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4. VANADIUM

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CONTENTS

INTRODUCTION

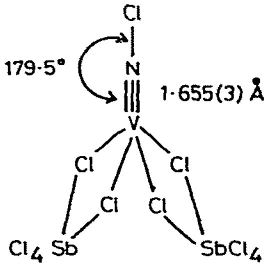
In reviewing the chemistry of vanadium for 1979 the decision was taken to omit the organo-metallic chemistry of the element, and all aspects of catalysis, as both these important areas are fully reviewed elsewhere.

There does not appear to have been a major development in the chemistry of vanadium in 1979, which remains dominated by vanadium-oxo species. This review is arranged in short sections. The major divisions are based upon valence states, and within a valence state sub-division is based upon the species bound to the metal.

4.1 VANADIUM (V)

4.1.1 Complexes with Group VII elements

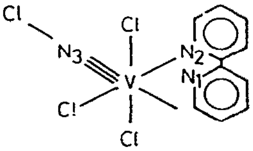
Vanadium(V) halide species containing a multiply-bonded V=X moiety (X = O, N—Cl or N—I) have been studied in a number of contexts. From the reaction of VCl_3O with either HF or KF in MeCN solution, evidence for the formation of $[VCl_4O(MeCN)]^-$, $[VCl_3FO(MeCN)]^-$, $[VCl_2F_2O(MeCN)]^-$, $[VClF_3O(MeCN)]^-$ and $[VF_4O(MeCN)]^-$ was obtained by ^{51}V NMR spectroscopy [1]. The major products of the reaction were the species containing two, three and four chlorine atoms, only traces of the others being detected. Strähle and co-workers isolated a number of vanadium(V) nitrene compounds and investigated the coordination chemistry of Cl_3VNCl [2]. From the reaction of Cl_3VNCl with $SbCl_5$, a 1 : 2 compound was isolated in which the $SbCl_5$ fragments are linked via chlorine bridges to the vanadium atom (1).



v(V≡N) = 1108 cm⁻¹

(1)

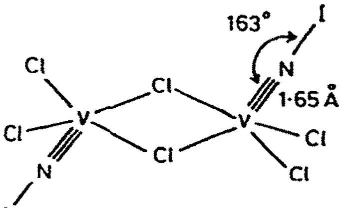
The Cl—N—V fragment is essentially linear {$\widehat{ClNV}$ = 179.5°, r(VN) = 1.655(3) Å; ν(V≡N) = 1108 cm^{-1}}. Other Lewis acids did not give stoicheiometric products with Cl_3VNCl. However, with Lewis bases, a whole range of adducts was isolated, namely $Cl_3(R_3P)VNCl$, $Cl_3(py)_nVNCl$ (n = 1 or 2) and [Cl_3(bipy)VNCl] (2), whose structure was determined. In (2), as in (1), the



r (VN_1) = 2·185(6) Å
r (VN_2) = 2·130(6) Å
r (VN_3) = 1·688(6) Å

(2)

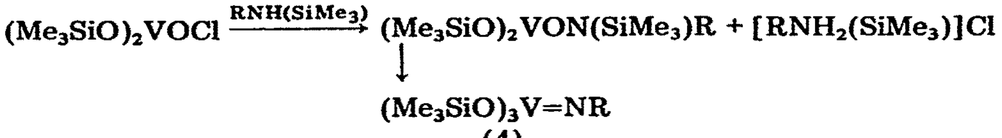
Cl—N—V fragment is linear, with r(V—NCl) = 1.688(6) Å; the mean $\bar{r}$(V—N_{bipy}) bond length is 2.16 Å. In contrast a bent V—N—Cl fragment is suggested (on the evidence of IR spectroscopy) to be present in $[Cl_5VNCl]^{2-}$, implying a double V=N bond {ν(V=N) = 925 cm^{-1}}. From the reaction of IN_3 with VCl_4 the dimeric compound [$(Cl_3VNI)_2$] (3) has been isolated, which contains a near linear V—N—I nitrene system {$\widehat{INV}$ = 163°; r(VN) = 1.65 Å}. This implies, as in the V—N—Cl species, a sp hybridised nitrogen atom which donates its lone pair to the vanadium atom [3].



(3)

4.1.2 Complexes with Group VI donor ligands

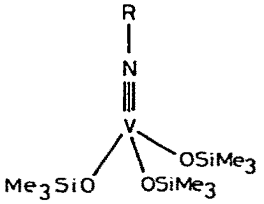
Related to the nitrene complexes discussed above is $(Me_3SiO)_3V{=}NR$ (R = CMe_3 or 1- adamantyl) which is prepared via a rearrangement reaction [4]



$$(Me_3SiO)_2VOCl \xrightarrow{RNH(SiMe_3)} (Me_3SiO)_2VON(SiMe_3)R + [RNH_2(SiMe_3)]Cl$$
$$\downarrow$$
$$(Me_3SiO)_3V{=}NR$$

(4)

The structure of (4; R = 1-adamantyl) has been determined and the V—N—C fragment is nearly linear {175.8(2)°}; the V—N bond is triple {r(V—N) = 1.614(2) Å) and the vanadium atom four coordinate.



