atoms. The rings are almost parallel and separated by only 3.45 Å. This geometric property is thought to render the molecule able to cleave plasmid DNA without exogenous oxidants or reductants. The interplanar spacing is suitable for the intercalation of both phenanthroline rings between base pairs in B-DNA and strand cleavage was observed when supercoiled (form I) pCW8 plasmid DNA was treated with various concentrations of the oxo-bridged V(III) dimers at pH 8.4. The phenanthroline dimer produced both single- and double-strand breaks with relatively short (15 min–2 h) incubation times. However, with longer incubation times, some oxidation of the dimer to the mononuclear V(IV) species was observed [83].

The synthesis and characterisation of two linear trinuclear V(III) complexes of formula $[\text{LV}(\mu\text{-(PhO)}_2\text{PO}_2)_3\text{-V-(}\mu\text{-(PhO)}_2\text{PO}_2)_3\text{VL}]\text{PF}_6$ (**66**) and $[\text{LV}(\mu\text{-(PhO)}_2\text{PO}_2)_2(\mu\text{-OH})\text{V-(}\mu\text{-(PhO)}_2\text{PO}_2(\mu\text{-OH})\text{VL)ClO}_4$ (**67**) ($\text{L} = \text{hydridotris(pyrazolyl)borate}$) have been reported. Complex (**66**) consists of two terminal V(III) ions capped by a hydridotris(pyrazolyl)borate group and linked to a central V(III) by three $(\mu\text{-O}, \mu\text{-O}')$ diphenyl phosphate bridges. The structure of (**67**) is analogous but with a hydroxide bridge replacing a diphenyl phosphate in each link. Magnetic measurements suggest that replacement of one phosphate bridge by a hydroxide leads to a change in the sign of the coupling between the terminal and central V(III) atoms from antiferromagnetic in (**66**) to ferromagnetic in (**67**) [84].



(66)



(67)

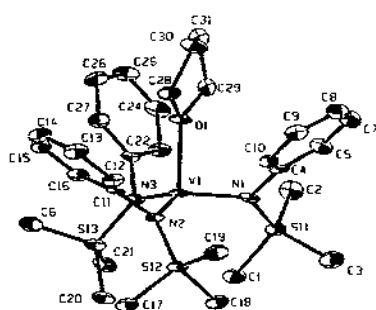
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Two different crystalline species, $[\text{VCl}_3(\text{thf})_2(\text{H}_2\text{O})]$ and $[\text{VCl}_3(\text{thf})_2(\text{H}_2\text{O})] \cdot \text{thf}$, have been isolated from the reactions of $[\text{mer-VCl}_3(\text{thf})_3]$ and water in thf or dichloromethane. An investigation of their crystal structures showed that in both species the V(III) ions are in a distorted octahedral environment surrounded by three *mer*-chlorine atoms, two *trans*-situated thf molecules and a water molecule [85].

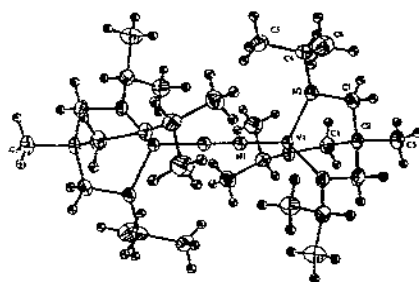
Continuing investigations into V(III) amide complexes in order to study the factors which promote or discourage the coordination of dinitrogen has led to the preparation of the tetrahedral complex $\{[(\text{CH}_3)_3\text{Si}]\text{NPh}_3\text{V}(\text{thf})\}$ (**68**) from reaction between $\text{VCl}_3(\text{thf})_3$ with $\{[(\text{CH}_3)_3\text{Si}]\text{NPhLi}\}$. Reaction of $\text{CH}_3\text{C}[(\text{CH}_2)\text{N}(i\text{-Pr})\text{Li}]_3(\text{TIAME})$ with $\text{VCl}_3(\text{thf})_3$ gave the new dinitrogen complex $(\text{TIAME})\text{VN}_2\text{V}(\text{TIAME})$ (**69**) whose structure was determined by X-ray analysis. The complex was found to be dinuclear with two identical (TIAME)V fragments linked together by a dinitrogen molecule. The coordination geometry around each V atom is tetrahedral with V–N distances in the expected range [86].

