

Vanadium 1995

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1. Introduction

This is the first annual review of the coordination chemistry of vanadium since that which highlighted the discoveries reported for the element during 1990 [1]. This chapter summarises the coordination chemistry of vanadium published during 1995. It was compiled using the online searching facilities of the University of Bath (Bids). The material is arranged initially in order of decreasing oxidation state. Following these sections, various aspects of the coordination chemistry of vanadium which enjoy current interest are discussed. There is a section on the solid state chemistry of vanadium, including a number of new phosphato- and phosphonato-compounds. The preparation and characterisation of these materials is currently an area of active research. There are also sections on biochemical and catalytic applications of vanadium compounds. These are not intended to be comprehensive surveys of the fields, but serve as a brief summary of the work published in 1995.

2. Reviews

A review of the coordination complexes of vanadium with multidentate ligands and imidazole and its derivatives has been published. The review describes the synthesis and characterisation of a large number of complexes by EPR and NMR spectroscopic and electrochemical techniques [2]. The structure of dinitrogen complexes with transition metals including vanadium is discussed in a review of biochemical nature. The function of nitrogenase with vanadium is described as is dinitrogen reduction in chemical systems in aprotic media. Dinitrogen reduction in protic media is also reviewed. Some soluble V(II) complexes including vanadium di-*tert*-butylcatecholate species are described [3].

A comprehensive review of the EPR spectra of many classical coordination complexes and organometallic molecules, including those of group V elements has been published. Spectral parameters are included for vanadium hexacarbonyl, trisbipyridyl complexes, nitrosyls and bis-arenes, all of which contain vanadium in the zero oxidation state [4].

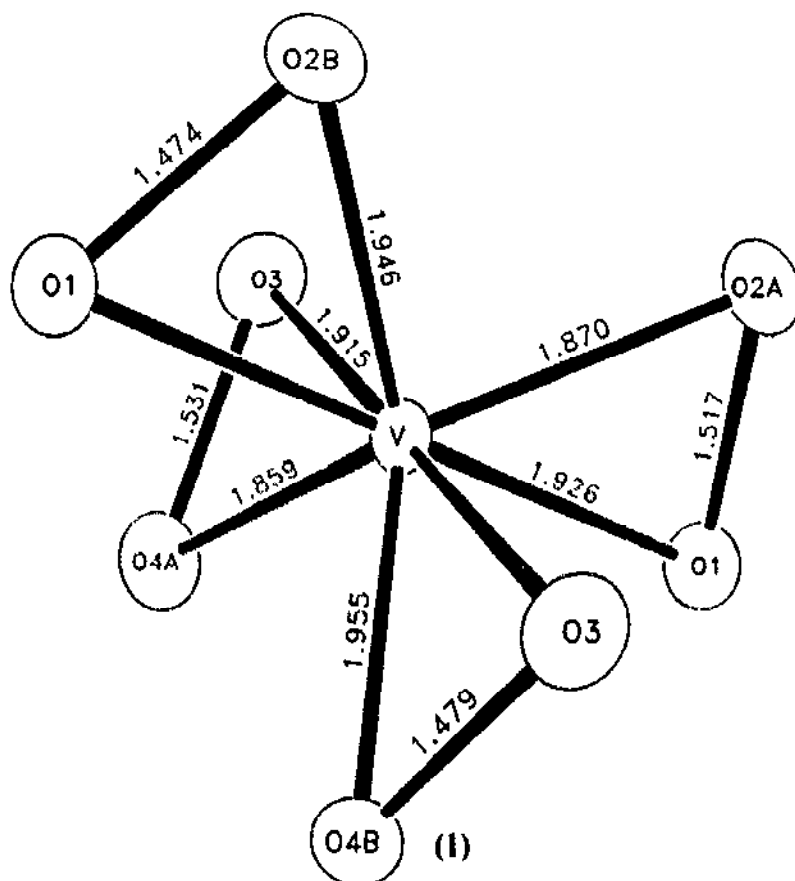
An article on metal ion chelation with reference to marine metabolites discusses the possible form of vanadium in tunichromes [5].

3. Vanadium(V)

The majority of V(V) coordination complexes reported in the literature during the past year contain V=O bonds and so these complexes are discussed in the first part of this section. They have been arranged loosely according to the basic structural V=O unit. Following this section species having V=N and V=S bonds are reported.

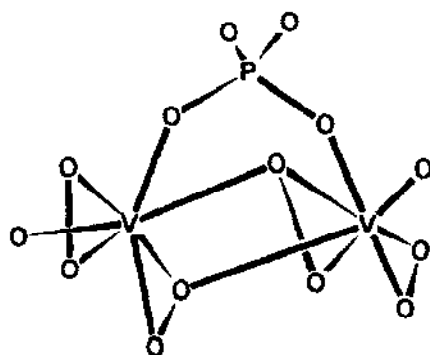
3.1. Complexes having V–O units

In an attempt to synthesise triperoxovanadate two complexes, each containing the tetraperoxovanadate(V) ion, were obtained and have been identified by low temperature X-ray diffraction methods. $\text{Na}_3[\text{V}(\text{O}-\text{O})_4] \cdot \text{H}_2\text{O}_2 \cdot 10.5\text{H}_2\text{O}$ and $\text{Na}_3[\text{V}(\text{O}-\text{O})_4] \cdot 14\text{H}_2\text{O}$ crystallise in the triclinic system with peroxo O–O and V–O_{peroxo} bond distances in the normal range. The tetraperoxovanadate ions, $\text{V}(\text{O}-\text{O})_4^{3-}$, (1), have approximately dodecahedral symmetry with peroxo ligands bound in an η^2 -fashion. A reinvestigation of the peroxovanadate equilibria in neutral and basic solutions by spectrophotometry was carried out in an attempt to determine whether tri- or tetraperoxovanadate should predominate under the experimental conditions used in this work. The results shed doubt upon the reliability of published formation constants and protonation constants for mononuclear peroxovanadium(V) [6].



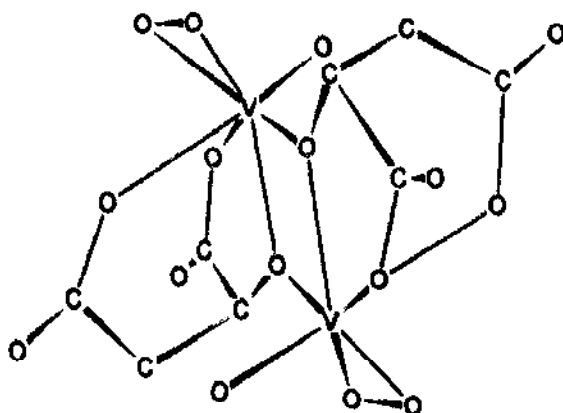
Reproduced from ref. [6] with permission.

The tetraperoxo phosphato complex $(\text{NH}_4)_5[\text{V}_2\text{O}_2(\text{O}_2)_4\text{PO}_4] \cdot \text{H}_2\text{O}$ has been obtained from the reaction between $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4VO_3 in H_2O_2 . The structure, (2), was found to consist of $[\text{V}_2\text{O}_2(\text{O}_2)_4\text{PO}_4]^{5-}$ anions, NH_4^+ cations and water molecules held together by extensive hydrogen bonding and electrostatic forces. Within the structure are 22 strong H bonds ($d < 2.9 \text{ \AA}$) [7].



$[V_2O_2(O_2)_4PO_4]^{5-}$
(2)

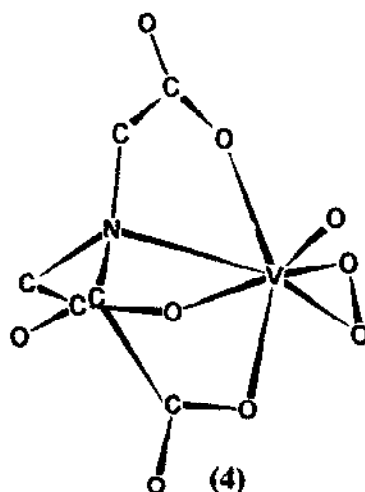
A series of peroxo malato vanadate(V) salts, $M [VO(O_2)(C_4H_4O_5)] \cdot H_2O$ ($M = NH_4, Na, K, Cs$) has been prepared from aqueous solutions of V_2O_5 or NH_4VO_3 and the appropriate hydroxide with malic acid. The structure of the ammonium salt showed it to be a dimer, $(NH_4)_2[VO(O_2)(C_4H_4O_5)]_2 \cdot 2H_2O$, (3), with the malato ligand exhibiting an unusual tridentate coordination. There are two independent half complexes in the asymmetric unit with a (V–O–V–O) bridging plane found in each ion formed by the hydroxyl oxygen atoms of the ligands. In addition there are two ammonium ions per dimer and lattice water molecules [8].



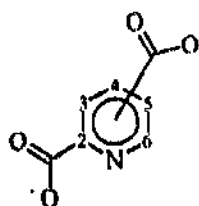
(3)

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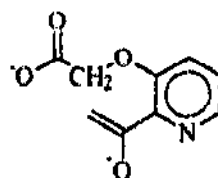
The monoperoxo vanadate $K_2[VO(O_2)(C_6H_6NO_6)] \cdot 2H_2O$, (4), has been synthesised from V_2O_5 and H_3NTA ($NTA = C_6H_6NO_6^{3-}$) in KOH and its structure determined. Unlike $(NH_4)_2[VO(O_2)(C_4H_4O_5)]_2 \cdot 2H_2O$ above, the NTA complex is monomeric. The V atom is seven coordinate and is enclosed in a distorted pentagonal bipyramidal arrangement by a tetradentate NTA ligand. The $V=O$ group occupies the apical position and the non-symmetrically coordinated peroxo group is *cis* to this in the pentagonal plane. Crystals of the complex were found to be stable in air for extended periods and showed a much reduced toxicity compared with other peroxoheteroligand vanadates [9].



A series of bisperoxovanadium complexes of general formula $K_3[VO(O_2)_2(L-L')]$, ($L-L'$ = pyridinedicarboxylate, (5), (2,3-pdc, 2,4-pdc, 2,5-pdc) or 3-acetatoxypicolinate (3-acetpic), (6)), has been prepared by a reaction between V_2O_5 in KOH and the appropriate dicarboxylic acid or potassium 3-acetatoxypicolinate. The structures of $K_3[VO(O_2)_2(2,4-pdc)]$, (7), and $K_3[VO(O_2)_2(3-acetpic)]$, (8), have been determined. The geometry around the vanadium atoms approximates to a distorted trigonal bipyramid if the peroxo ligand is assigned one coordination site. The vanadyl oxo ligand and the carboxylate oxygen occupy the two axial positions and the two peroxo groups form the trigonal plane. The compounds were found to rapidly oxidise sodium tris(3-sulfonatophenyl)phosphine which is evidence for the potential role of this type of compound as an efficient biological oxidant [10].