(4)

The oxo-anions of vanadium continue to have an important part in the chemistry of vanadium. Corner-sharing {VO_4} tetrahedra, giving rise to $[V_2O_7]^{4-}$, have been shown to be present in $Na_4V_2O_7 \cdot 18\ H_2O$ [5]. Two environments were observed for the sodium ions, namely infinite chains of face-sharing octahedra and $Na_2(H_2O)_9$ units.

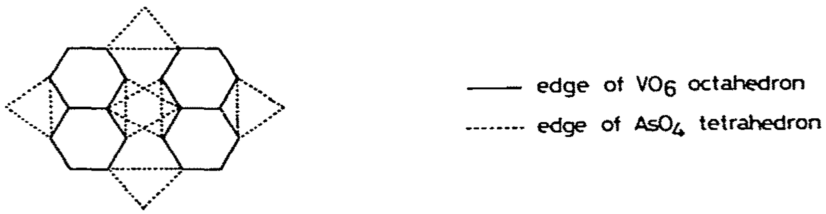
The reaction of NpO_2 with V_2O_5 in a 1 : 2 molar ratio gives rise to $Np(VO_3)_4$, which contains {VO_4} tetrahedra linked by corner-sharing to form infinite parallel $(VO_3)_n$ chains. In between these chains are eight coordinate neptunium atoms, which bridge adjacent chains [6]. The IR spectra of a series of metavanadates MVO_3 (M=NH_4, ND_4, K, Rb or Cs) have been measured at room and low temperature, and the VO_2 and V—O—V bending modes assigned to 390—330 and 280—210 cm^{-1}, respectively [7].

The mixed cation orthovanadate $Cd_4Na[VO_4]_3$ contains chains of {CdO_6} octahedra that are linked through shared oxygen atoms to {VO_4} tetrahedra. The resulting three-dimensional framework contains voids, some of which contain sodium or cadmium atoms in a tetrahedral environment [8].

Full details of the preparation of two decavanadates $Na_6[V_{10}O_{28}] \cdot 18\ H_2O$ and $[NH_4]_6\ [V_{10}O_{28}] \cdot 6\ H_2O$ are available. The sodium salt is prepared by an ethanoic acid-induced condensation of Na_3VO_4, while the ammonium compound is obtained from the reaction of V_2O_5, ammonia and water [9].

The intercalation of lithium ions into V_2O_5 has been shown to yield a series of bronzes. Treatment of V_2O_5 with an ethanenitrile solution of LiI at room temperature yields a series of bronzes $Li_xV_2O_5$ ($0 < x \leqslant 1.0$) whose structure is different from compounds with the same stoicheiometry that were formed at high temperature. The new compounds appear to have structures closely related to that of V_2O_5 [10]. Confirmation of these results came from electrochemical studies. Open circuit voltages in systems in which $Li_xV_2O_5$ is an electrode show that three phases exist: I, where $0 < x < 0.1$; II, where $0.35 < x < 0.5$; and III, where $0.9 < x < 1.0$. All these phases have orthorhombic cells similar to that of V_2O_5 [11]. The β-phase of $Na_xV_2O_5$ behaves partly as a one-dimensional metal and partly as an anisotropic semiconductor. The structure of $Na_xV_2O_5$ ($x = 0.287$) was examined by X-ray techniques and it was shown that disordered strings of sodium atoms exist in the tunnels formed by the chain-like array of vanadium and oxygen atoms (see Figs. 1 and 2) [12].

A new type of vanadium—arsenic condensed anion $[As_6V_4O_{30}]^{10-}$ (5) has been characterised by X-ray studies upon $[NH_4]_4H_6[As_6V_4O_{30}] \cdot 4\ H_2O$. The anion consists of a double pair of edge-sharing octahedra linked by AsO_4 tetrahedra (5) [13].



(5)

Björnberg has reported structural studies on $[Mo_4V_8O_{36}]^{8-}$ [14] and $[Mo_6V_2O_{26}]^{6-}$ [15]. The $[Mo_4V_8O_{36}]^{8-}$ anion (Fig. 3) has an inversion centre,