The room temperature reactions of $(\text{Ph}_2\text{N})_3\text{V}(\text{thf})$ with $\{[(\text{CH}_3)_3\text{Si}]\text{N}_3\}$ and $\{[(\text{CH}_3)_3\text{Si}]\text{CHN}_2\}$ have been found to afford $(\text{Ph}_2\text{N})_3\text{V}[\text{N-Si}(\text{CH}_3)_3]$ and $(\text{Ph}_2\text{N})_3\text{V}[\text{N}_2\text{CHSi}(\text{CH}_3)_3]$ respectively. Reactions of both these products with lithium isopropylamide led to the anionic vanadium nitride species $[(\text{Ph}_2\text{N})_3\text{V}(\mu\text{-N})\text{Li}(\text{thf})_3](\text{thf})_{0.5}$. This undergoes reaction with $(\text{CH}_3)_3\text{SiCl}$ and MeI to form the complexes $(\text{Ph}_2\text{N})_3\text{V}(\text{N-R})$ ($\text{R} = \text{Si}(\text{CH}_3)_3$ and Me) [87].

The three-coordinate V(III) species $\{(\text{Me}_3\text{Si})_2\text{N}_2\text{VER}\}$ ($\text{E} = \text{Se}, \text{Te}$; $\text{R} = \text{Si}(\text{SiMe}_3)_3, \text{SiPh}_3$) have been obtained by reaction between



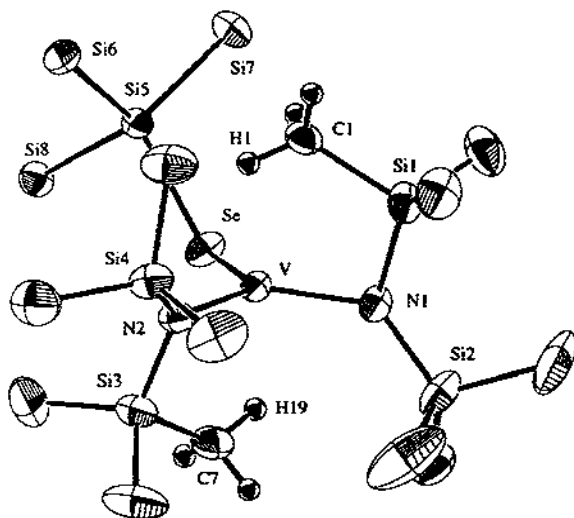
(68)



(69)

(Reproduced from ref. [86] with permission.)

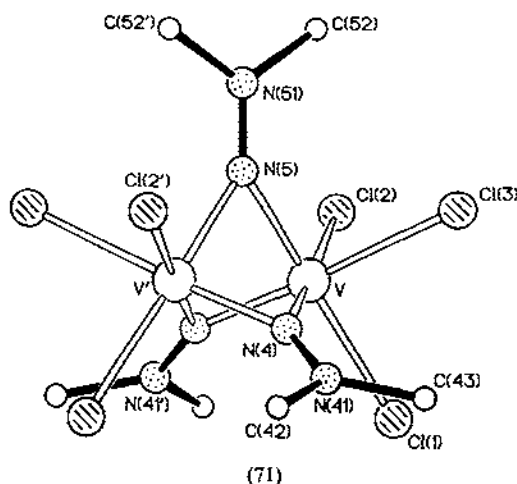
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}(\text{Br})(\text{thf})$ and $(\text{thf})_2\text{LiER}$. The structures of the $-\text{SeSi}(\text{SiMe}_3)_3$ (70) and both $-\text{TeR}$ derivatives have been determined crystallographically. The structures all possess a three-coordinate V centre with agostic interactions between two C–H groups of the amido trimethylsilyl ligands at the vacant apical coordination sites of the V atom. Oxidation of the V(III) species by styrene oxide, propylene sulfide and Ph_3PSe or Se to V(V) chalcogenides is described and the derivatives characterised by ^1H , ^{13}C and ^{51}V NMR spectroscopy. The X-ray crystal structure of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}(\text{Se})[\text{SeSi}(\text{SiMe}_3)_3]$ showed it to possess a rare example of a $[\text{V}=\text{Se}]^{3+}$ unit. The stability of these V(V) chalcogenates to reduction and isomerisation was investigated, the selenolates being found more stable than the tellurolates [88].



