7. Vanadium 1990

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CONTENTS

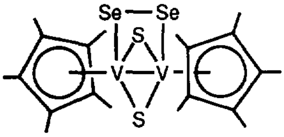
INTRODUCTION

Vanadium is one of the most interesting and reactive elements with a very rich chemistry in all of its formal oxidation states from +5 to –1. Its most stable oxidation state is +4. The lower oxidation states are strongly reducing and stable only at low temperatures. The first reports of organovanadium complexes can be traced back to the days of the discovery of ferrocene (1950s); however, progress since then has been slow. This review highlights some of the discoveries reported in the year 1990 in the area of coordination chemistry of vanadium. It is by no means a complete and comprehensive survey of such complexes, and it is hoped that selected literature will depict the highly exciting but yet unexplored nature of this field. We would like to thank Ms. Maria G.L. Petrucci (McGill University) and Dr. Catherine E. Housecroft (Institut für Anorganische Chemie, Universität Basel) for editorial corrections.

7.1 COORDINATION COMPLEXES

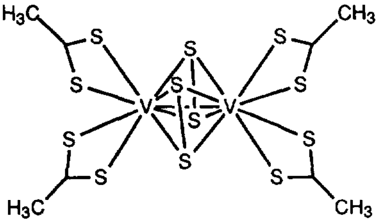
7.1.1 Complexes containing vanadium-vanadium bonds:

Mixed chalcogen dinuclear complexes of vanadium containing both sulfur and selenium bonded to the metal have been prepared [1] by the reaction of the compounds of the type, $[Cp^*{}_2V_2E_n]$ (E = S, Se; n = 3, 4) with chalcogen donors of compositions Na_2S_{22} and Na_2Se_5. A single crystal X-ray structure determination of $[Cp^*{}_2V_2Se_2S_2]$ (**1**) revealed that the vanadium centres are triply bridged [V-V bond length of 264.1(2)pm] with a diselenide bridge parallel to the V-V bond.



(1)

Divanadium tetrakis(dithioacetate) containing two μ-η^2-S_2 bridges, $[V_2(S_2)_2(S_2CCH_3)_4]$ (2), has been prepared by reacting bis(benzene)vanadium(0) with dithioacetic acid [2].

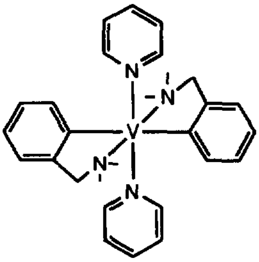


(2)

The results of a study involving metal-metal and metal-ligand interactions using *ab initio* SCF/CI calculations on a cyclopentadienylvanadium butanediyl dimer have been reported [3].

7.1.2 Vanadium(II)

A convenient method for the synthesis of octahedral high-spin vanadium(II) complexes, *trans*-$[L_4VCl_2]$, involves bridge splitting reactions of $[V_2(\mu\text{-}Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with nitrogen donor ligands such as *N,N,N′,N′*-tetramethylethylenediamine, pyrrolidine and pyridine. These complexes were then used to prepare the first dinitrogen derivative $[\{py(Mz)_2V\}_2(\mu\text{-}N_2)]$ [Mz= *o*-$C_6H_4CH_2N(CH_3)_2$] and the monomeric complex *trans*-$[Vpy_2(Mz)_2]$ (3) which has been crystallographically characterized [4].



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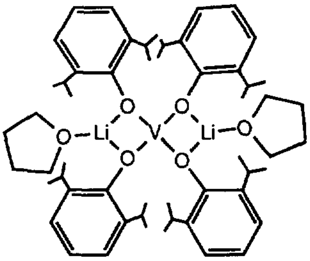


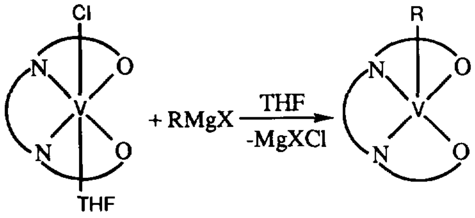
(4)

The first example of a four coordinate and planar V(II) complex, $[V(DIPP)_4\{Li(thf)\}_2]$ (DIPP= 2,6-diisopropylphenoxide) (4) has been prepared and structurally characterized [5]. As expected, this low valent and coordinatively unsaturated complex was found to be extremely reactive towards a variety of reagents at room temperature.