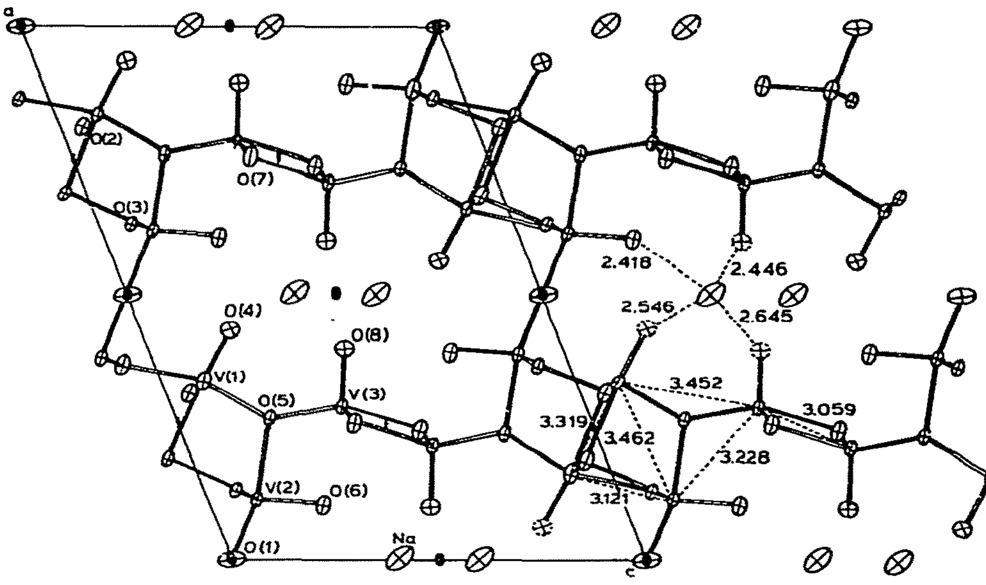


Fig. 1. Projection of the crystal structure of $Na_xV_2O_5$ [12].

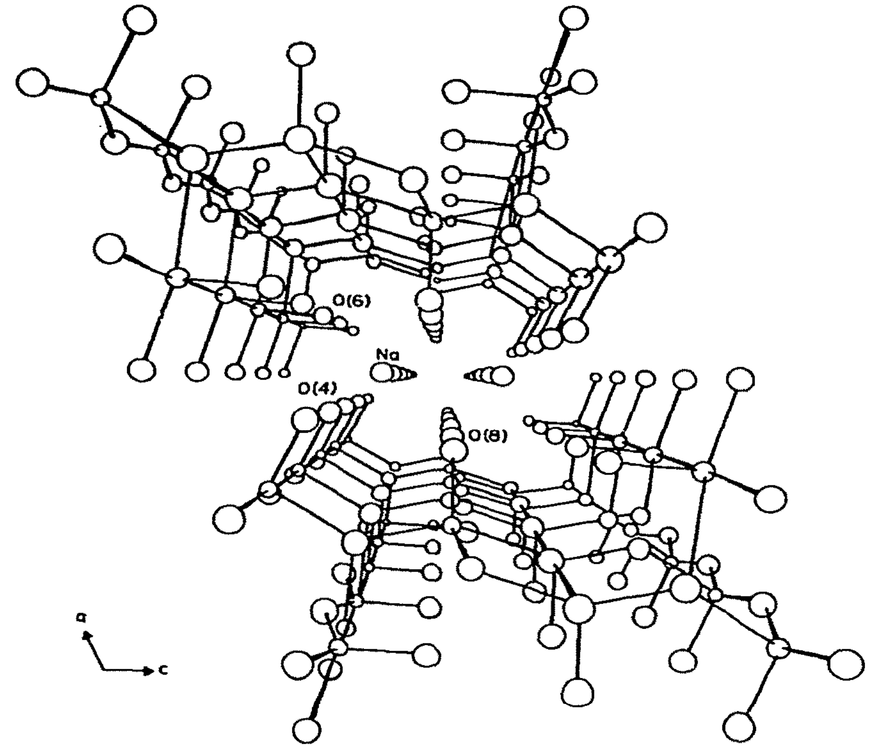


Fig. 2. Perspective view of the tunnel structure of $Na_xV_2O_5$ [12].

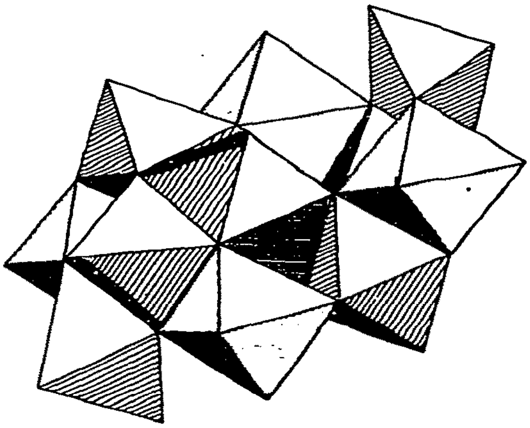
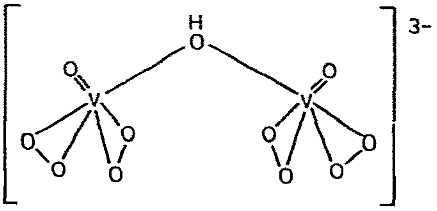


Fig. 3. The $[Mo_4V_8O_{36}]^{8-}$ anion, with the $\{MoO_6\}$ octahedra only lightly shaded [14].

around which two $\{MoO_6\}$ and four $\{VO_6\}$ octahedra are arranged in a ring. The ring is capped by a $\{VO_5\}$ square pyramid. The remaining two Mo and two V atoms are attached to the edge of the ring as $\{MoO_6\}$ octahedra and $\{VO_5\}$ trigonal bipyramids (Fig. 4) [14]. The second anion, $[Mo_6V_2O_{26}]^{6-}$, consists of a flat ring of six $\{MoO_6\}$ octahedra sharing edges with two $\{VO_4\}$ tetrahedra, one above and one below the ring [15].