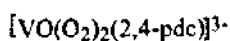
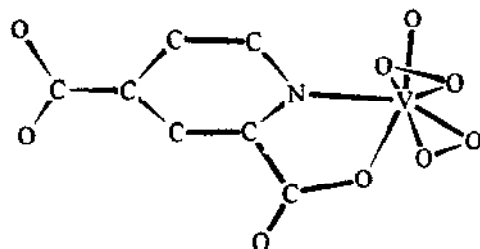


pdc
(5)

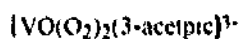
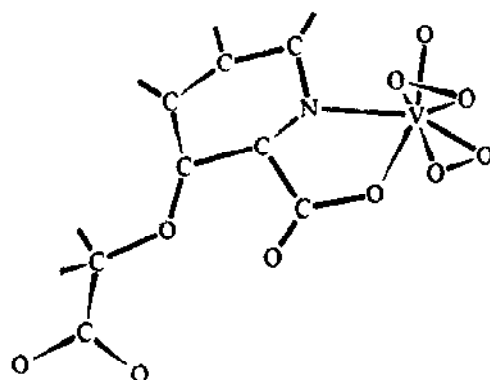


3-acetpic
(6)

The X-ray crystal structure of a product from the reaction of adenosine with vanadate in aqueous solution has been determined. The structure which contains two V nuclei and two adenosine moieties possesses the cyclic VOVO fragment seen in several other dinuclear V complexes. Each V atom is in an irregular pentacoordinate arrangement. 1H and ^{51}V NMR spectroscopic studies at reduced temperature in acetone/water media provided strong evidence that the crystal structure is maintained in solution [11]. Prior to the publication of this paper, a study of the vanadate-adenosine aqueous system was made using Aden (Aden is an adenosine derivative

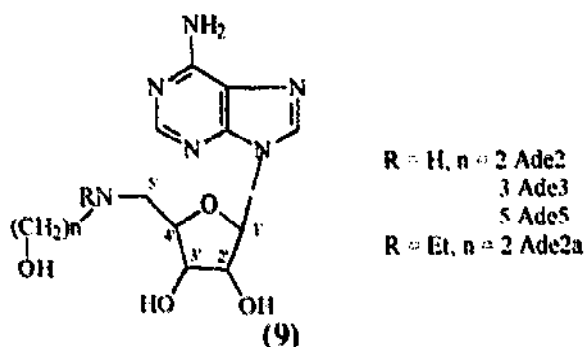


(7)



(8)

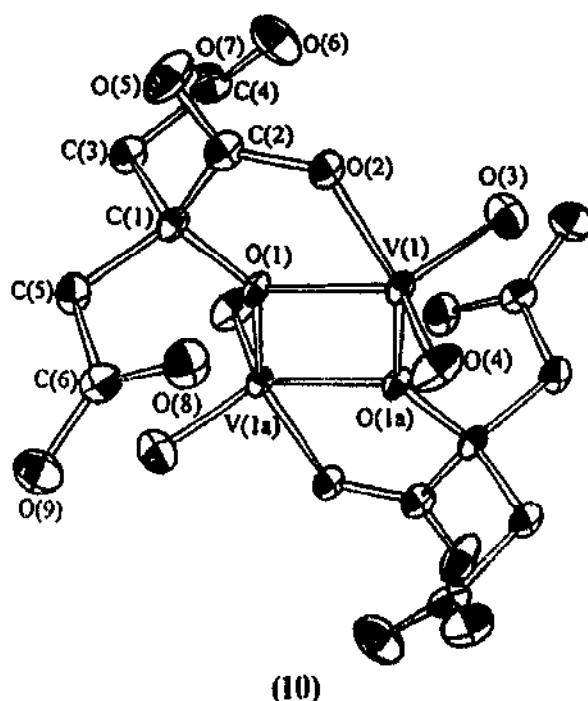
with O5' replaced by a secondary amine nitrogen tailed by n CH_2 groups and a terminal OH; $n = 2, 3, 5$; (9)). Complex formation constants were reported for the dinuclear biligate complexes formed and possible structures for the products proposed [12].



(9)

There is currently considerable interest in citrato complexes of vanadium. The complex $\text{K}_2[\text{V}(\text{O})_2(\text{C}_6\text{H}_6\text{O}_7)]_2 \cdot 4\text{H}_2\text{O}$ has been isolated and characterised both spectroscopically and by X-ray diffraction. The citrate ligand (cit^{3-}) is coordinated didentately to the vanadium atom *via* the bridging hydroxyl group and a unidentate

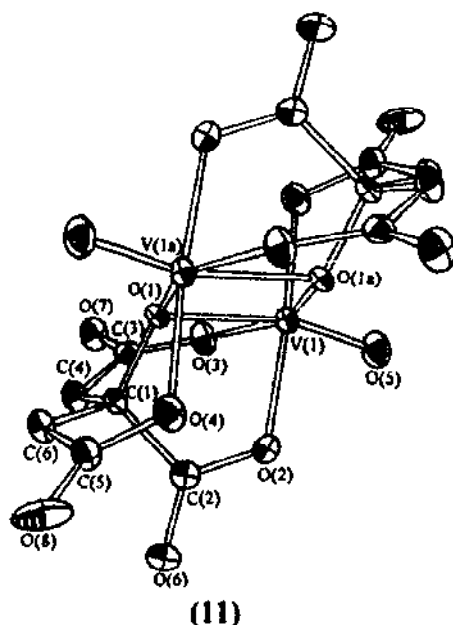
carboxylate group in an arrangement which is thought to be unique. The complex may be of relevance to the understanding of physiological forms of metabolised vanadium as it represents the first model of a tricarboxylic acid coordinated to the heteroatom found in the cofactor of nitrogenase [13]. Two further dimers, $K_2(NH_4)_4[VO_2(cit)]_2 \cdot 6H_2O$ and $Na_4[VO(cit)]_2 \cdot 6H_2O$, have been prepared by the reactions of citric acid and metavanadate in neutral solution. The anion in the vanadium(V) complex, $K_2(NH_4)_4[VO_2(cit)]_2 \cdot 6H_2O$, (10), contains a centrosymmetric planar four membered V_2O_2 ring with the bridging hydroxyl oxygens. Coordination of the citrate ion is again *via* oxygen atoms of the hydroxyl and α -carboxylato groups. The vanadium(IV) dimer $Na_4[VO(cit)]_2 \cdot 6H_2O$, (11), has citrate ligands coordinated in a tetradentate fashion *via* hydroxyl and α -carboxylato oxygens to one vanadium and *via* two acetato branches to the two vanadium atoms, making each metal atom 6-coordinate [14].



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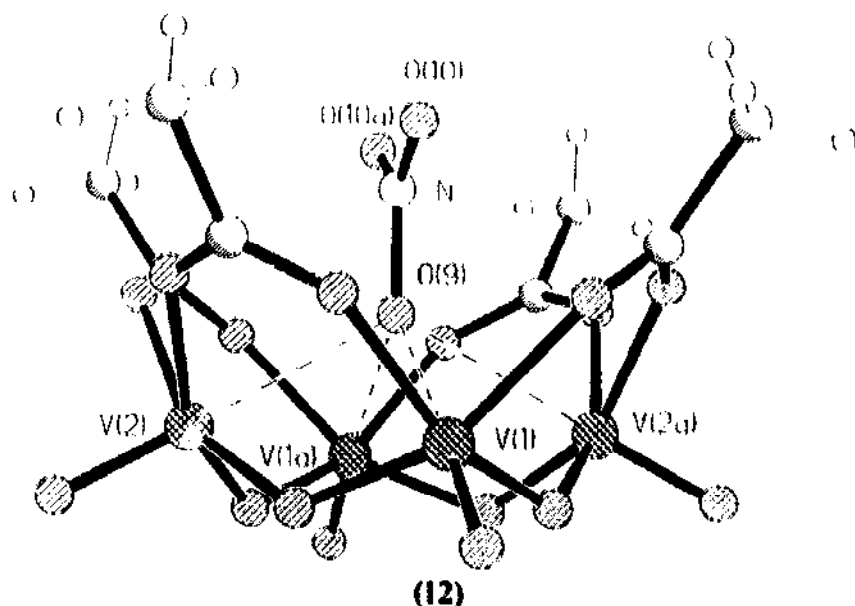
^{13}C NMR spectroscopy has been used to study the reactions of vanadate, $H_2VO_4^-$, with ^{13}C labelled oxalate in aqueous and acetic acid media. Results from the aqueous studies suggest the formation of both mono(oxalato)-, $[VO_2(ox)(OH_2)]^-$ and bis-oxalato *cis*- $[VO_2(ox)_2]^{3-}$ V(V) complexes. The results from acetic acid media suggested that other species are also present [15].

The tetrameric monoanion $[\{ VO_2(O_2CMe) \}_4(NO_3)]^-$, (12), has been obtained in a reaction between $VO(NO_3)_3$ with acetonitrile in the presence of Ph_4AsCl in which the acetonitrile is oxidised to acetate. The crystal structure of the product showed it to contain a tetrakis(μ -acetato μ -oxo oxovanadium) crown with all four vanadium atoms linked to one oxygen of the nitrate ion. The compound is thought to be the



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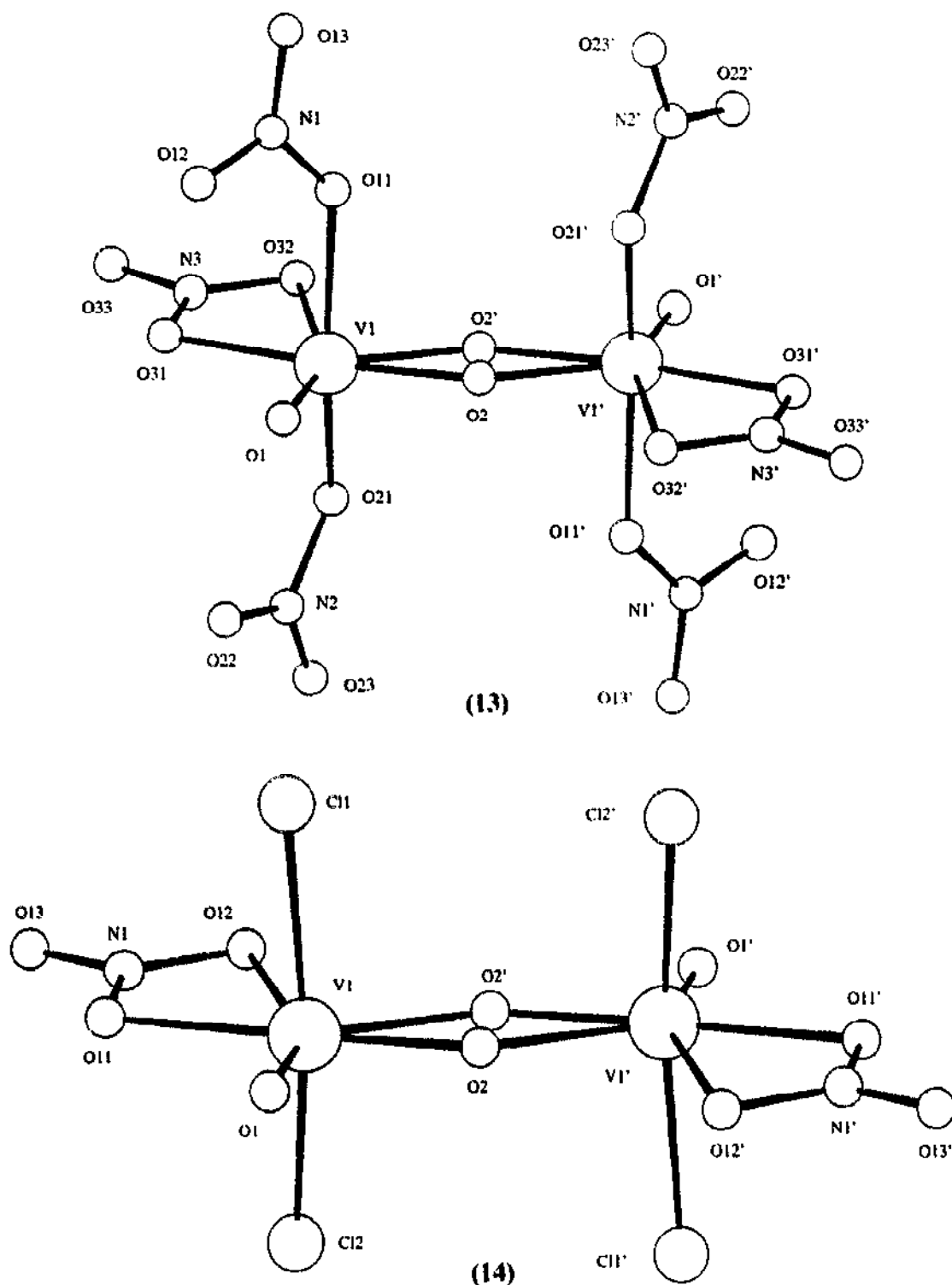
first example of a neutral polynuclear vanadium carboxylate to accommodate a guest anionic species inside the cavity [16].