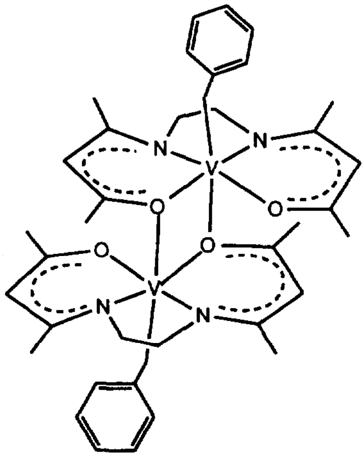
A hexaaquavanadium(II) salt $[V(H_2O)_6](CF_3SO_3)_2$ was conveniently prepared from metallic vanadium and aqueous trifluoromethylsulfonic acid [6]. This water-soluble salt is a good starting material for the preparation of a variety of vanadium(II) complexes by displacing water molecules with other donor ligands *e.g.*, treatment of $[V(H_2O)_6](CF_3SO_3)_2$ with ethylenediamine affords $[V(en)_3](CF_3SO_3)_2$.

7.1.3 *Vanadium(III)*

Schiff-base vanadium(III) complexes containing V-C bonds, V(acen)R (6) (R = CH_3, $CH_2C_6H_5$, C_6H_5, 2,4,6-$(CH_3)_3C_6H_2$) have been prepared by the reaction of [(thf)V(acen)Cl] (5) with Grignard reagents [7]. The compound, $[V(acen)C_6H_5]$ is monomeric while $[V(acen)CH_2C_6H_5]$ consists of centrosymmetric dimers (7) as determined from their X-ray crystal structure characterization. These compounds exhibited hydrogen-bonding between aryl groups and the oxygen atoms of the Schiff-base ligand.



(5) (6)



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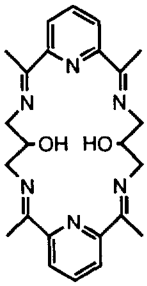
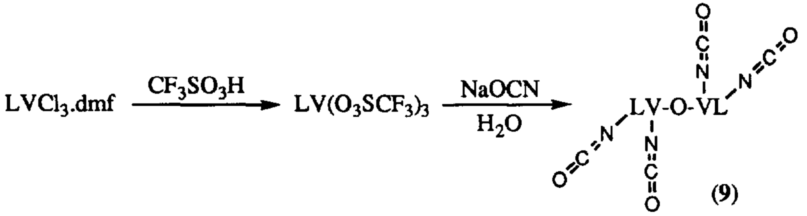


H_2L

(8)

A dinuclear vanadium (III) complex containing the Schiff base macrocycle, H_2L (**8**) (1,7,14,20-tetramethyl-2,6,15,19-tetraaza[7,7](2,6)pyridinophane-4,17-diol) has been prepared [8] by transmetallation of $[Ba(H_2L)(H_2O)_2](ClO_4)_2$ with VCl_3 to give $[V_2L(H_2O)_4](ClO_4)_4.2H_2O$. The crystal structure of this compound contains a symmetrical complex cation surrounded by four perchlorate ions. Dinuclear complexes containing a $[V^{III}–O–V^{III}]$ bridging unit such as $[L_2V_2(OCN)_4(\mu\text{-}O].2H_2O$ (**9**) have been prepared by first reacting $[LVCl_3.dmf]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) with CF_3SO_3H to give $[LV(O_3SCF_3)_3]$, and then reacting the latter with NaOCN (scheme 1) [9].