The addition of H_2O_2 to metavanadate solutions (6 : 1 molar ratio) readily yields peroxovanadium(V) species. By varying the pH and measurements of ^{51}V NMR spectra of the resulting mixtures, Howarth and Hunt obtained evidence for the compounds of notional formula $[VO(O{-}O)]^+$, $[HVO_2(O{-}O)_2]^{2-}$, $[H_2VO_2(O{-}O)_2]^-$, $[VO(O{-}O)_3]^{3-}$, $[HVO(O{-}O)_3]^{2-}$, $[V(O{-}O)_4]^{3-}$, $[H\{VO(O{-}O)_2\}_2O]^{3-}$, and $[VO(NH_3)(O{-}O)_2]^-$ [16]. Similar studies on $[NH_4]^+/NH_3/H_2O_2/[NH_4]VO_3$ mixtures have led to the isolation of $[NH_4]_4[O\{VO(O{-}O)_2\}_2]$, $[NH_4][VO(O{-}O)_2(NH_3)]$ and $[NH_4]_3[HV_2O_{11}] \cdot 2\ H_2O$. IR studies on the last compound, and upon caesium and potassium analogues, have been interpreted assuming the anion to be $[HO\{VO(O{-}O)_2\}_2]^{3-}$ (6)



(6)

[17]. The kinetics of the conversion of $[VO(O{-}O)_2L]^{n-}$ to $[VO(O{-}O)L(H_2O)]^{(n-2)-}$ by H^+ have been deduced as evidence for the mechanism given below [18].

$$[VO(O{-}O)_2L]^{n-} + H^+ \xrightarrow{\text{rapid}} [VO(O{-}O)(OOH)L]^{(n-1)-}$$

$$[VO(O{-}O)(OOH)L]^{(n-1)-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [VO(O{-}O)L]^{(n-2)-} + H_2O_2$$

$$[VO(O{-}O)L]^{(n-2)-} + H_2O \xrightarrow{k_4} [VO(O{-}O)L(H_2O)]^{(n-2)-}$$

(Where L = bipy, phen, $[C_2O_4]^{2-}$ or picolinic acid.)

Volume of activation determinations for the formation of $[VO(O{-}O)\{N(CH_2COO)_3\}]^{2-}$ from $[VO_2\{N(CH_2COO)_3\}]^{2-}$ and H_2O_2 reveal a negative volume of activation of -3.3 ± 0.6 cm^3 mol^{-1}. The negative activation volume is consistent with an associative mechanism in which H_2O_2 enters the coordination sphere of the metal during the activation process [19].

Stability constants for the reactions of vanadium(V) with $HN(CH_2COOH)_2$, $N(CH_2COOH)_3$, $\{CH_2NH(CH_2COOH)\}_2$ and $\{CH_2N(CH_2COOH)_2\}_2$ (collectively, H_nY) have been determined, and the log of pH-independent equilibrium constants for the 1 : 1 species are 11.70, 13.80, 15.98 and 15.54, respectively. These 1 : 1 compounds all have the formula $[VO_2Y]^{(n-1)}$ [20].

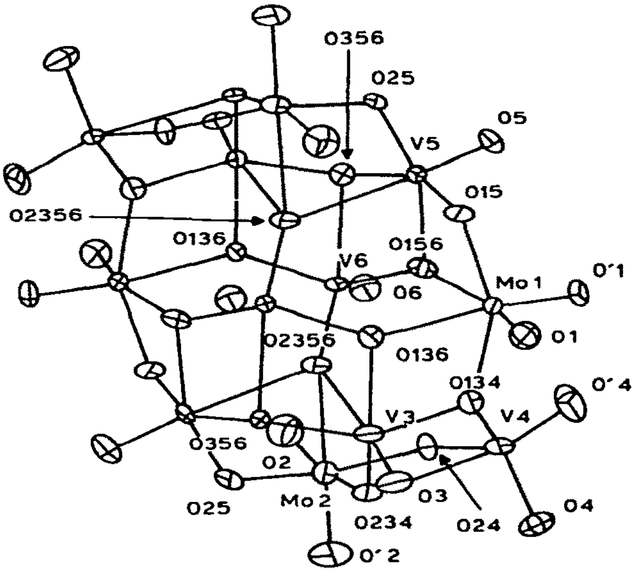


Fig. 4. The structure of the $[Mo_4V_8O_{36}]^{8-}$ anion [14].