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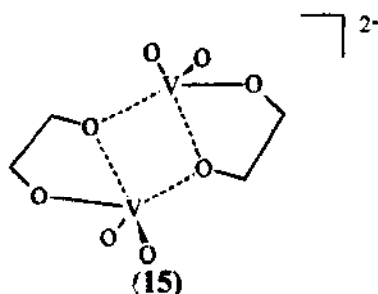
Two dinuclear vanadium species containing the $(V_2O_5)^{4+}$ central core have been obtained from the reactions of tetraphenylarsonium nitrate with $VO(NO_3)_3$ and $VOCl_3$. The compounds, $[Ph_4As]_2[V_2O_5(NO_3)_6]$, (13), and $[Ph_4As]_2[V_2O_5Cl_4(NO_3)_2]$, (14), are structurally related, each V atom having octahedral coordination achieved by two oxygen atoms, a didentate nitrate and two other

monodentate groups. The bridging oxygen atom is disordered in each structure over two positions related by the inversion centre. $[\text{Ph}_4\text{As}]_2[\text{V}_2\text{O}_3\text{Cl}_4(\text{NO}_3)_2]$ is the first example of a halonitrato species to be isolated [17].



(13) and (14) Reproduced from ref. [17] with permission.

The solution structure of the complex formed by the condensation of 2 mol of vanadate with 2 mol of a vicinal diol in aqueous solution has been determined in order to compare it with the known solid state structure. The solution structure is of particular relevance to phosphoryl transfer reactions and there already exist four different proposed structures for vanadate-diol complexes in solution. Using a variety of spectroscopic techniques the structure was shown to contain a four membered V_2O_2 unit within the framework of two VO_5 clusters that are each part of a five-membered ring involving the diol (15) [18]

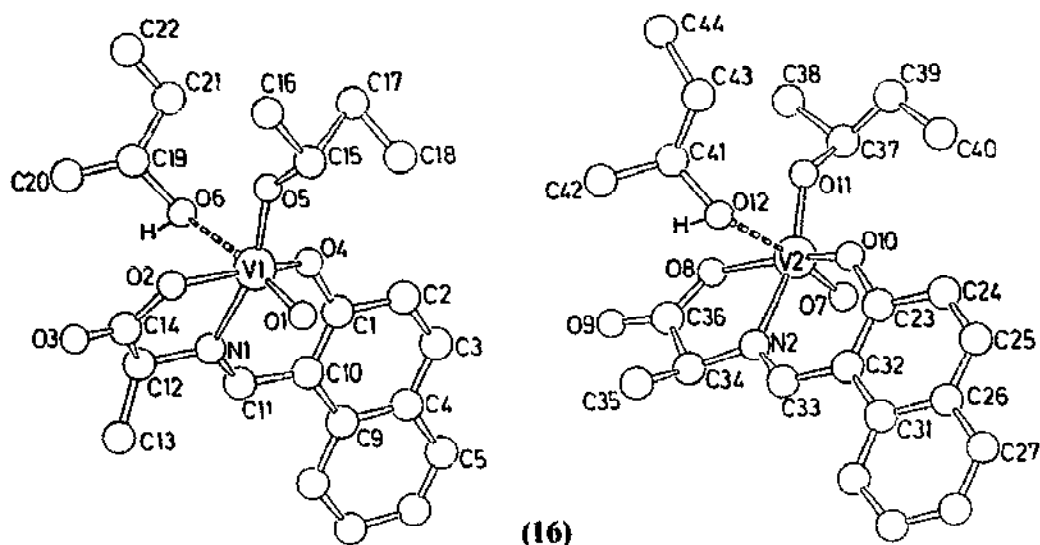


The past year has seen the publication of several structures possessing the VO^{3+} centre containing a mixed ON-coordination sphere as a result of interest in vanadate-dependent bromoperoxidases. Reaction of vanadyl sulfate, L-alanine and 2-hydroxynaphthaldehyde followed by aeration in D,L-*sec*-butyl alcohol produced the Schiff base complex $[VO\{N-(2-oxido-1-naphthylmethylene)-L-al\} O^tBu (HO^tBu)]$, (16). The molecule possesses four centres of chirality resulting in eight possible diastereoisomers and two of the isomers are found in the same asymmetric unit in the crystalline structure. The geometry around the V atom in each unit is that of a highly distorted octahedron with the terminal O atom at one apex and three O atoms and one N atom from the ligand forming the plane. The sixth position is occupied by *sec*-butanol coordinated through the hydroxyl oxygen at an extremely long distance [19].

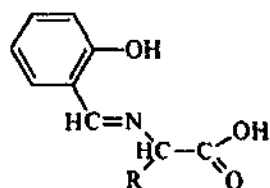
Interest in the binding of carboxyl oxygen atoms to VO^{3+} has resulted in the isolation of the complexes $[VO(L^1)(hquin)]$ and $[VO(L^2)(hquin)]$ (H_2L^1 and H_2L^2 are shown in (17); $Hhquin$ =quinolin-8-ol) which incorporate *N*-salicylidene-glycinate and L-phenylalaninate respectively. The crystal structure of $[VO(L^2)(hquin)]$ showed the $[L^2]^{2-}$ ligand to be coordinated tridentately through carboxyl and phenolic oxygen atoms and the azomethine nitrogen atom. The CD spectrum, 1H NMR spectrum and electroreduction of the species were studied [20].

Five further complexes of VO^{3+} with Schiff bases formed from trishydroxymethylaminomethane with salicylaldehyde and its derivatives have been prepared and characterised by 1H and ^{13}C NMR, UV-VIS, and FTIR spectroscopies and cyclic voltammetry. The complexes were shown to have trigonal bipyramidal NO_4 -coordination at the vanadium atom [21].

The same group has prepared a series of mononuclear *cis*-dioxovanadium(V) anionic complexes, $[VO_2L]^-$ ($H_2L=[1+1]$ Schiff base derived from salicylaldehyde or substituted derivatives and 2-amino-2-methylpropan-1-ol). Three of the com-



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R
H H₂L¹
CH₂Ph H₂L²

(17)

pounds, when structurally characterised, were shown to be mononuclear having distorted square pyramidal geometry at the V atom which is displaced from the equatorial plane by ≈ 0.5 Å. Each V atom is surrounded by two *cis*-terminal oxygen atoms and tridentate ONO from the ligand. Two of the compounds have the longest yet reported V=O bond lengths for *cis*-dioxo mononuclear vanadium(V) complexes. There is extensive hydrogen bonding between the anions and cations in the crystal lattices of all three structures which is thought to be relevant to vanadium in biological systems [22].

Bromide oxidation by hydrogen peroxide catalysed by *cis*-dioxovanadium(V) in acidic, aqueous and aqueous/ethanolic solutions was found to be second order in V concentration and first order in Br concentration. The catalytic reaction is thought to proceed via coordination of H₂O₂ by V(V) and the reaction has been studied spectroscopically [23].

The reaction of KBr with aromatic compounds C₆H₄XY (X = NHCOMe, Y = H or 4-Me; X = CHO, Y = 2-OH) and 5,5-dimethylcyclohexa-1,3-dione in aqueous media in the presence of [V₂O₂(O₂)₃(GlyH)₂(H₂O)₂] was found to result in the corresponding brominated compounds. The reaction is proposed as a mimic for the enzyme bromoperoxidase [24].

Rate constants have been determined for the oxidation of the Re_2^{IV} complex, $[(\text{C}_2\text{O}_4)_2\text{Re}(\mu\text{-O})_2\text{Re}(\text{C}_2\text{O}_4)_2]^{4-}$ by *cis*- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ acting as a one-equivalent oxidant [25]. Reaction of VOCl_3 with equimolar and bimolar amount of $4\text{-}^t\text{BuC}_6\text{H}_4\text{OSiMe}_3$ led to the isolation of $[\text{VOCl}_2(\text{OC}_6\text{H}_4^t\text{Bu}_4)]$ and $[\text{VOCl}(\text{OC}_6\text{H}_4^t\text{Bu}_4)_2]$ respectively. Reactions of the complexes with various aldehydes, ketones and carboxylic acid salts were investigated [26].

The synthesis and structural characterisation of a number of new V(V) and V(IV) complexes using pyrazole and its 3,5-dimethyl- and 3(5)-*tert*-butyl-substituted derivatives as ligands have been reported. The compounds were obtained by aerial oxidation of acetonitrile solutions containing VCl_3 and pyrazole or the relevant derivative in a 1:1 molar ratio. The compounds, namely, $[(\text{pz})_4\text{VOCl}]\text{Cl} \cdot \text{H}_2\text{O}$, $(3,5\text{-Me}_2\text{pz})_2\text{VOCl}_2(\text{H}_2\text{O})$, $(^t\text{Bupz})_2\text{VOCl}_2$, $[(^t\text{Bupz})_4\text{VO}(\text{H}_2\text{O})]\text{Cl}_2 \cdot 4\text{CH}_3\text{CN}$, $(^t\text{Bupz})_2\text{VOCl}_2(\text{F})\text{VOCl}(^t\text{Bupz})_3$ and $(^t\text{Bupz})_2\text{VO}_2\text{F}$ have all been characterised by X-ray crystallography and were found to contain six-coordinate vanadium with a terminal $\text{V}=\text{O}$ bond [27].

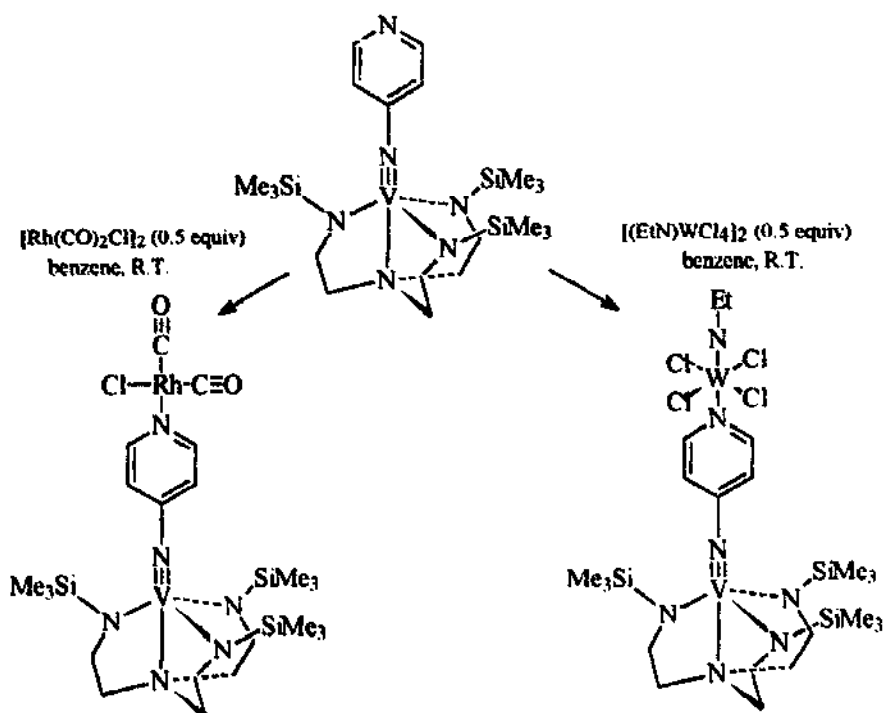
3.2. Complexes having V–N bonds

Reaction of $[(\text{N}_3\text{N})\text{V}^{\text{III}}]$ ($\text{N}_3\text{N} = [\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$) with 4-azidopyridine in pentane yields $[(\text{N}_3\text{N})\text{V}=\text{N}-\text{C}_5\text{H}_4\text{N}]$. The structure consists of a central V atom surrounded by five N atoms in a pentagonal bipyramidal arrangement. One of the apical V–N bond lengths is extremely short, consistent with a $\text{V}=\text{N}(\text{py})$ triple bond. The exposed nitrogen atom of this *p*-pyridylimido ligand provides a reactive site capable of complexing with a second metal fragment to form heterodimetallic complexes linked by a compact conjugated bridge as shown in Scheme 1 [28].