(70)

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The reactions of $\text{Me}_3\text{SiNHNMe}_2$ with $[\text{VCl}_3(\text{PMePh}_2)_2]$ or $[\text{VCl}_3(\text{thf})_3]$ led to the first example of a triply hydrazide-bridged complex, namely $[\text{NH}_2\text{Me}_2]_2[(\text{VCl}_3)_2(\mu\text{-NNMe}_2)_3]$ (71). Cation exchange reactions of the complex were investigated. Treatment of $[\text{V}(\text{OC}_6\text{H}_3^i\text{Pr}_{2-2,6})_4\text{Li}(\text{thf})]$ with NH_2NMe_2 gave the low melting point compound $[\text{V}(\text{OC}_6\text{H}_3^i\text{Pr}_{2-2,6})_3(\text{NH}_2\text{NMe}_2)_2]$ which was shown to possess monomeric V centres in a trigonal bipyramidal arrangement with axial hydrazine ligands [89].

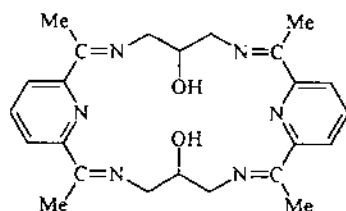


(Reproduced from ref. [89] with permission.)

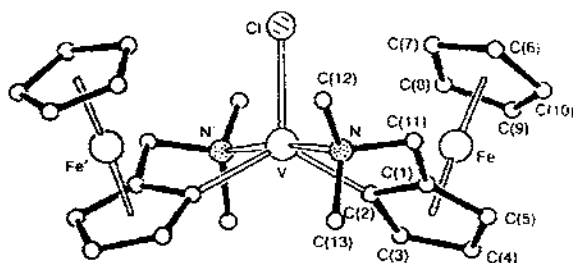
The reaction of VCl_3 with the amide ligand *N*-[2-((2-pyridylmethylene)amino)phenyl]pyridine-2-carboxamide (Hcapca) led to the formation of *trans*- $[\text{VCl}_2(\text{capca})]$ which is thought to be the first example of a V(III) complex containing a vanadium-deprotonated amide nitrogen bond. Reactions of $\text{VO}(\text{acac})_2$ with the related ligands H_2phepc , H_3hypb and H_4hybeb yielded the complexes $[\text{VO}(\text{phepc})]$, $\text{Na}[\text{VO}(\text{hypb})] \cdot 2\text{CH}_3\text{OH}$ and $\text{Na}_2[\text{VO}(\text{hybeb})] \cdot 3\text{CH}_3\text{OH}$ respectively. The crystal structures of a series of complexes of V(III), $\text{V}^{\text{IV}}\text{O}^{2+}$ and $\text{V}^{\text{VO}}\text{O}^{3+}$ each containing a vanadium-deprotonated amide nitrogen bond were determined. Various spectroscopic and magnetic measurements are reported for the complexes [90].