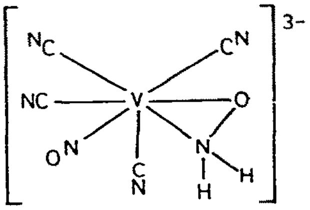
The nature of the compound formed between the anion of 8-hydroxyquinoline, $[OX]^-$, and $VO_2{}^+$ depends upon the acidity of the solution, and by carefully controlling the pH, $[VO_3(OX)]^{2-}$, $[VO_3H(OX)]^-$ or $VO_2(OX)$, or $[VO_2(OX)_2]^-$ can be obtained in solution. The trends in stability and possible structures of the species can be seen from the scheme given below [21].

$$\begin{tikzcd}
{[VO(OH)_3(H_2O)_2]} \arrow[r, rightleftharpoons, "3.8"] \arrow[d, rightleftharpoons, "1.8"] & {[VO_2(OH)(H_2O)_2]} \arrow[r, rightleftharpoons, "-8.1"] \arrow[d, rightleftharpoons, "0.3"] & {[VO_3(OH)(H_2O)_2]^{2-}} \arrow[r, rightleftharpoons, "13"] \arrow[d, rightleftharpoons, "-1.0"] & {[VO_4]^{3-}} \\
{[VO(OH)_2(OX)(H_2O)]} \arrow[r, rightleftharpoons, "5.3"] & {[VO_2(OH)(OX)(H_2O)]^-} \arrow[r, rightleftharpoons, "9.3"] \arrow[d, rightleftharpoons, "0.1"] & {[VO_3(OX)(H_2O)]^{2-}} & \\
 & {[VO_2(OX)_2]^-} & &
\end{tikzcd}$$

(n.b. Numbers on equilibria signs are log values of appropriate equilibrium constants.)

Fluoro-alkoxides of VO^{3+} have been prepared by allowing $LiOCH_2CF_3$ to react with $VO(OCHMe_2)_{3-x}Cl_x$. By examination of the results of IR and NMR spectroscopy, the electron donation power of OCH_2CF_3 is put between those of Cl and $OCHMe_2$ [22].

Stable hydroxylamidovanadium(V) complexes have been isolated by a number of routes. An example is the isolation of $[VO(bipy)(H_2NO)_2]Cl \cdot H_2O$ by the interaction of NH_4VO_3, 2,2-bipyridine and $[NH_3OH]Cl$ [23]. A range of nitrosyl complexes also containing the $[H_2NO]^-$ ligand are obtained if similar reactions to those above are carried out at higher pH. For example, the reaction of NH_4VO_3, pyridine-2,6-dicarboxylic acid (dpH_2) and $[NH_3OH]Cl$ in the presence of strong ammonia gave $[NH_4][V(dp)(H_2NO)(NO)(NH_3)] \cdot H_2O$. For the cyanide species $Cs_3[V(NO)(H_2NO)(CN)_4] \cdot 2\ H_2O$, the structure (7)



(7)

is envisaged for the anion [24].

From the reaction of $VOCl_3$ with $PhCS_2H$, $VO(SSCPh)_3$ was isolated and shown to be monomeric in solution. The IR spectrum of the species shows complex absorptions in a number of regions which may be evidence for a pentagonal-bipyramidal structure with the oxygen atom in an axial position, but the evidence is not unequivocal [25].

4.2 VANADIUM(IV)

4.2.1 Complexes with Group VII elements

The molecular structure and vibronic interactions of VBr_4 have been studied by gas-phase electron-diffraction. The gaseous sample was prepared by the disproportionation of $VBr_3(s)$ at 390°C. The molecule, which is tetrahedral with a V—Br distance of 2.276(4) Å, exhibits a dynamic Jahn—Teller effect [26].

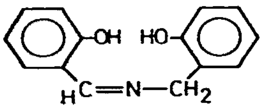
A compound previously thought to be $Cs_2[VF_6]$ has been re-examined by neutron and X-ray diffraction methods and shown to be $Cs_2[VF_4O(H_2O)]$. The metal atom has a strongly deformed octahedral coordination sphere and adjacent anions are linked by hydrogen bonds (O—H···F). The important bond lengths are $r(V{=}O) = 1.602(8)$ Å, $r(V{-}O)$ (*trans* to V=O) = 2.268(8) Å, $r(V{-}F) = 1.919(4)$ Å [27]. A related crystallographic study concerns $2\{Cs(VF_3O)\} \cdot H_2O$. In this compound, two crystallographically different VF_5O octahedra are linked via an F—F edge to form a complex chain. The V=O distances (1.583(7) and 1.595(7) Å) are shorter than that in the $[VF_4O(H_2O)]^{2-}$ anion, whilst the V—F distances span the range 1.881—2.205 Å [28].

4.2.2 Complexes with Group VI donor ligands

Vanadium(IV) chemistry is dominated by the VO^{2+} moiety (see also Section 4.2.1). A recent development has been the successful isolation of the sulphur analogue of VO^{2+} by the reaction of [VO(L)] [LH_2 = *N,N'*-ethylenebis(salicylideneamine) or *N,N'*-ethylenebis(acetylacetonylideneamine)] with B_2S_3. The resulting products have a ν(V=S) in the region 543—556 cm^{-1} [29].