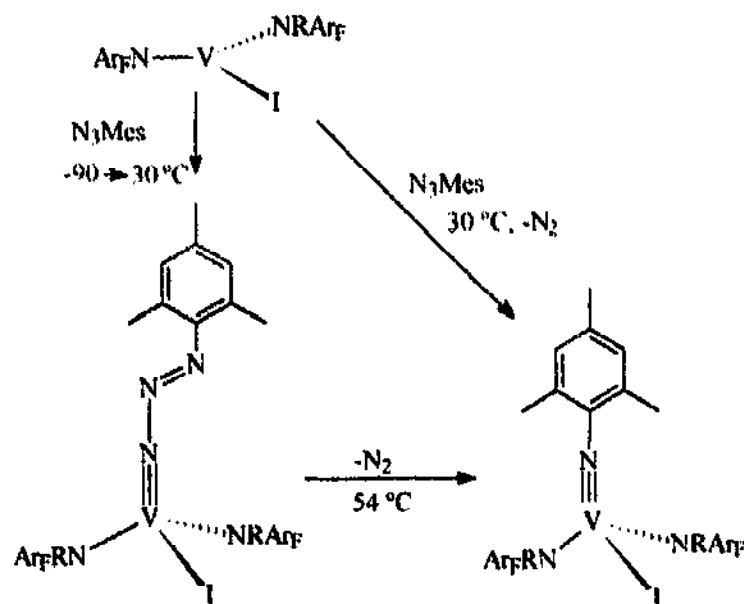
The V(III) complex $\text{V}(\text{I})(\text{NRAr}_F)_2$ has been synthesised in a three step reaction starting from $\text{VCl}_3(\text{THF})_3$ and $\text{Li}(\text{NRAr}_F)(\text{OEt})_2$ ($\text{R} = \text{C}(\text{CD}_3)_2\text{CH}_3$). Reaction of $\text{V}(\text{I})(\text{NRAr}_F)_2$ with mesityl azide at -100°C yielded $\text{V}(\text{N}_3\text{Mes})(\text{I})(\text{NRAr}_F)_2$ whose structure was determined by X-ray crystallography. At 54°C the azide complex loses N_2 in a reaction with second order kinetics to give the imido complex $\text{V}(\text{NMes})(\text{I})(\text{NRAr}_F)_2$ as shown in Scheme 2. The compound $\text{V}(\text{NMes})(\text{I})(\text{NRAr}_F)_2$ can also be prepared directly from $\text{V}(\text{I})(\text{NRAr}_F)_2$ by dropwise addition of mesityl azide to an ether solution of $\text{V}(\text{NMes})(\text{I})(\text{NRAr}_F)_2$ [29].

Treatment of VOCl_3 with 1 equivalent of $^t\text{BuNCO}$ or ArNCO ($\text{Ar} = 2,6\text{-}^t\text{Pr}_2\text{-C}_6\text{H}_3$) yields $\text{V}(\text{N-}^t\text{Bu})\text{Cl}_3$ and $\text{V}(\text{NAr})\text{Cl}_3$ respectively which, when treated with 1 equivalent KTp or KTp^* produce the complexes $\text{TpV}(\text{N-}^t\text{Bu})\text{Cl}_2$, $\text{Tp}^*\text{V}(\text{N-}^t\text{Bu})\text{Cl}_2$, $\text{TpV}(\text{NAr})\text{Cl}_2$ and $\text{Tp}^*\text{V}(\text{NAr})\text{Cl}_2$. The X-ray crystal structures of $\text{TpV}(\text{N-}^t\text{Bu})\text{Cl}_2$ and $\text{Tp}^*\text{V}(\text{NAr})\text{Cl}_2$ have been determined and the polymerisation of ethylene and propylene in the presence of $\text{Tp}^*\text{V}(\text{NAr})\text{Cl}_2$ and methylalumoxane investigated [30].

The reactions of $^t\text{BuNVCl}_3$ with cyclic ethers, ethylene carbonate and thiethane have been studied. The reactions of $^t\text{BuNVCl}_3$ with 2-chloroethanol, 3-chloropropanol and 5-chloropentanol yield the complexes $^t\text{BuN}:\text{V}(\text{OR})\text{Cl}_2$ ($\text{R} = (\text{CH}_2)_n\text{Cl}$, $n = 2, 3, 5$) and $^t\text{BuN}:\text{V}(\text{OR})\text{Cl}_2 \cdot \text{ROH}$. In the presence of triethylamine the disubstituted compounds $^t\text{BuN}:\text{V}(\text{OR})_2\text{Cl}$ are formed. The



Scheme 1.



Scheme 2.

crystal structures of ${}^t\text{BuN}:\text{VCl}_3 \cdot \text{dme}$ and ${}^t\text{BuN}:\text{V}(\text{OCH}_2\text{CH}_2\text{Cl})\text{Cl}_2 \cdot \text{OHCH}_2\text{CH}_2\text{Cl}$ have been determined [31].

Reaction of ArNVCl_3 ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-(}{}^i\text{Pr)}_2$) with CpSiMe_3 results in the formation of the half sandwich imido vanadium complex $\text{CpV}(\text{NAr})\text{Cl}_2$. Attempts at

alkylation of $\text{CpV}(\text{NAr})\text{Cl}_2$ and $\text{CpV}(\text{N-}p\text{-tolyl})\text{Cl}_2$ led to extensive reduction of the vanadium. Reaction of $\text{CpV}(\text{N-}p\text{-tolyl})\text{Cl}_2$ with AlMe_3 led to a mixture of diamagnetic dimeric, imido-bridged complexes $(\text{CpV})_2(\mu\text{-N-}p\text{-tolyl})_2\text{MeR}$ ($\text{R} = \text{Me}$ or Cl) which were converted to the pure chloro compound $[\text{CpV}(\mu\text{-N-}p\text{-tolyl})\text{Cl}]_2$ by reaction with HCl . Alkylation of $[\text{CpV}(\mu\text{-N-}p\text{-tolyl})\text{Cl}]_2$ with MeLi gives $[\text{CpV}(\mu\text{-N-}p\text{-tolyl})\text{Me}]_2$. The structures of $[\text{CpV}(\mu\text{-N-}p\text{-tolyl})\text{Cl}]_2$ and $[\text{CpV}(\mu\text{-N-}p\text{-tolyl})\text{Me}]_2$ have been determined and both have a planar cyclovanadazene core with a vanadium-vanadium single bond [32].

3.3. Complexes having V–S bonds

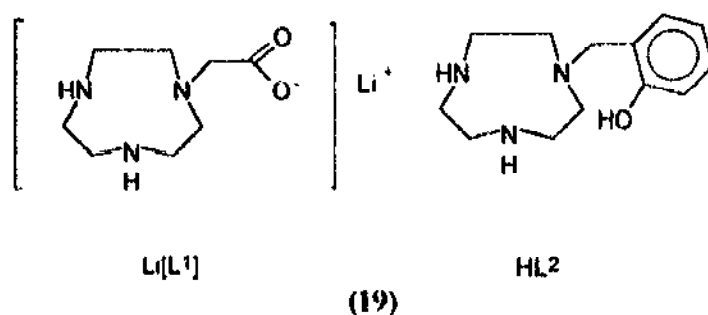
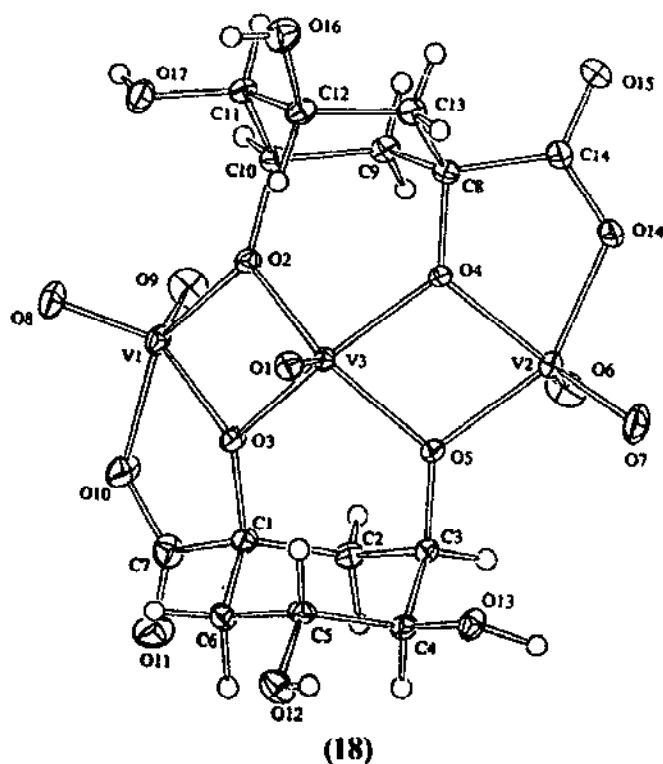
The compounds $[\text{VS}_4(\text{CuPPh}_3)_5\text{Br}_2\text{CuX}]$ and $[\text{VS}_4(\text{CuPPh}_3)_5\text{Br}_2\text{CuX}] \cdot \text{CH}_2\text{Cl}_2$ ($\text{X} = 0.5 \text{ Br}$ and 0.5 Cl), prepared by heating a mixture of $(\text{NH}_4)_3\text{VS}_4$, CuCl , PPh_3 and Et_4NBr , have been characterised by single crystal X-ray diffraction. The clusters were found to consist of a tetrahedral VS_4 core bound to an octahedral array of six copper atoms having both trigonal planar and tetrahedral coordinations [33].

4. Complexes containing vanadium(V) and vanadium(IV)

The mixed valence $\text{V(V)}\text{--V(IV)}\text{--V(V)}$ trinuclear complex $(\text{NH}_4)_2[\{\text{V}^{\text{V}}(\text{O})_2\}_2\{\text{V}^{\text{IV}}(\text{O})\}(\mu\text{-(}-)\text{-quinato(3-)}\}_2) \cdot \text{H}_2\text{O}$ has been prepared by two different routes each involving quinic acid and V_2O_5 . In the molecule each quinic acid trianion coordinates to all three vanadium ions as shown in (18). The V(IV) atom occupies the central position and the alcoholate donors of the quinic acid act as bridging groups between this and the outer V(V) ions. The geometry around the V ions tends more towards square pyramidal rather than trigonal bipyramidal [34].

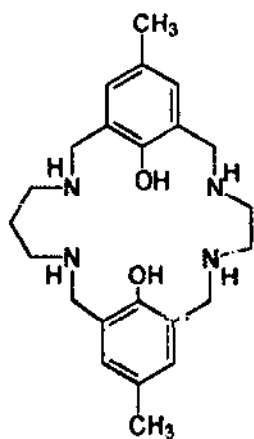
The tetradentate ligands $\text{Li}[\text{L}^1]$ and HL^2 , (19), have been prepared and used to synthesise a series of mono- and dinuclear complexes of V(IV) and V(V) . The syntheses of the following complexes is described: $[\text{L}^1\text{V}^{\text{IV}}\text{O}(\text{NCS})]$, $[\text{L}^1\text{VO}_2] \cdot \text{H}_2\text{O}$, $[\text{L}^2\text{VO}(\text{NCS})]$, $[\text{L}^2\text{VO}(\text{NCS})]\text{Cl}$ and $[\text{L}^2\text{VO}_2]$ along with those of the dinuclear, mixed valence compounds $[\text{L}_2^1\text{V}_2\text{O}_3]\text{Br}$ and $[\text{L}_2^1\text{V}_2\text{O}_3](\text{ClO}_4) \cdot 0.5\text{acetone}$. The latter two complexes contain the $[\text{OV} \cdots \text{O} \cdots \text{VO}]^{3+}$ core. In $[\text{L}_2^1\text{V}_2\text{O}_3]\text{Br}$, the bridging O atom lies on a crystallographic two-fold axis and the two $\text{L}^1\text{V} \cdots \text{O}$ fragments are therefore identical despite the mixed valence nature of the complex. No sign of disorder could be detected in the structure. The second mixed valence complex $[\text{L}_2^1\text{V}_2\text{O}_3](\text{ClO}_4) \cdot 0.5\text{acetone}$ again contains two L^2VO fragments bridged by an oxo group but in this case there is no crystallographic symmetry and the fragments are geometrically different [35].