Antiferromagnetically coupled V(III) macrocyclic compounds $[\text{V}_2\text{L}(\text{H}_2\text{O})_4]^{4+}$ [H_2L = tetraimine Schiff base (72)] have been formed via transmetallation reactions of $[\text{Ba}(\text{H}_2\text{L})(\text{H}_2\text{O})_2][\text{ClO}_4]_2$ with either V(III) or vanadyl(IV) species. They were also formed through the template action of oxovanadium(IV) salts upon 2,6-diacylpyridine and 1,3-diaminopropan-2-ol [91].

The complex 1,2-*N,N*-dimethylaminomethylferrocenyl (L^-), acting as a ligand, reacts with $\text{VCl}_3(\text{thf})_3$ to give $[\text{VClL}_2]$ (73) which contains two didentate L^- ions. Reduction of the complex to V(II) by N_2 is under investigation [92].

 H_3L

(72)



(73)

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The intermolecularly stabilised V(III) amide complexes VL_3 and VL_2 have been obtained from reaction of $VBr_3(thf)_2$ with LiL ($HL = 2$ -(dimethylaminomethyl)pyrrolyl) and spectroscopic measurements carried out [93].

A series of macrocyclic thioether complexes of V(II), V(III) and (IV) has been synthesised and the structure of the V(III) crown thioether $[VCl_3\{9\}aneS_3]$ has been determined [94].

8. Vanadium(II)

Reaction of VI_2 with liquid NH_3 at room temperature led to the formation of $[V(NH_3)_6]I_2$ which was found to crystallise with the $K_2[PtCl_6]$ structural type in a high-spin configuration [95]. When the same reaction was carried out in the presence of traces of H_2O or O_2 the complex $[(NH_3)_5V-O-V-(NH_3)_5]I_4 \cdot NH_3$ was obtained. This structure was found to consist of corner-sharing octahedra, the double units of $[(NH_3)_5V-O-V-(NH_3)_5]^{4+}$ having an eclipsed conformation. Infrared spectra of the undeuterated and 5% deuterated samples suggested the presence of N–H...I bridge bonds and also the possibility of π -bonding between the V atom and the bridging O atoms [96].

(Bismesitylene)vanadium(0), $V(Mes)_2$, is oxidised to $VCl_2(dme)_n$ by CPh_3Cl in dme according to Eq. (7) [97].



Reaction of $[\text{VCl}_2(\text{tmeda})_2]$ with the tetralithium salt of octaethyl porphyrin, $(\text{oepg})[\text{Li}(\text{thf})]_4$, initially yielded a monomeric V^{II} complex $[(\text{oepg})\text{VLi}_4\text{Cl}_2(\text{thf})_4]$. Treatment of this complex with tetramethylethylenediamine resulted in a mixture from which $[(\text{oepg})\text{V}(\text{thf})_2][\text{Li}(\text{tmeda})_2] \cdot 0.5\text{toluene}$ and the unprecedented nitrido-bridged dimeric species $\{[(\text{oepg})\text{V}]_2(\mu\text{-N})(\mu\text{-Li})_4\}[\text{Li}(\text{tmeda})_2]$ were isolated and characterised. When the reaction was carried out in the absence of N_2 , $[(\text{oepg})\text{VO}][\text{Li}(\text{tmeda})_2]$ was obtained which suggested that the bridging N atom in the former complex is derived by cleavage of molecular dinitrogen. The O atom in this latter complex was thought to originate from deoxygenation of thf [98].

9. Solid-state compounds of vanadium

9.1. Vanadium silicates

The compound $\text{Nd}_4\text{V}_5\text{Si}_4\text{O}_{22}$ was found to be isostructural with $\text{Pr}_4\text{V}_5\text{Si}_4\text{O}_{22}$, consisting of rutile-like vanadium–oxygen layers and neodymium–oxygen layers formed by $[\text{Nd}_2\text{O}_{13}]$ dimers in a quasi-two-dimensional chevkinite-type structure [99].