The oxygen atom in the VO^{2+} group has been readily replaced by chlorine atoms by allowing [VO(chelate)$_2$] {chelate = acac, 8-*O*-quin, or $\frac{1}{2}${*N,N'*-ethylenebis(salicylideniminato)}*N*-butyl(salicylideneniminato)}, to react in benzene solution with $SOCl_2$, or in 1,4-dioxan with PCl_5, to give [VCl_2-(chelate)$_2$] [30]. The structure of bis[*N*-butyl(salicylideniminato)]dichlorovanadium(IV) has been determined; the metal atom sits at a centre of symmetry with V—Cl distances of 2.354(2) Å. The preparation of [VCl_2(chelate)$_2$] by the new method is found to be much easier than from VCl_4 [30]. The same authors have prepared [VO(chelate)$_2$] and [VO(chelate)$_2$(py)] (chelate = 8-*O*-quin) by a replacement reaction involving the displacement of $[acac]^-$. Both compounds react readily with dioxygen, and a detailed study of the reactions of [VO(chelate)$_2$(py)] showed that at atmospheric pressure a dinuclear vanadium(V) species [O{VO(chelate)$_2$}] was formed [31]. Nitrosobenzene and 2-nitrosobiphenyl (ArNO) also react in a similar manner giving [O{VO(chelate)$_2$}], the reduced product being [ArN(O)=NAr]. Oxidation with *p*-benzoquinone gives a different product namely [(chelate)$_2$V(O)—O—C_6H_4—O—(O)V(chelate)$_2$] [31].

The reactions of Schiff's bases with VO^{2+} are still of considerable interest. From a study of Schiff's bases (SBH_2) derived from *o*-hydroxybenzylamine and salicylaldehyde (8), it was suggested that the resulting VO(SB) compounds are dimeric. The evidence is provided by magnetic measurements, and the bridging atoms are thought to be the oxygen atoms from the *o*-hydroxybenzylamine [32]. Dimeric oxovanadium(IV) compounds are also reported to be formed when certain hydrazones (9; R = H, Me, Et or Pr) are allowed to react with the VO^{2+} moiety. The major evidence for the dimeric structure was provided by magnetic measurements [33]. Monomeric compounds were obtained when $VOSO_4$ or VCl_2O were allowed to react with three hydrazides derived from pyridine-2,6-dicarboxylic acid (LH_2; **10**). Two series of compounds were isolated, [VO(LH_2)]X_2 (X = Cl or $\frac{1}{2}[SO_4]$) and [VO(L)], and in all the species the ligands are believed to be pentadentate [34]. An interesting development of the above work is the formation of a



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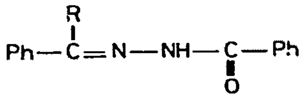
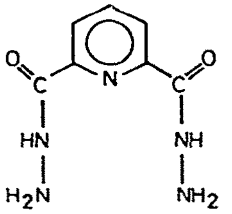


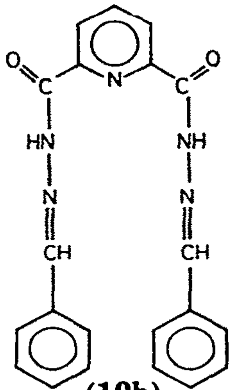
$$Ph-\overset{R}{\overset{|}{C}}=N-NH-\underset{\underset{O}{\|}}{C}-Ph$$

(9)

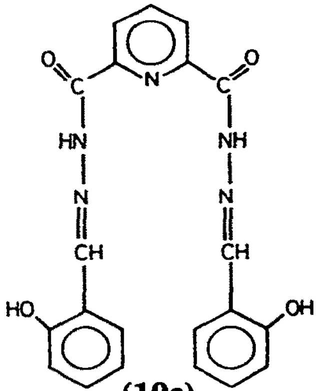
(R=H, Me, Et or Pr)



(dphH$_2$)
(10a)

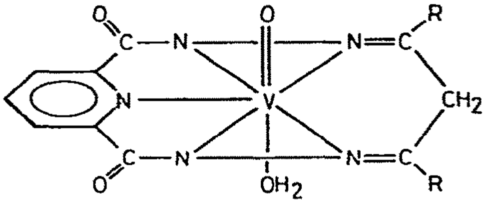


(10b)



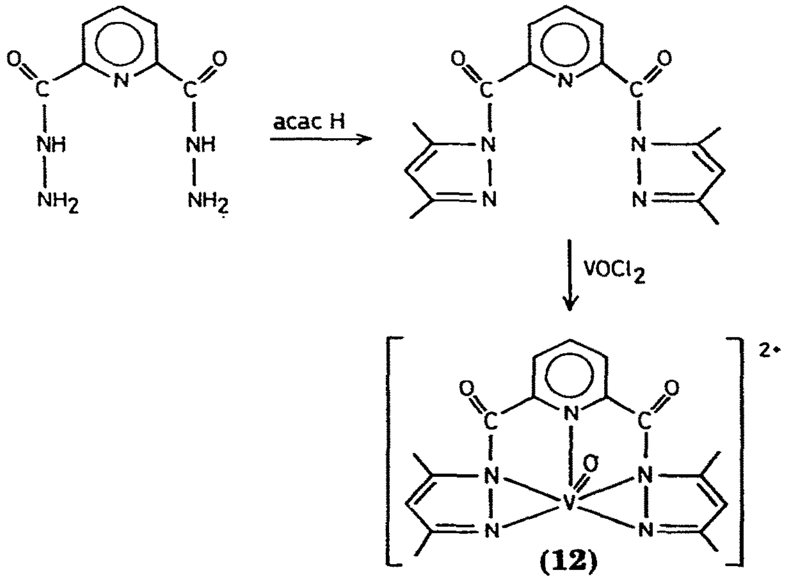
(10c)

macrocyclic oxovanadium(IV) compound by the reaction of [VO(L)] {LH$_2$ = **(10a)**} with a range of β-diketones; **(11)** represents the structure suggested