The macrocyclic tetraamine-diphenol ligand (H_2L^2) (20) with two different cavity sizes provided by an ethylene and propylene bridge, respectively, between the two sets of amine groups, produces a mixture of monomeric oxoV(IV) and (V) complexes of the $[\text{L}^2]^{2-}$ anion on reaction with $\text{VO}(\text{acac})_2$. The mixture reacts with nickel(II) perchlorate yielding three compounds of composition

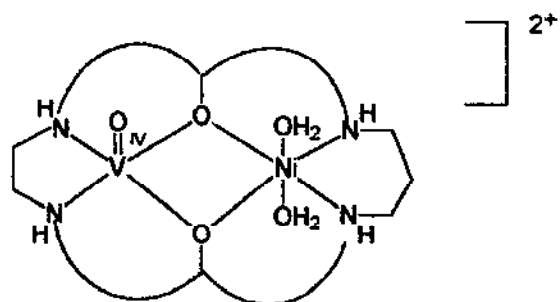


$[(V^{IV}O)L^2Ni(H_2O)_2](ClO_4)_2$ (**21**), $\{[(V^{IV}O)L^2Ni(H_2O)]\} \{[(V^{VO}_2)(HL^2)]\} (ClO_4)_2 \cdot 3H_2O \cdot 2.5CH_3OH$ (**22**) and $[NiL^2(V^{IV}O)](ClO_4)_2$ (**23**). Complex (**23**) reacts with pyridine to produce $[(V^{IV}O)L^2Ni(py)](ClO_4)_2 \cdot H_2O$ (**24**). Reaction of $VO(SO_4)$ with H_2L^2 yields the V(IV) complex $[(V^{IV}O)(H_2L^2)(SO_4)] \cdot 5H_2O$, (**25**), as the sole product in which both of the amino nitrogen atoms of the $-NH(CH_2)_2NH-$ moiety are protonated [36].

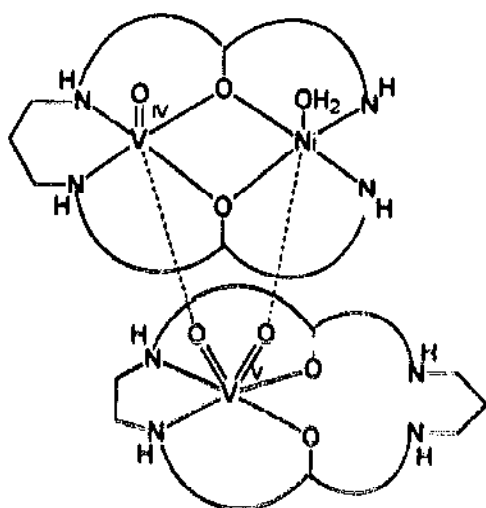
The synthesis and X-ray structure of the mixed valence complex $[V^{IV}V^{VO}_2O_7(phen)]$ have been described. The compound was obtained by heating a mixture of V_2O_5 and phenanthroline at $180^\circ C$ in an autoclave for 2 days. The material has a layered structure comprising repeated asymmetric units each with three unique V centres as shown in (**26**) [37].



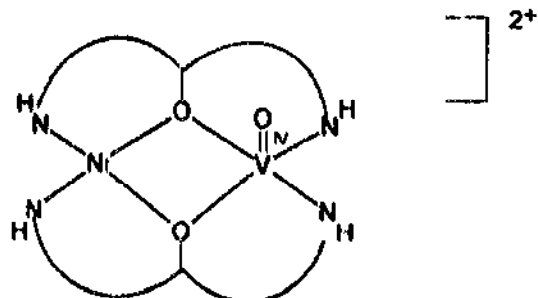
H_2L_2
(20)



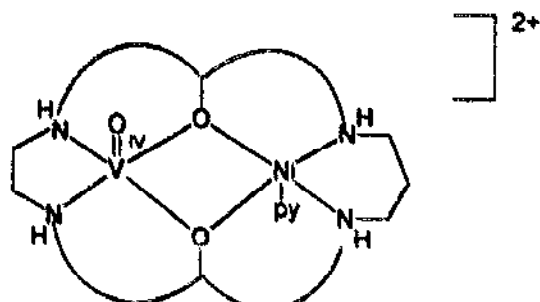
$[(V^{IV}O)L_2Ni(H_2O)_2](ClO_4)_2$
(21)



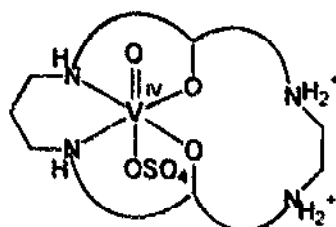
$[(V^{IV}O)L_2Ni(H_2O)](VVO_2)(HL_2)_2^{2+}$
(22)



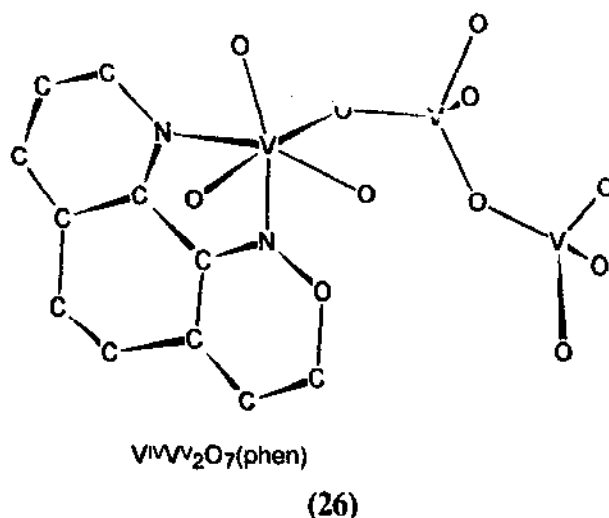
$[NiL_2(V^{IV}O)]^{2+}$
(23)

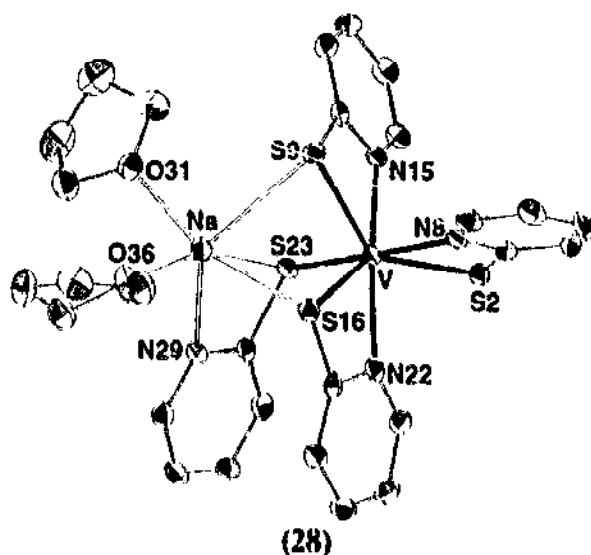
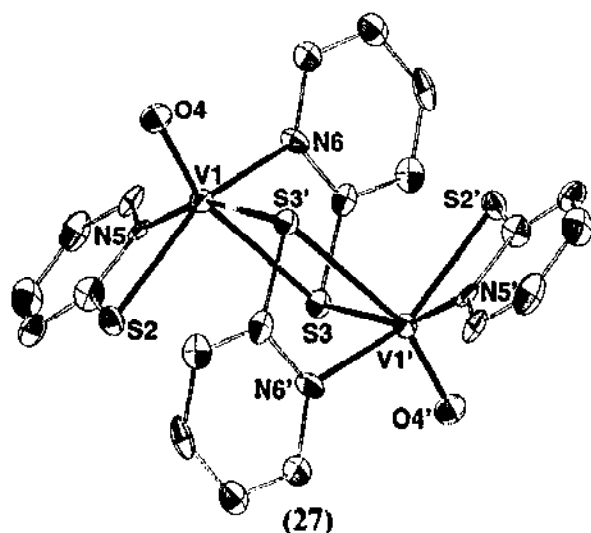


$[(V^{IV}O)L_2Ni(py)]^{2+}$
(24)



(25)

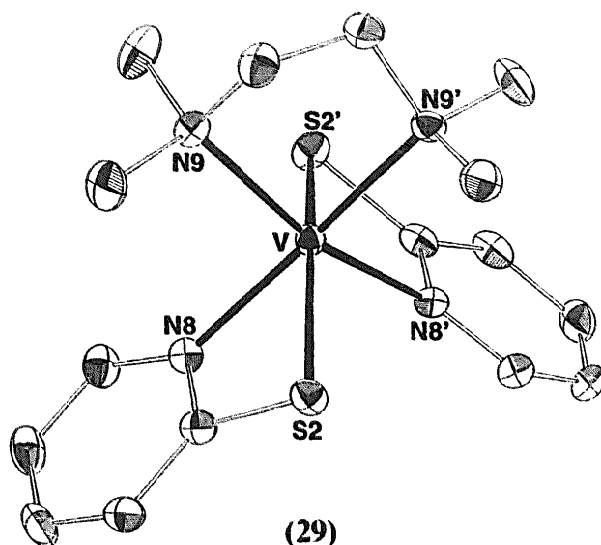




(27) and (28) reproduced from ref. [40] with permission.

5.2. Vanadyl complexes

A series of V(IV) and V(V) complexes having hydrazine derivatives as ligands has been prepared from the reactions between $\text{VCl}_2(\text{acac})_2$ and $\text{VCl}_2(\text{acpn})$ (acpn = propylenediiminobis(acetylacetonato(2-))) and benzoylhydrazine. The complexes, $(\mu\text{-PhCONNCOPh})\{\text{VOCl}(\text{NHNHCOPh})\}_2 \cdot 5\text{CH}_3\text{CN}$ and $(\mu\text{-PhCONNCOPh})\{\text{V}(\text{dbh})\}_2 \cdot 2\text{CH}_3\text{CN}$ both contain doubly deprotonated *N,N'*-dibenzoylhydrazine (dbh) as a bridging, doubly *N,O*-chelating ligand. In $(\mu\text{-PhCONNCOPh})\{\text{VOCl}(\text{NHNHCOPh})\}_2 \cdot 5\text{CH}_3\text{CN}$ the two remaining coordination sites at the VOCl group are occupied by the hydrazido(1-) ligand $[\text{NHNHCOPh}]^-$. In the non-oxo V(IV) complex $(\mu\text{-PhCONNCOPh})\{\text{V}(\text{dbh})\}_2 \cdot 2\text{CH}_3\text{CN}$ the coordination geometry at the V atom is approximately trigonal prismatic. Back donation from