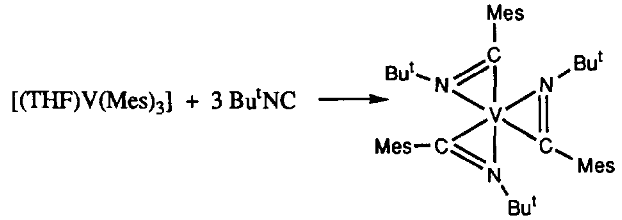


(**9**)

Scheme 1

Vanadium(III) chloride has been shown to react with 2,2'-bipyridine in de-aerated water to give an oxo-bridged dinuclear complex containing the dication $[\{VCl(bpy)_2\}_2O]^{2+}$ which has been structurally characterized [10].

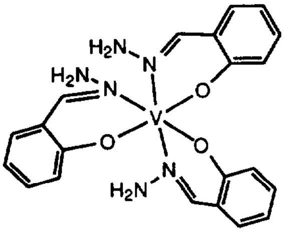
A tris(η^2-iminoacyl) complex, $[V(\eta^2\text{-}Bu^tNCMes)_3]$ (Mes = 2,4,6-$(CH_3)_3C_6H_2$) (**10**) was prepared by the insertion of tert-butylisocyanide into the V-C bonds of $[V(Mes)_3(thf)]$ at room temperature [equation (i)] [11].



(**10**) (i)

The compound, tris(salicylaldehyde hydrazonato)vanadium(III) $[V(OC_6H_4CHNNH_2)_3]$ (**11**) has been synthesized by reacting (i) $[V(NH_2NHPh)_2(salen)]I$ with anhydrous hydrazine in methanol, (ii) [VO(salen)] with hydrazine in acetonitrile-methanol at reflux, (iii) $[VCl_3(thf)_3]$ with salicylaldehyde, salicylaldehyde hydrazone or salazine, and an excess of hydrazine, or (iv) $[VCl_3(thf)_3]$ with 3-methoxysalicylaldehyde or 5-bromosalicylaldehyde and an excess of hydrazine [12]. The crystal structure of the red coloured vanadium(III) salicylaldehyde hydrazone complex was determined.

A dihydrogen complex of vanadium, $[(\eta^5\text{-}C_5H_5)V(CO)_3(H_2)]$ obtained by photolysis of $[(\eta^5\text{-}C_5H_5)V(CO)_4]$ and H_2 in n-heptane at 25°C and liquid xenon at –78°C has been spectroscopically characterized in solution [13].

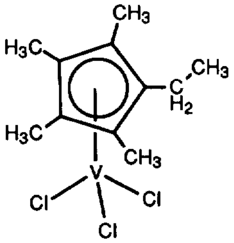


(11)

7.1.4 Vanadium(IV)

Spectroscopic and single-crystal X-ray diffraction studies of $[(\eta^5\text{-}C_5Me_4Et)VCl_3]$ have been reported [14]. The molecule is shown to adopt a three-legged piano-stool structure **(12)**.

Vanadium tetrafluoride, a light green moisture sensitive compound, has been prepared by reacting vanadium powder with fluorine at 280°C [15]. A comparison of its structure with that of SnF_4 revealed that the two structures are related. However, VF_6-octahedra in the vanadium tetrafluoride layers are tilted with the bond angle of V-F-V 150.7° while that in SnF_4 is 180°.



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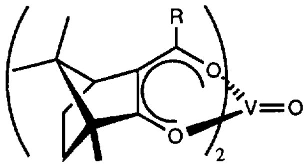


(13)

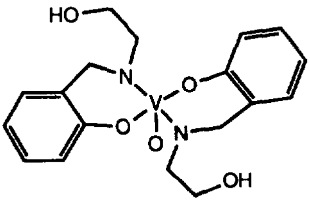
Oxo-vanadium(IV) complexes, bis(3-acylcamphorate)oxovanadium(IV) **(13)** have been prepared [16] by reacting vanadyl sulfate, $VOSO_4.5H_2O$, with the camphor ligands and NEt_3 in ethanol/water mixture, or reacting $[VO(acac)_2]$ and the camphor ligands in toluene, xylene or mesitylene at 100-180°C. The compound, bis(3-heptafluorobutyrylcamphorato)oxovanadium was found to catalyse the cycloaddition of aldehydes to activated dienes to give pyrones.