9.2. Vanadium antimonates

New titanium-substituted vanadium antimonates have been prepared with nominal compositions $\text{VSb}_{1-x}\text{Ti}_x\text{O}_4$ and $\text{V}_{1-x}\text{Ti}_x\text{SbO}_4$ ($0 < x < 1$). Solid-state reactions over 2 days gave rutile-related vanadium antimonates of formula $\text{V}_{1-y}\text{Sb}_{1-y}\text{O}_4$ whereas material prepared by microwave for 15 min gave $\text{VSb}_{1-y}\text{O}_{4-2y}$ or $\text{VSb}_{1-y}\text{O}_{4-3/2y}$ type structures [100].

9.3. Vanadium nitrides

Polycrystalline vanadium oxynitrides have been prepared by heat treating V_2O_5 at high temperature in a flowing ammonia atmosphere. Single phase cubic samples with the rock salt structure were produced by this method at 600–700 °C. X-ray diffraction was not successful in unambiguously determining the structure due to various problems. Measurements were carried out on the electrical resistivity and magnetic susceptibility and lithium intercalation studies carried out. Only a small concentration of Li^+ ions were found to insert into the cathode due to the close packed nature of the structure [101].

9.4. Vanadium phosphates/phosphonates

A family of new alkali-metal/ammonium vanadium(V) methylphosphonates, $\text{M}(\text{VO}_2)_3(\text{PO}_3\text{CH}_3)_2$ ($\text{M} = \text{K}, \text{NH}_4, \text{Rb}, \text{Tl}$), has been synthesised hydrothermally and the single crystal X-ray structures of the K and NH_4 derivatives determined.

The isostructural, noncentrosymmetric phases are built up from hexagonal tungsten oxide-like sheets of vertex-sharing VO_6 octahedra, capped on both sides of the V/O sheets by PCH_3 entities from $[\text{PO}_3\text{CH}_3]^{2-}$ groups [102].

Dark green single crystals of $\text{Sr}_2(\text{VO})(\text{P}_2\text{O}_8)$ have been prepared in solid-state reactions in closed quartz tubes. X-ray studies showed the compound to be isotypic with $\text{Sr}_2(\text{VO})(\text{V}_2\text{O}_8)$ having V^{4+} cations in split positions [103].

Complex formation between oxovanadium(IV) and phosphonate ligands has been investigated by pH potentiometric techniques, UV and EPR spectroscopy. In contrast to the situation with monophosphate which binds the metal-forming four-membered chelated rings, methylphosphonate acts only as a monodentate ligand [104].

The new vanadium phosphate $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NH}_2[(\text{VO})_4(\text{H}_2\text{O})_4(\text{HPO}_4)_2(\text{PO}_4)_2]$ has been prepared from the reaction of VCl_4 with phosphoric acid, 1,4-diaminopiperazine hydrochloride, tetra-*n*-butylammonium hydroxide and water in a sealed glass tube at 200 °C for 3 h. The phosphate was found to have a three-dimensional covalently bonded network of vanadium phosphate with occluded organic cations occupying tunnels within the oxide framework [105].

A series of mononuclear, one-, two- and three-dimensional species, namely $\text{Cs}[\text{VO}(\text{HO}_3\text{PCH}_2\text{PO}_3\text{H})_2(\text{H}_2\text{O})]$, $\text{Cs}[\text{VO}(\text{HO}_3\text{PCH}_2\text{PO}_3)]$, $\text{Cs}[(\text{VO}_2)_2\text{V}(\text{O}_3\text{PCH}_2\text{PO}_3)_2(\text{H}_2\text{O})_2]$ and $[\text{V}(\text{HO}_3\text{PCH}_2\text{PO}_3)(\text{H}_2\text{O})]$, has been isolated by varying the reaction temperatures, times and stoichiometries of the reactants in the CsVO_3 /methylenediphosphonate system. The $[\text{VO}(\text{HO}_3\text{PCH}_2\text{PO}_3\text{H})_2(\text{H}_2\text{O})]^-$ anion consists of isolated V(IV) octahedra. Two-dimensional $\text{Cs}[\text{VO}(\text{HO}_3\text{PCH}_2\text{PO}_3)]$ adopts a chain structure constructed from corner-sharing V(IV) octahedra forming infinite $\{-\text{V}=\text{O}-\text{V}=\text{O}-\}$ linkages. The layer structure of $\text{Cs}[(\text{VO}_2)_2\text{V}(\text{O}_3\text{PCH}_2\text{PO}_3)_2(\text{H}_2\text{O})_2]$ contains trinuclear units of corner-sharing VO_6 octahedra having central V(III) atoms and V(IV) centres at the extremities of the cluster. The compound $[\text{V}(\text{HO}_3\text{PCH}_2\text{PO}_3)(\text{H}_2\text{O})]$ has isolated V(III) O_6 octahedra linked by diphosphonate groups in a three-dimensional framework [106].