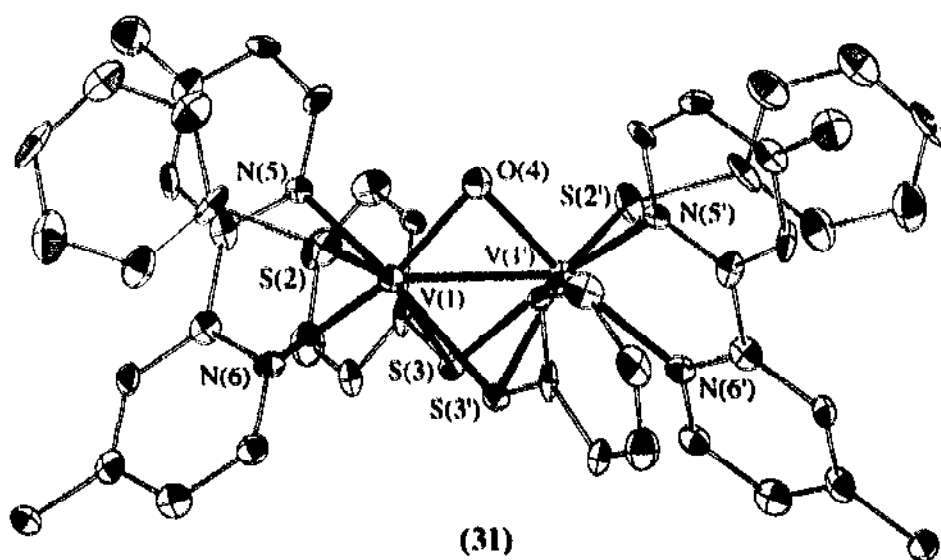
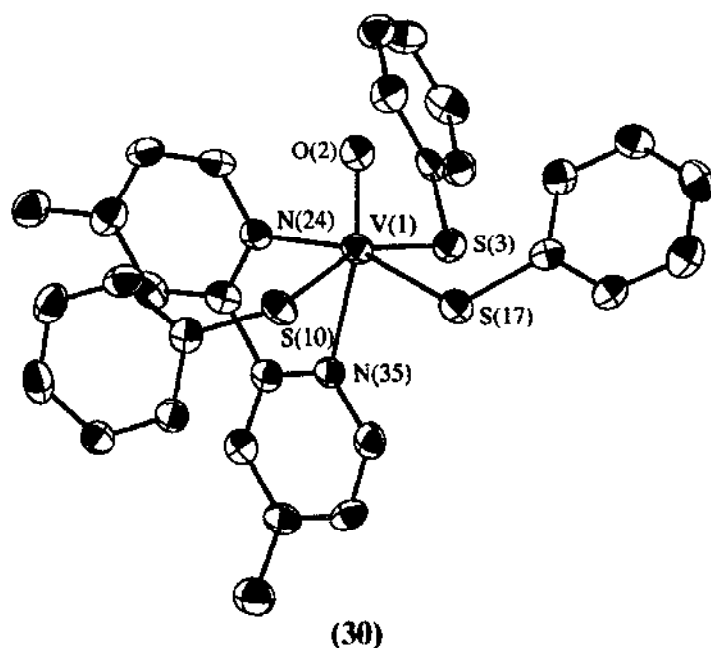


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three negatively charged enolic oxygen atoms compensates for the lack of π -back donation from the vanadyl oxygen atom. The third complex, $[\{VO\}_2(tbh)]$, contains a highly symmetrical octadentate ligand formed during the synthesis. The ligand is coordinated to two VO(IV) centres by *N,O*-chelation resulting in a square pyramidal geometry [41].

Investigation into non-organometallic organosulfur chemistry has led to the synthesis of mononuclear $(NEt_4)[V(SPh)_4(bpy)]$ from $VCl_3(thf)_3$ and NaSPh with NEt_4Cl and bipyridine in MeCN. The complex can also be prepared from $(NEt_4)[VCl_4(bpy)]$ and NaSPh in MeCN. Controlled aerial oxidation of the 4,4'- Me_2 -bpy (Me_2 -bpy) analogue resulted in the $[VO(SPh)_3(Me_2-bpy)]^-$ ion which can be isolated as the NR_4^+ salts. Structural analysis of the NMe_4^+ salt showed the anion to consist of a distorted-octahedral species with three equatorial PhS⁻ groups and one Me_2 -bpy N atom, (30). Controlled hydrolysis of $[V(SPh)_4(Me_2-bpy)]^-$ leads to $V_2O(SPh)_4(Me_2-bpy)_2$ (31) which has a $[V_2(\mu-O)(\mu-SPh)_2]^{2+}$ core with a terminal PhS⁻ and chelating Me_2 -bpy ligand on each metal. The V–V distance of 2.579(3) Å suggests a V^{III} – V^{III} single bond is present. Extended Hückel calculations were carried out on the model complex $V_2O(SH)_4(NH_3)_4$ along with variable temperature magnetic measurements and 1H NMR spectroscopic solution studies to investigate the metal-metal bonding and the possibility of antiferromagnetic exchange interaction [42].

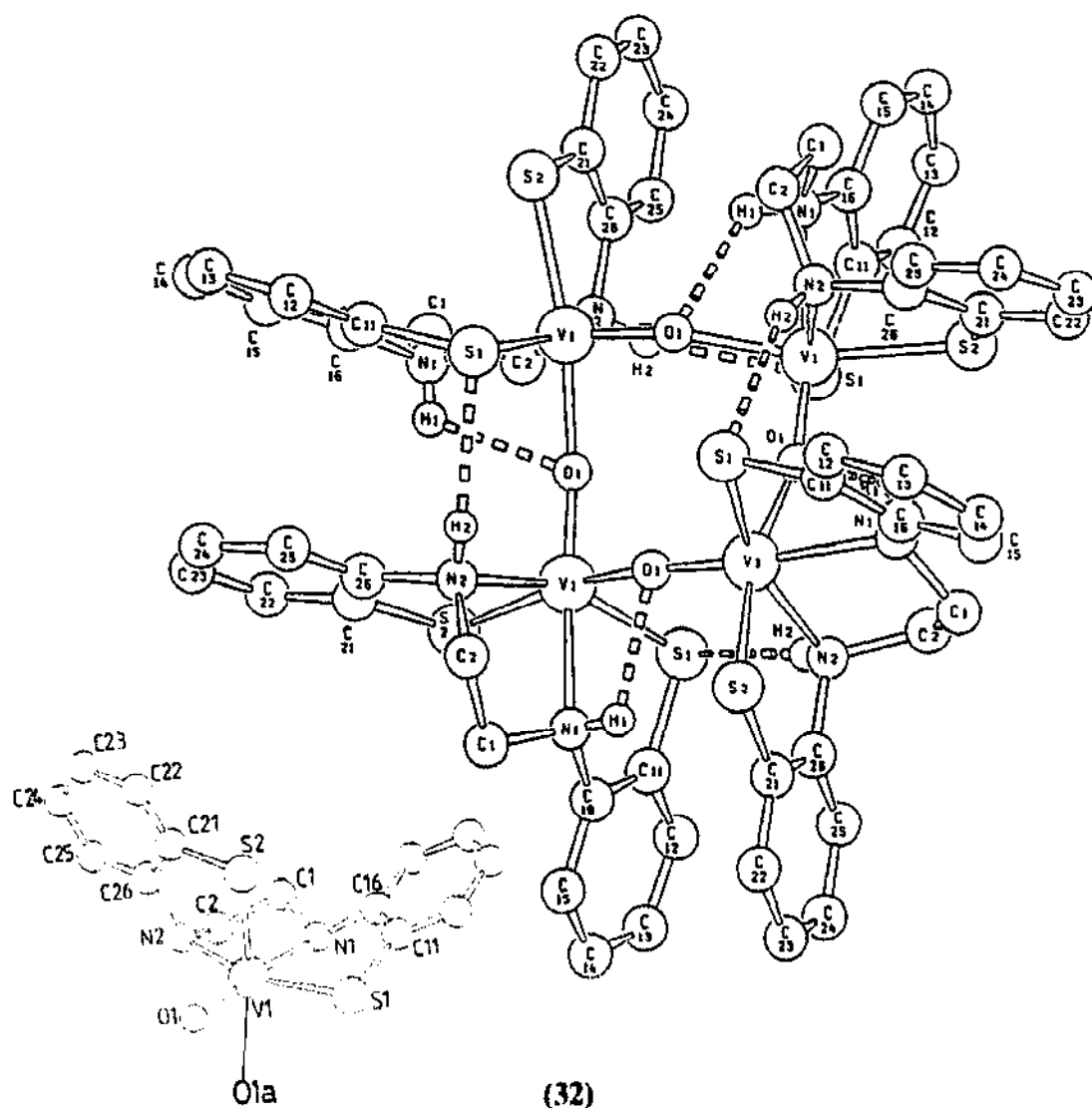
Reaction of $VOCl_2(thf)_2$ with the disodium salt of the tetradentate ligand *N,N'*-bis(*o*-mercaptophenyl)ethylenediamine ($NaSNNSNa$) led to the tetranuclear V(IV) complex $\{V(SNNS)^-\}_4(\mu-O)_4$, (32), along with the oxidation product of the ligand. The absence of air suggests that oxidation is brought about by V(IV), but the formation of any V(III) complex was not proved unambiguously. The structure of the product consists of a central V_4O_4 ring, each V atom having a distorted octahedral environment being coordinated by two ligand S and N atoms as well as the bridging O atoms [43].



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Reaction of colourless $V^V(O)(O^iPr)_3$ with $Ti(NRAr)_3$ in ether is accompanied by a colour change to yellow and marked shifts in the 2H NMR spectroscopic signal of the Ti complex consistent with the formation of a heterodinuclear μ -oxo complex, $(^iPrO)_3V^{IV}OTi^{IV}(NRAr)_3$ whose structure was determined [44].

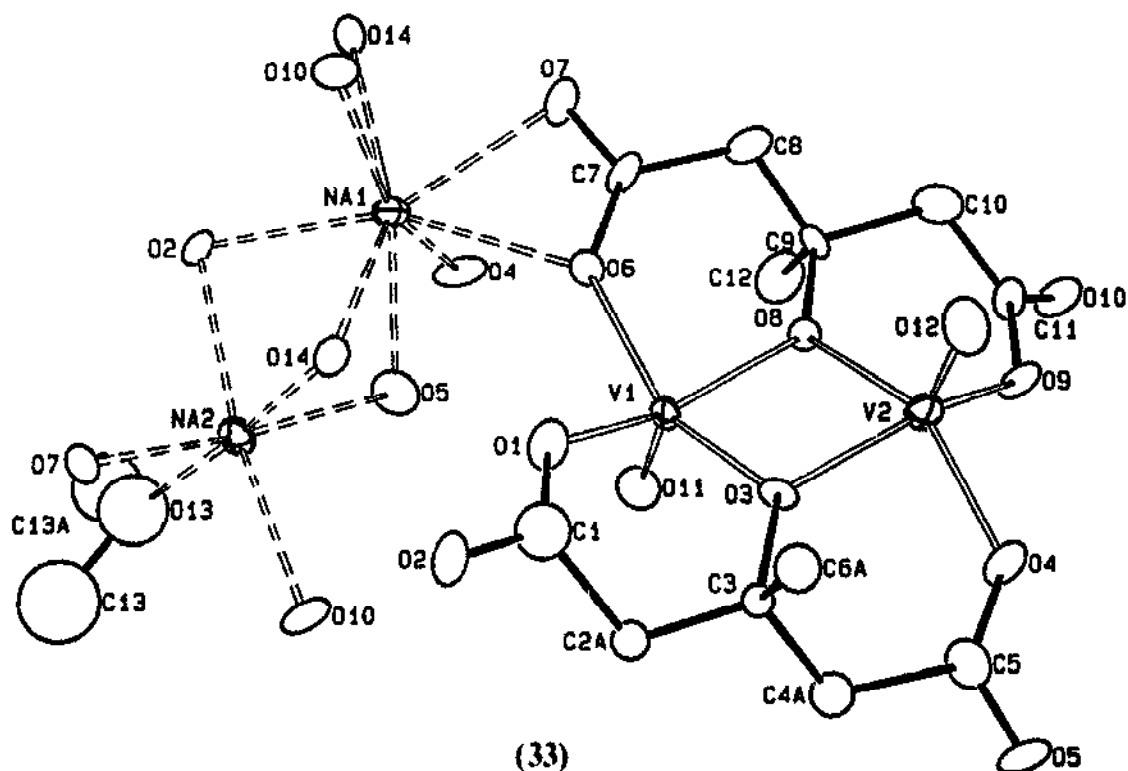
The reaction chemistry of the potent insulin-mimetic agent bis(maltolato)oxovanadium(IV) (BMOV or $VO(ma)_2$) has been investigated. In aqueous solution it is slowly oxidised to $[VO_2(ma)_2]^-$ by molecular O_2 and in alcohols $VO(OR)(ma)_2$ ($R = CH_3, C_2H_5, iso-C_3H_7$) species are formed. With pyri-



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dine, the six-coordinate $\text{VO}(\text{ma})_2\text{py}$ can be formed which undergoes aerial oxidation much more slowly indicating that a vacant site is required for O_2 coordination. A complete study by ^{51}V NMR spectroscopy and electrochemistry was made of the aqueous chemistry of $\text{VO}(\text{ma})_2$ and $[\text{VO}_2(\text{ma})_2]^-$. The X-ray crystal structures of $\text{VO}(\text{ma})_2$ and $[\text{cis-VO}_2(\text{ma})_2]^-$ were determined [45].