A vanadium(IV) complex containing a nitrogen rich ligand, [VO(pycac)], is prepared by reacting *N*-[2-(4-oxopentan-2-ylideneamino)phenyl]pyridine-2-carboxamide (H_2pycac) with bis(pentane-2,4-dionato)oxovanadium(IV) $[VO(acac)_2]$ in methanol [eqautions (ii) and (iii)] [17]. The crystal structure of the title vanadium(IV) amide complex shows a square pyramid vanadium in which the oxo ligand occupies the apical position and the tetradentate amide ligand, the basal plane.

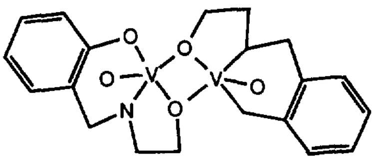
$$N\text{-(2-aminophenyl)pyridine-2-carboxamide} + \text{pentane-2,4-dione} \longrightarrow H_2\text{pycaac} \qquad \text{(i)}$$

$$[VO(acac)_2] + H_2\text{pycac} \longrightarrow [VO(\text{pycac})] + 2\,\text{Hacaac} \qquad \text{(ii)}$$

Monomeric and dimeric vanadium(IV) complexes of *N*-(hydroxyalkyl)salicylideneamine ligands, 2-(salicylideneamino)-1-hydroxyethane (H_2SALAHE), 3-(salicylideneamino)-1-hydroxypropane (H_2SALAHP), 2-(salicylieneamino)-2-methyl-1-hydroxypropane (H_2SALAMHP), 2-(salicylideneamino)-2-methyl-1-hydroxyethane (H_2SALAMHE), tris(hydroxymethyl)(salicylideneamino)methane (H_2SALATHM) have been prepared by varying the metal to ligand ratio [18]. In a 2:1 ligand to metal ratio, monomeric complexes such as [VO(HSALAHE)$_2$] crystallize out while in 1:1 ratio, dimeric [VO(SALAHE)]$_2$ complexes are obtained. Crystal structures of VO(HSALAHE)$_2$ and dialkoxy-bridged dimers, [VO(SALAHE)]$_2$ and [VO(SALAMHP)]$_2$O, and the magnetic properties of these complexes are also reported.



(14) VO(HSALAHE)$_2$

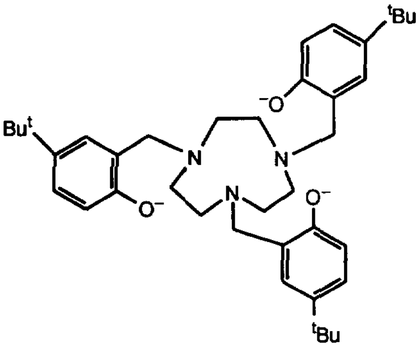


(15) [VO(SALAHE)]$_2$

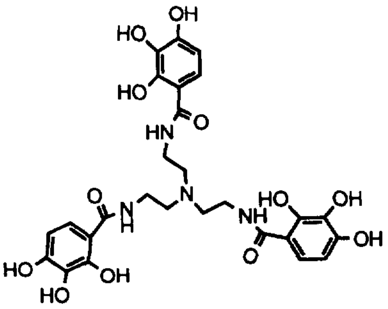
The nature of a tris(catecholato)vanadate(IV) complex in aqueous solution has been determined using ESR spectroscopy [19].

Synthesis, differential thermal analysis and the crystal structure of the high temperature β-polymorph of a vanadium(IV) pyrophosphate, $K_2V_3P_4O_{17}$ have been reported [20].