A further five mixed-ligand vanadium(III) phosphate/phosphonate complexes have been isolated and structurally characterised. The complexes $[\text{LVCl}\{\mu-(\text{PhO})_2\text{PO}_2\}]_2$, $[\text{LVCl}\{\mu-\text{Ph}_2\text{PO}_2\}]_2$, $[\text{LVCl}\{\mu-\text{PhP}(\text{H})\text{O}_2\}]$, $[\text{LV}\{(\text{PhO})_2\text{POS}\}_2\text{DMF}]$ and $[\text{LV}\{(\text{PhO})_2\text{PO}_2\}]_2 \cdot \text{H}_2\text{O}$ ($\text{L} = \text{hydrotris}(\text{pyrazolyl})\text{borate}$) are thought to provide good models for the possible modes of bonding between V(III) and biological phosphates such as DNA [107].

The first vanadium aluminophosphates, $\text{Cs}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$, $\text{Rb}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$, $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$ and $\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2]$, have been hydrothermally prepared. The phosphates are built up from tetrahedrally coordinated Al and P atoms and either octahedral $\text{Cs}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$, $\text{Rb}[(\text{VO})\text{Al}(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$ and $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[(\text{VO})\text{Al}(\text{PO}_4)_2]$ or square pyramidal V atoms $(\text{CH}_3\text{NH}_3[(\text{VO})\text{Al}(\text{PO}_4)_2])$ [108].

Kinetic studies have been carried out on the reactions of PAPr (purple acid phosphatase) from porcine uteri with VO_4^{3-} ions using stopped-flow monitoring of the systems by UV-vis absorbance [109].

9.5. Vanadium arsenates

A new polymorph of strontium vanadium(IV) arsenate, $\text{Sr}(\text{VOAsO}_4)_2$, has been synthesised hydrothermally at 450 °C in a quartz glass tube and characterised by single crystal X-ray diffraction and magnetic susceptibility measurements. The three-dimensional $[\text{V}_2\text{As}_2\text{O}_{10}]_x$ network consists of infinite chains of *cis*-corner-sharing octahedra linked by arsenate groups along [010] and [001]. The strontium atoms are located in one-dimensional channels along the chain direction. Magnetic measurements confirmed the presence of V(IV) [110].

9.6. Vanadium oxides

A report has been made upon the influences of different parameters such as molar ratio of precursors, relative humidity, etc. on the nature of the final products in the V–Nb–O system. The mixed oxides MVO_5 ($\text{M}=\text{Nb}, \text{Ta}$), prepared using sol–gel techniques, are isostructural with orthorhombic unit cells. The thermal behaviour of the materials has been investigated and the effect of lithium insertion into the mixed oxides tested with a view to possible usage of the materials in lithium cells [111]. The hydrothermal synthesis of a new class of solid-state materials, $(\text{L}_2\text{M})_x[\text{VO}_x]$ (L =didentate amine, $\text{M}=\text{Cu}$ or Zn) has been reported. The compounds comprise mixed-valence vanadium oxide layers with interlamellar coordination complexes [112].