The V(IV) dimer $\text{Na}_2[(\text{VO})(3\text{-hydroxy-3-methylglutarate})]_2 \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$, (33), has been obtained by reaction of 3-hydroxy-3-methylglutarate with $\text{VO}(\text{SO}_4)$. The structure has two 3-hydroxy-3-methylglutarate trianions acting as tridentate ligands each bridging the V atoms through the hydroxy O and bonding to the different V atoms by the carboxylate oxygen atoms. The overall structure consists of dianions linked together in a three dimensional structure by chains of sodium ions which are additionally coordinated and bridged by oxygen atoms from the glutarate ligands, a water molecule and a methanol molecule [46].



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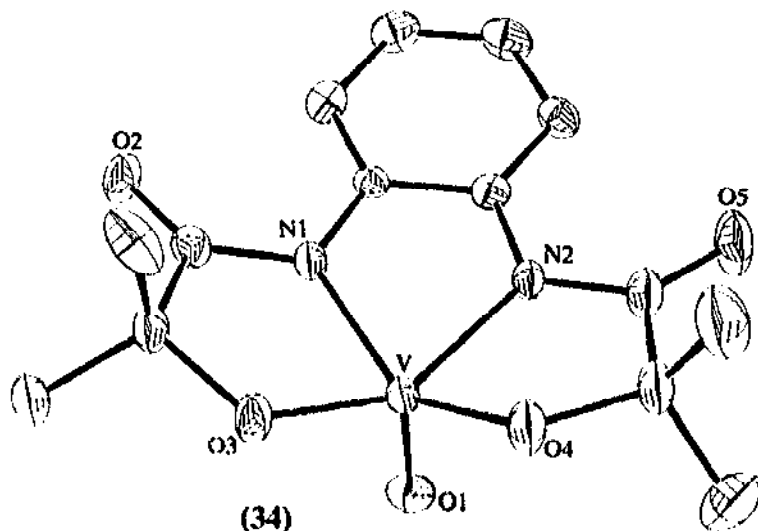
The structure of oxobis(pentane-2,4-dionato)vanadium(IV), $[\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2]$, has been redetermined using high resolution Mo data but no significant differences from those previously reported were found in the geometrical parameters [47].

The mechanism of complex formation between species containing VO^{2+} and D-, L-, DL- or *meso*-tartaric acid or citric acid in aqueous solution has been re-examined by the combined use of pH potentiometry and spectroscopic methods. The dinuclear species existing in the VO^{2+} -D-, L- and DL-tartrate systems were fully characterised and a different mode of complexation was observed to that in the *meso*-tartrate system. The *meso* ligand was found to yield predominantly cyclic trinuclear species. Dinuclear species, different from those of the tartrates, were predicted for the VO^{2+} -citrate system [48].

Complex formation between VO^{2+} and ADP, ATP, adenine, adenosine and 2'-deoxyadenosine 5'-diphosphate (dADP) has been investigated in aqueous solution by EPR, absorption spectroscopy and pH-potentiometry. The results suggest that in acidic media the nucleotides chelate the metal through unshared oxygen atoms of the polyphosphate chain whereas in alkaline solution vicinal *cis*-oriented hydroxyls of the ribose moiety bind. Dihydroxy bridged dimers were observed with ATP and ADP molecules coordinating through both the phosphate and ribose residues but mixed chelation seemed to be the most favoured arrangement. Because of the poor affinity of VO^{2+} for N-donors, adenine is not able to bind VO^{2+} over a large pH range [49].

The effect of amide coordination on the parallel coupling constant has been

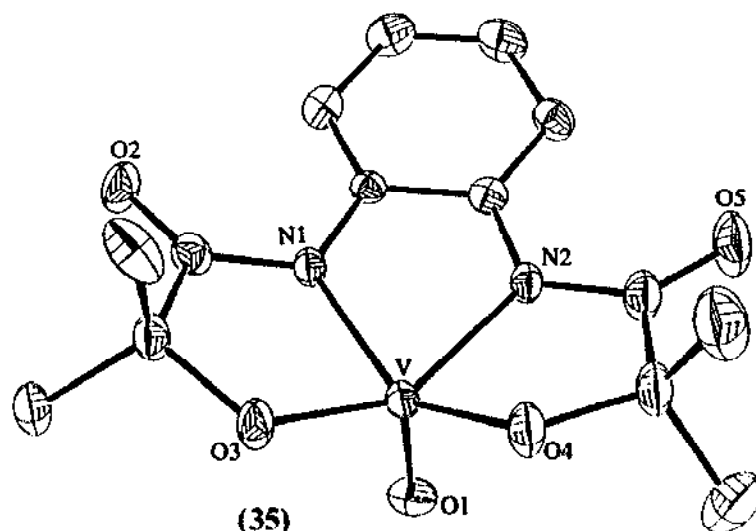
determined for three square pyramidal vanadyl complexes. The complexes $V^{IV}O(PAAP)$, $V^{IV}O(PAIS)$ and $[Bu_4N][V^VO(HIBA)]$ have been prepared and the structures of the latter two investigated. (PAAP=dianion of 1,2-bis(2-carboxamidopyridyl)benzene, PAIS=dianion of [*N*-(salicylideneamino)phenyl]pyridine-2-carboxamide), HIBA=tetraanion of 1,2-bis(2-hydroxy-2-methylpropanamido)benzene). The $V^{IV}O(PAIS)$ structure, (34), consists of an equatorial tetradentate ligand that provides pyridyl, amido, imino and phenolato coordination to the $V=O$ group which has a distorted square pyramidal geometry. The compound $[Bu_4N][V^VO(HIBA)]$, (35), is the first structurally characterised $V(V)$ complex containing a $V-N_{amide}$ bond. The immediate coordination sphere of the V atom consists of an O atom, two alkoxide oxygen donors and two deprotonated amide-nitrogen donors. Again the coordination geometry is best described as distorted square pyramidal. Measurements of A_{\parallel} for vanadyl-bleomycin and vanadyl-serum were carried out and compared with calculated values. Conclusions were drawn from these upon the nature of vanadyl–amide nitrogen coordination in vanadium(V) peptides and dipeptides [50].



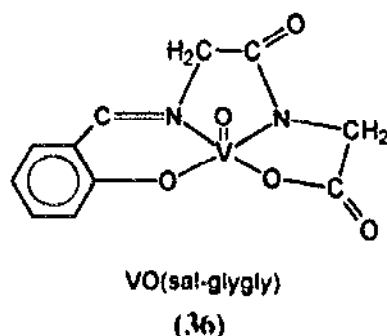
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The complex $VO(\text{sal-glygly})(H_2O)_n$, (36), (sal-glygly = *N*-salicylidene-glycylglycinate; $n = 1.5\text{--}3.0$), has been isolated from concentrated solutions containing VO^{2+} , glycylglycine and salicylaldehyde. Dilute solutions used in the preparation of (36) on standing, yielded the decavanadate $(NH_4)_4(Na)_2[V_{10}O_{28}] \cdot 10H_2O$, (37), whose structure was determined [51].

The same group has studied the solution structures of various species of oxovanadium(IV) with derivatives of L-histidine and related ligands by investigating the pH dependence of the circular dichroism, isotropic absorption and ESR spectra and comparing them with structures of the corresponding complexes of L-histidine. The results confirm the tridentate coordination of one of the L-histidine ligands in the pH range 6–8 and show that most natural amino acids solutions with low ligand to metal ratios contain high concentrations of hydrolysed VO^{2+} [52].

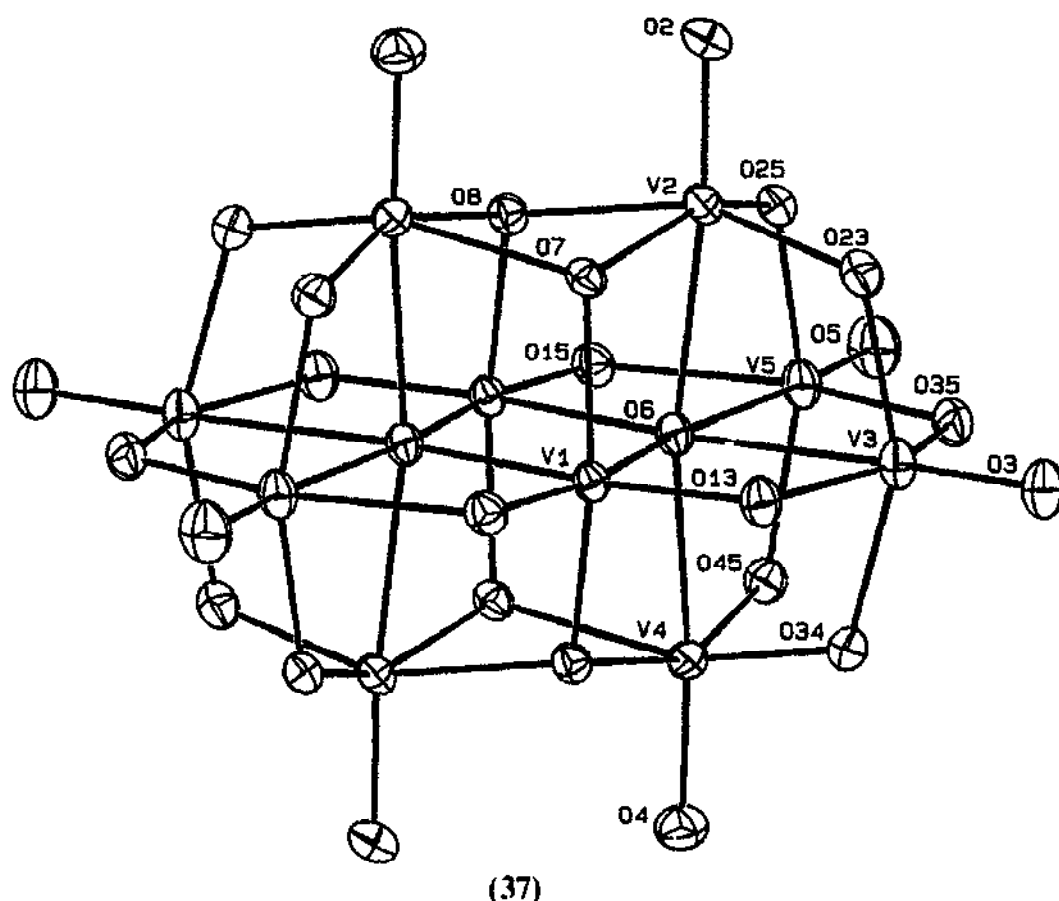


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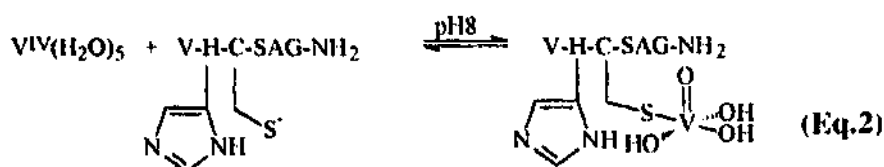
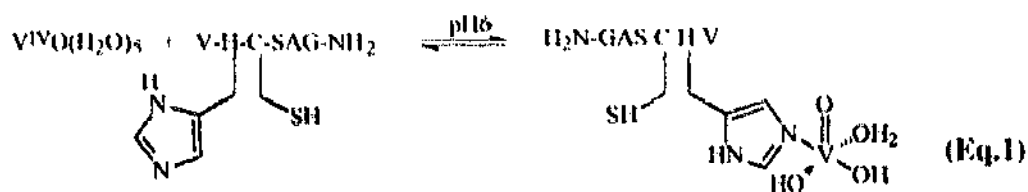


Vanadyl complexes of the peptides VIICGAG-NH₂, VIIMxurSAG-NH₂ and VFCSAG-NH₂ (single letter amino acid nomenclature) have been examined by EPR spectroscopy to determine which heteroatoms of the peptide interact with the metal in some protein tyrosine phosphatase complexes. Structures were proposed for the complexes on the basis of the EPR results which are summarised in equations (i) and (ii) [53].