(11)

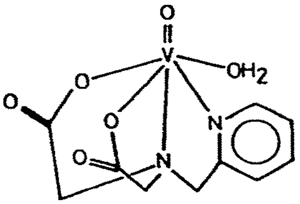
for the macrocyclic product. The influence of VO^{2+} on the course of reaction was investigated by allowing **(10a)** to react with acacH and then allowing the product to react with VCl$_2$O. The final product, **(12)**, was a 1 : 2 electrolyte



(12)

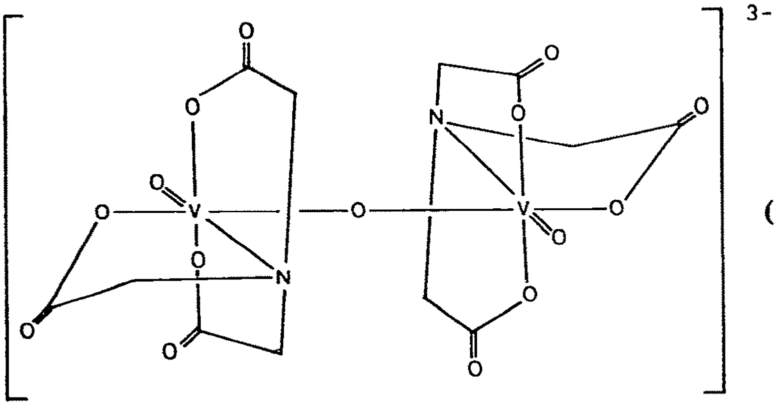
and the route to its formation is shown in the scheme [35].

From the reaction between 2-pyridylmethyliminodiacetic acid (H_2L) and $VO(acac)_2$, $[VO(L)(H_2O)] \cdot 2H_2O$ (**13**) was obtained, and its structure has



(13)

been determined; the tertiary amine nitrogen atom is *trans* to V=O and the remaining four positions of the six-coordinate coordination sphere are filled by three oxygen atoms (two from COO^-, one from H_2O) and a pyridine nitrogen atom [36]. Another interesting carboxylate formed by nitrotriacetic acid ($ntaH_3$) is $[NH_4]_3[V_2O_3(nta)_3] \cdot 3\ H_2O$. In solution an equilibrium exists between $[VO(nta)(H_2O)]^-$ {V(IV)}, $[VO_2(nta)]^{3-}$ {V(V)} and the parent ion $[V_2O_3(nta)_3]^{3-}$ (**14**). From the evidence of solution EPR measurements, an electron is delocalised over both centres in the binuclear ion. The structure of (**14**) has been determined; it has a centre of symmetry and the V=O bond length at 1.607 Å is within the range of V(IV)=O distances rather than V(V)=O distances [37].



(14)

The [VO(β-diketone)₂] compounds have been studied in research into a number of aspects of inorganic chemistry. The fluorinated compound $[VO(CF_3COCHCOCF_3)_2]$ forms 1 : 1 and 2 : 1 compounds with pyrazine (pz) and the equilibrium constants for the reactions have been determined. In the 2 : 1

$$\begin{tikzcd}
{[VO(CF_3COCHCOCF_3)_2] + pz} \arrow[r, shift left, "K=1.5 \times 10^6\ l\ mol^{-1}"] & {[VO(CF_3COCHCOCF_3)_2(pz)]} \arrow[l, shift left] \arrow[d, shift left, "K \simeq 2 \times 10^3\ l\ mol^{-1}"] \\
 & {[\{VO(CF_3COCHCOCF_3)_2\}_2(pz)]} \arrow[u, shift left]
\end{tikzcd}$$

complexes, the pyrazine bridges between two equatorial sites on adjacent vanadium atoms and promotes, although only poorly, some exchange interaction [38]. The nitroxide radical 2,2,6,6-tetramethylpiperidinyl N-oxide forms an adduct with $[VO(CF_3COCHCOCF_3)_2]$ in which there is strong interaction between the electrons on the metal and nitroxide [39]. The EPR spectrum of bis(dibenzoylmethanato)oxo vanadium(IV) dissolved in a number of pyrene and fluoranthrene complexes with polynitrocompounds (just above their melting points) indicates that the motion of the spin probe is more or less restricted [40].