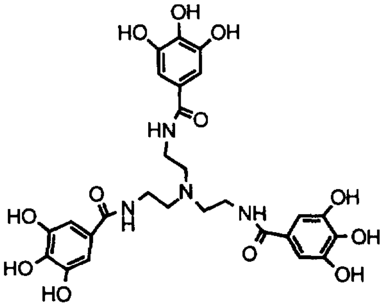
Vanadium(IV) complexes of the type [LV]X (X = ClO_4 or BPh_4) where H_3L = 1,4,7-tris(5-t-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane have been prepared by first reacting the tripotassium salt of the anion **(16)** with VCl_3 in CH_3CN, and then oxidizing the LV^{III} complex thus obtained with $HClO_4$ followed by metathesis with $NaBPh_4$ [21]. Vanadium(IV) complexes of the isomeric tris(pyrogallol) derivatives, 2,3,4-TRENPAM amd 3,4,5-TRENPAM ligands **(17)** and **(18)** have been prepared [22].



(16)



(17) 2,3,4-TRENPAMH$_9$



(18) 3,4,5-TRENPAMH$_9$

7.1.5 *Vanadium(V)*

Vanadium(V) (trimethylsilyl)imido compounds of the type $[V(NSiMe_3)Cl_3(4\text{-}Etpy)_2]$ and $[V(NSiMe_3)Cl_3(4\text{-}^tBupy)_2]$ have been prepared by reacting $[V(NSiMe_3)Cl_3]$ with ethyl- or ^{t}butylpyridine (scheme 2) [23]. These complexes undergo facile loss of chlorotrimethylsilane to give $[V(N)Cl_2L_2]$.

$$\begin{tikzcd} V(NSiMe_3)Cl_3 + 2L \arrow[r] & V(NSiMe_3)Cl_3L_2 \arrow[d] \\ & V(N)Cl_2L_2 + SiMe_3Cl \end{tikzcd}$$

L = 4-ethylpyridine
= 4-^{t}butylpyridine

Scheme 2

Hydrothermal growth of oxocopper(II) vanadate(V) hydrates, $Cu_3V_2O_8(H_2O)$ and $CuV_2O_6(H_2O)_2$ from $[Cu_3V_2O_8.3H_2O)$ or $[Cu_3V_2O_8]$ in ammonium fluoride solution at 493K, and their crystal structures have been reported [24].

The synthesis and structure determination of peroxo-glycine-vanadium complexes of the type $[NH_4][VO(O_2)_2GlyH].H_2O$, $K[VO(O_2)_2GlyH].H_2O$ and $[V_2O_2(O_2)_3(GlyH)_2(H_2O)_2]$ have been carried out [25].

7.1.6 *Vanadium(-I)*

The synthesis, ESR spectra and reactivity with CO and CO_2 of potassium salts of bis(arene)vanadium anions (arene = benzene, mesitylene) have been reported. The salts are prepared according to equation (iv) [26].

$$[V(arene)_2] + K \longrightarrow K[V(arene)_2] \quad arene = C_6H_6;\ C_6H_3\text{-}1,3,5\text{-}Me_3 \qquad (iv)$$

The syntheses of dinitrosyl complexes of vanadium(-I), $[V(NO)_2(bpy)_2]CN$ and $[V(NO)_2(bpy)_2]ClO_4$, and their decomposition and hydrolytic chemistry have been reported [27].

7.2 CATALYSIS

Vanadium bromoperoxidase has been shown to catalyse the oxidation of chloride by hydrogen peroxide and the chloride-assisted disproportionation of hydrogen peroxide [28].

A vanadium pillared clay, prepared from montmorillonite and vanadia, has been shown to catalyse molecular recognition of primary and para-substituted benzyl alcohols [29]. It has also been demonstrated that a vanadium pillared montmorillonite catalyst exhibits regioselectivity in epoxidation reactions towards internal allylic double bonds compared to terminal allylic double bonds [30].

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