The syntheses and properties of various mixed-metal oxovanadates have been reported. Single crystals of KBaVO_4 and KSrVO_4 have been prepared by crystallisation from a V_2O_5 flux. Both compounds show an ordered distribution of K^+ , Ba^{2+} and Sr^{2+} ions [113]. The same group has reported investigations into the Ba/vanadyl/vanadate system. Single crystals of $\text{Ba}_2(\text{VO})\text{V}_2\text{O}_8$ were prepared from the reaction of $\text{Ba}_2\text{V}_2\text{O}_7$, V_2O_3 and V_2O_5 in sealed silica tubes. The compound was found to be monoclinic comprising tetrahedral V^{5+} ions and V^{4+} ions inside $\frac{1}{2}[\text{V}(3)\text{O}_4]$ chains having square pyramidal coordination with a short apical V–O distance. The structure type is therefore different from that of $\text{Sr}_2(\text{VO})\text{V}_2\text{O}_8$ [114].

Hydrothermal reactions in the V_2O_4 – SeO_2 – KOH system under controlled conditions led to the formation of a new compound, $\text{K}(\text{VO})(\text{SeO}_3)_2\text{H}$, composed of chains of V(IV) atoms linked by double bridges of selenite groups. Spectroscopic evidence suggests that there is a H atom between the chains which forms a strong hydrogen bond. Low temperature antiferromagnetic behaviour confirmed the one-dimensional nature of the material [115].

Single crystals of $\mu\text{-Mg}_2\text{CuV}_2\text{O}_8$ and $\text{MgCu}_2\text{V}_2\text{O}_8$ have been prepared in solid-state reactions. Both were found to be monoclinic with ordered metal distributions and with the V atoms tetrahedrally coordinated by oxygen. $\mu\text{-Mg}_2\text{CuV}_2\text{O}_8$ has elongated CuO_6 octahedra and $\text{MgCu}_2\text{V}_2\text{O}_8$ has trigonal CuO_5 bipyramids [116].

Mercury vanadates having the empirical formulae HgVO_3 and Hg_2VO_4 have been prepared by annealing mercury(II) oxide with an amorphous mercury vanadate of approximate composition HgV_2O_6 in molar ratios varying from 1:1 to 4:1 in evacuated sealed silica tubes at 400 °C. The crystal structures of both compounds were

determined and in both compounds the V atoms were found to be irregularly surrounded by five oxygen atoms. The resulting coordination polyhedra form infinite $(VO_3^-)_n$ chains aligned parallel to each other. The compounds differ in the situations of the Hg atoms [117].

The X-ray crystal structure of β -AgVO₃ has been determined and was found to consist of a three-dimensional network of V atoms and three Ag atoms with the associated O atoms in the surroundings to constitute $[Ag_3V_4O_{12}]_n^{3-}$ units. The fourth Ag cation is inserted in a monocapped trigonal prism and is thought responsible for conductivity in the material. The structure of the compound is compared with other silver vanadium oxide bronzes such as Ag₂V₄O₁₁ and δ -Ag_xV₂O₅ [118].

The compound (CsCl)Cs₂(TeV₂O₇)₂ was obtained at 700 K during the crystallisation of a mixed tellurium–caesium vanadate using TeCl₄ as a transport agent. The structure consists of stacks of [V₂TeO₇] sheets alternately separated by layers of Cs atoms and layers of Cs and Cl atoms. Within the sheets the V atoms are distributed over two sites: a tetrahedral site containing V⁵⁺ ions and a square pyramidal site containing V⁴⁺ ions. The Te⁴⁺ ion lies within a tetrahedron formed by three O atoms and a lone pair, which is expected to act as a maximum in the electron density map [119].