Fundamental crystal structures of VO^{2+} complexes reported this year include a study of $[VO(dmso)_5][ClO_4]_2$ {where $r(V{=}O) = 1.591(9)$ Å, $\bar{r}(VO_{eq})(dmso) = 2.034$ Å, $r(VO_{ax})$ (*trans* to V=O) = 2.18(9) Å} [41] and the re-examination of $VOSO_4 \cdot 5\ H_2O$ [42]. In $VOSO_4 \cdot 5\ H_2O$, four of the water molecules are coordinated to the metal. The vanadium atom is six coordinate, one of the positions *cis* to V=O being filled by an oxygen atom from $[SO_4]^{2-}$ [42].

An oxovanadium(IV) substituted bovine carbonic anhydrase B has been characterised. It was prepared by the combination of the oxovanadium(IV) ion and apocarbonic anhydrase. Measurements of EPR and NMR spectra indicate that a water molecule is bound to the metal atom. Thus it is suggested that the active site in carbonic anhydrase contains two sites for water coordination [43].

Three mixed Mo(VI)—V(IV) isopolyanions have been detected from the reaction of $[MoO_4]^{2-}$ and $VOSO_4$ under oxygen-free conditions. The three compounds are $[Mo_4V_2^{IV}O_{19}H_3]^{3-}$, $[Mo_3V_3^{IV}O_{19}H_6]^{2-}$ and $[Mo_2V_4^{IV}O_{19}H_7]^{3-}$ and preparation of each one requires specific conditions of temperature, concentration and pH [44].

4.3 VANADIUM(III)

4.3.1 Complexes with Group VII elements

Compounds of formulation M_xVF_3 (M = K, Rb, Tl or Cs; $x < 0.33$) having the hexagonal tungsten bronze structure have been isolated by the reaction of $MF/VF_2/VF_3$ mixtures. The products were examined by X-ray techniques and, from Debye—Scherrer films, evidence was obtained for ordering of the M^+ ions in partially filled sites; superlattice reflections were observed [45].

Vanadium(III) chloride after reduction with $Li^+[np]^-$ (np = naphthalene) or with Li and $Li_2^+[np]^{2-}$ binds N_2. The study of the fixation process with VCl_3 is complicated as dinitrogen is also *directly* reduced by Li and $Li_2[np]$ [46].

The kinetics of the reaction of vanadium(III) chloride in pyridine solution with dioxygen have been studied and a two stage mechanism proposed to explain the observed kinetic data:

$$V(III) + O_2 \overset{K}{\rightleftharpoons} V(III)\,O_2$$

$$V(III)\,O_2 \xrightarrow{k} \text{products}$$

In the presence of large concentrations of VCl_3, when $[VCl_3(py)_3]$ is formed, $K = 40 \pm 24\ l\ mol^{-1}$ and $k = (9.2 \pm 6.3) \times 10^{-2}\ s^{-1}$ at 25°C. At small concentrations of VCl_3, and high dioxygen concentrations, $K = 265 \pm 18\ l\ mol^{-1}$ and $k = (7.1 \pm 0.5) \times 10^{-2}\ s^{-1}$ [47].

The vanadium compound VClO has a layer structure. Intercalation studies in which the Li^+ ion is placed in the lattice either electrochemically or via BuLi lead to the detection of the new compound $Li_{0.8}VClO$ [48]. Heating of VClO in an argon stream leads to disproportionation reactions [49]

$$3\ VClO(s) \xrightarrow{T < 400^\circ C} V_2O_3(s) + VCl_3(s)$$

$$2\ VCl_3(s) \rightarrow VCl_2(s) + VCl_4(g)$$

Above 120°C, VClO reacts with dioxygen to give a mixture of V_2O_5, Cl_2 and VCl_3O [49].

4.3.2 Complexes with Group VI donor ligands

The kinetics of the vanadium(III)/4-aminosalicylic acid system have been investigated and the mechanism shown to be associative [50].

The temperature-dependent isotropic shift in a range of vanadium(III)-β-diketone complexes have been examined in detail [51] and paramagnetic contact shifts for a range of new β-diketone species measured [52].

4.4 VANADIUM(II)

4.4.1 Complexes with Group VII elements

Crystalline VF_2 having a rutile type structure has been prepared by the reduction of VF_3 in $H_2/HF(3:1)$ mixtures [53]. The magnetic ordering in VF_2 has been examined, as has that in VI_2 [54].

Sodium chloride doped with vanadium(II) has been examined spectroscopically. With decrease in temperature, the oscillator strength of the bands decreases and the bands shift to higher wavelengths. At low temperature, vibrational fine structure was detected on the $^4T_{2g} \leftarrow {}^4A_{2g}$ band [55].

4.4.2 Complexes with Group V donor ligands

Vanadium(II) thiocyanate complexes with a wide range of nitrogen bases have been isolated. The pyridine complex $[V(py)_4(NCS)_2]$ contains nitrogenbonded $[NCS]^-$ ions and is isomorphous with $[Ni(py)_4(NCS)_2]$, a compound known to have *trans* $[NCS]^-$ ions [56].

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