The new compounds Ln₃VO₄Cl₆ (Ln = La, Ce, Pr, Nd) were prepared by heating a mixture of LnCl₃, LnOCl and V₂O₅ (3:3:1) in evacuated, sealed silica ampoules at 850 °C for 5 days. Single crystals of the lanthanum compound were obtained by chemical vapour transport using Cl₂ gas as the transport agent. Apart from the lower coordination number of V⁵⁺ as compared to Nb⁵⁺, the structure is closely related to that of Pr₃NbO₄Cl₆ [120]. In a similar system, the La vanadate La₃VO₄Cl₅ was prepared by heating a mixture of LaOCl, LaCl₃ and VO₂ (2:1:1) at 900 °C for 8 days and has been investigated using electron microscopy [121].

Intercalation of V₂O₅ · *n*H₂O xerogels with neutral organic species usually results in compounds which retain the lamellar structure with the guest species occupying the interlayer regions. When organic amines are used as the intercalation species partial reduction of the V to V⁴⁺ is often observed with simultaneous oxidation of the guest species. The materials formed can be viewed as molecular or polymer bronzes and interest in their properties has led to the formation of various examples such as $[(HN(C_2H_4)_3NH)][V_6O_{14}] \cdot H_2O$. This compound was obtained from the hydrothermal reaction of V₂O₅, 1,4-diazabicyclo[2,2,2]octane and H₂O in a sealed bomb at 170 °C for 45 h. The structure was found to consist of layers of composition $[(V^{5+})_2(V^{4+})_4O_{14}]^{2-}$ with protonated $[HN(C_2H_4)_3NH]^{2+}$ dications and water molecules in the interlayer region [122]. The same group has prepared a further four mixed-valence vanadium oxides containing interlamellar organic cations, α -(H₃N-(CH₂)₂NH₃)[V₄O₁₀], β -(H₃N(CH₂)₂NH₃)[V₄O₁₀], α -(H₂N(C₂H₄)₂NH₂)[V₄O₁₀] and β -(H₂N(C₂H₄)₂NH₂)[V₄O₁₀]. The hydrothermal syntheses and crystal structure determinations are reported for all four complexes. Each compound was found to contain mixed valence V⁴⁺/V⁵⁺ vanadium oxide layers made up of V⁵⁺O₄ tetrahedra and pairs of edge-sharing V⁴⁺O₅ square pyramids with protonated organic amines occupying the interlayer spaces [123].

9.7. Vanadium sulfates

Crystal structure determinations of the alums $MV(SO_4)_2 \cdot 12H_2O$ ($M = K, Rb, Cs$) showed them all to belong to the β -structural class. Analysis of the neutron structures enabled a fairly good prediction of the hydrogen atom positions in the H_2O molecules and showed the water to be coordinated to V(III). This behaviour is not observed in analogous Cr(III) and Fe(III) alums and is thought to occur due to a lifting of the degeneracy of the $^3T_{2g}(O_h)$ ground term resulting from unsymmetrical occupancy of these orbitals [124].

9.8. Vanadium chalcogenides

The quaternary sulfides K_2AgVS_4 and Rb_2AgVS_4 have been shown to crystallise as dark violet needles from a molten reactive flux. In the structures infinite Ag- and V-centred tetrahedra of S^{2-} anions, sharing common edges, run parallel to the crystallographic a axis. The chains are separated by K^+ or Rb^+ ions in an eight-fold environment and the tetrahedra are arranged in an ordered fashion. The V–S distances are in the normal range for this type of compound but the Ag–S distances are very short, indicating a degree of covalent bonding between Ag^+ and S^{2-} [125].

A low temperature synthesis has been reported for the vanadium selenides V_2Se_9 and V_5Se_4 using the average composition of the amorphous reaction intermediate to control phase nucleation. The approach is focused on the use of superlattice reactants which are designed to form amorphous alloys at low temperatures. These are then used as metastable reaction intermediates for the preparation of solid state compounds. Evidence is presented for a new kinetically stable vanadium selenide with composition close to $V_{0.8}Se$ which disproportionates upon heating [126].

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