An electron spin echo envelope modulation (ESEEM) study has been performed on VO²⁺ introduced into the high-affinity metal binding site of D-xylose isomerase. The results showed the existence of an equatorially coordinated N from the histidine residue and provided fairly detailed information concerning the geometry of N ligation in such complexes [54]. The technique has been applied to further studies on metalloprotein active sites in VO-(imidazole)₄ and VO-(histidine)_n complexes. Studies using ¹⁵N enriched ligands showed that the coordinated and remote ring N atoms in the [¹⁵N]imidazole complex have very different isotropic hyperfine coupling whereas in the [¹⁵N]histidine complex equatorial coordination by both imine and amine nitrogen takes place. As such it was concluded that the VO²⁺-histidine complex cannot be considered an adequate model for coordination by the histidine side chain in proteins and that the imidazole ligand provides a better model [55].



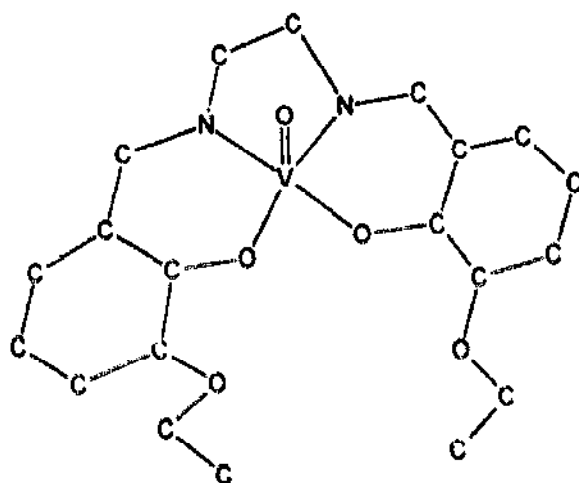
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Vanadyl perfluorophthalonitrile, VOPcF_{16} , has been prepared from V_2O_5 and tetrafluorophthalonitrile in pentan-1-ol. An investigation of the spectroscopic and electrochemical properties of the complex showed it to exist as a monomer in non-polar solvents and to dimerise in polar solvents [56]. Vanadyl β -alkyl-corrolate has been synthesised by the reaction of the corrole, $\text{H}_3\text{L} = 2,3,7,8,12,13,17,18$ -octaalkylcorrole) with $\text{VO}(\text{acac})$. The complex retains the

aromatic π -electron system and NMR spectroscopy showed the proton to be located at the inner nitrogen atom position. EPR spectroscopy was used to confirm the +4 oxidation state for the metal [57].

The Schiff base complex $(VO)[salphen]CH_3CN$ has been obtained from the reaction of $(C_2H_5)_4NVO_3$ with salphen in CH_3CN . The complex was characterised by elemental analysis, EPR, IR and electronic absorption spectroscopy and conductance measurements. A structural determination showed the salphen ligand to be acting as a doubly negative quadridentate ligand coordinating to the V atom through two N and two O atoms. The V atom is in a distorted square pyramidal conformation [58]. The structurally similar complex $[VO(3-EtOsalen)]$, (38), (3-EtOsalen = Schiff base *N,N'*-ethylene(3-ethoxysalicylideneamine)) has been prepared from $VOSO_4$ and the Schiff base with sodium acetate trihydrate in methanol. The IR and electronic absorption spectra of the complex were recorded and interpreted and the X-ray crystal structure determined [59]. A report has been made of the synthesis and spectral properties of vanadyl complexes with Schiff bases derived from 5-nitrosalicylaldehyde, 2-hydroxy-1-naphthaldehyde and 2,2'-diamino-diphenyl-disulfide [60].

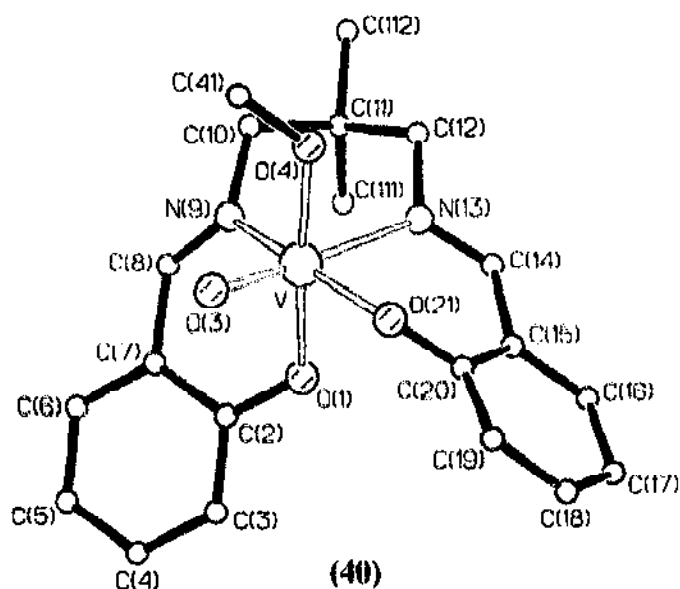
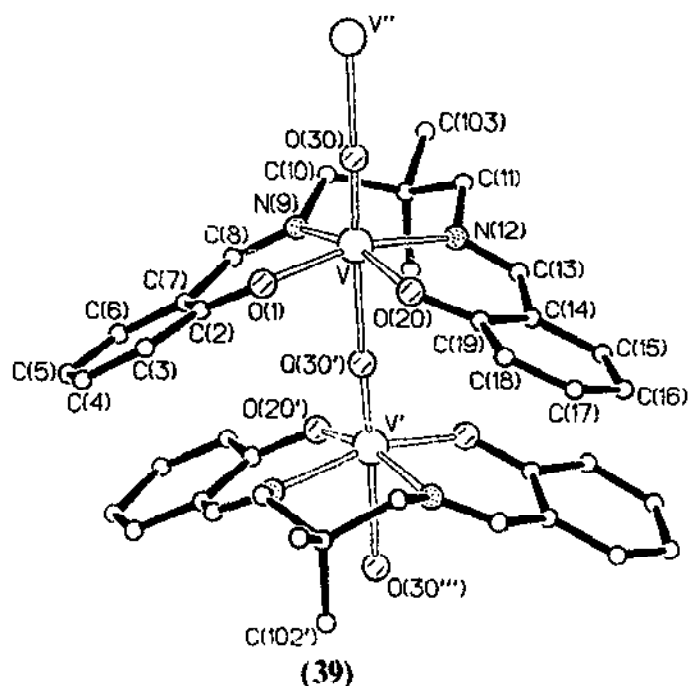


$[V(IV)O(3-EtOsalen)]$

(38)

The structure of $[VO(salnptn)]$ (salnptn = *N,N'*-2,2-dimethyltrimethylenebis-[salicylideneimine(2-)]) has been determined and was found to be polymeric in the solid state having... $V=O \rightarrow O=V=O \rightarrow O=V=O$...chains. The *O,O',N,N'*-donor atoms of the Schiff base are coplanar and the V atom is pseudo six-coordinate (39). The derivative $[VO(OMe)(salnptn)]$ (40) was found unexpectedly to have the OMe and vanadyl oxygen atoms coordinated *cis* to each other, so that the Schiff base occupies three equatorial and one axial position. Similar behaviour was found for the ethylene analogue of salnptn which is normally planar [61].

Vanadyl complexes of Schiff bases derived from isonicotinic acid hydrazide with general composition $VO(L).nX_2$ ($X=Cl, Br, I, NCS$ or NO_3 , $n=1$; $X=ClO_4$, $n=$



(39) and (40) reproduced from ref. [6] with permission.

2; L = Schiff base) have been synthesised and characterised by chemical and spectral analysis. No evidence was found for metal-metal interactions between the V atoms [62].

A number of new mixed ligand complexes consisting of three ligands have been obtained from the reactions of $[VO(acac)(BH).EtOH]$ (BH = benzohydroxamato) with bases such as Ph_3P , dppe, dppp and pyridine. An octahedral structure was proposed for the complex on the basis of spectral data and conductivity measure-

ments [63]. The redox chemistry of some oxovanadium(IV) complexes containing substituted dibenzotetraaza[14]annulene ligands has been investigated by cyclic voltammetry. Reversible oxidation to the corresponding oxoV(V) cations was observed in each case and the cations could be prepared in high yield by the oxidation of the oxovanadium(IV) precursors with $[(C_5H_5)_2Fe]SbF_6$ [64].

5.3 Non-oxo vanadium(IV) complexes

An extensive series of spectroscopic studies has been carried out for the eight coordinated V(IV) and (V) complexes $[V(hida)_2]^{2-}$ and $[V(hida)_2]^-$ ($H_3hida = N$ -hydroxyiminodiacetic acid) and $[V(hidpa)_2]^{2-}$ and $[V(hidpa)_2]^-$ ($H_3hidpa = (S,S)$ - N -hydroxy-2,2'-iminodipropionic acid). Vanadium is concentrated by fungi of the *Amanita* genus as amavadin, a complex of H_3hidpa , which has not hitherto been fully characterised. The studies reported here suggest that amavadin consists of an approximately equal mixture of $[A-V\{(S,S)\text{-}hidpa\}_2]^{2-}$ and $[A-V\{(S,S)\text{-}hidpa\}_2]^{2-}$, both of which ions contain eight-coordinated V(IV) but no V=O group. The electronic structure and the nature of the metal-ligand bonding in these V(IV) and V(V) centres is described [65].

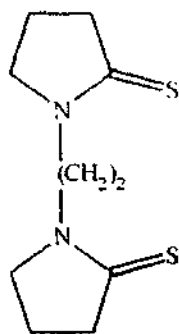
Reaction of tris(acetylacetonato)vanadium(III) with salicylaldehyde-2-hydroxyanil yielded the non-oxo compound bis{salicylaldehyde-2-hydroxyanilato(2-)}vanadium(IV) whose crystal structure was determined [66]. Similarly reaction of $V(acac)_3$ with tridentate diacidic ligands led to non-oxo V(IV) complexes such as bis[2,2'-dihydroxy-azobenzenato(2-)]vanadium(IV) [67]. The reactions of these non-oxo V(IV) complexes in $CH_2Cl_2/CH_3OH/H_2O$ solutions were studied by UV-VIS spectroscopy and were shown to lead to V(V) products [68].

A similar non-oxo V(IV) complex [vanadium(salen)benzilate] has been prepared from a different route in which the initial step is the deoxygenation of $VO(salen)$ by $SOCl_2$. This reaction leads to *trans*- $VCl_2(salen)$ which when treated with the Li_2 -salt of benzilic acid yields the product [vanadium(salen)benzilate] $\cdot 1.5CH_2Cl_2$. The X-ray crystal structure of the complex showed the V(IV) ion to be in a distorted octahedral environment as shown in (41). This is thought to be the first example of a monomeric non-oxo V(IV) complex with concomitant vicinal carboxylate and hydroxylate coordination [69].

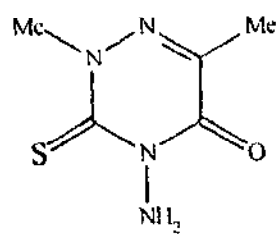
Ab initio CASSCF and CASPT2 (second-order perturbation theory correction) calculations have been carried out on the $V_2N_2H_6$ complex as a model of a series of (cyclobutane)diazadivanadium complexes in order to study the electronic structure and bonding in these complexes. Analogous calculations were also carried out on the cationic and anionic species in order to study the behaviour of the complexes on oxidation and reduction. The results indicate a weak σ metal-metal bond and a relatively large singlet-triplet splitting with the singlet as the ground state [70].

6. Vanadium(III)

Reaction of the V(III) complex $\{[(Me_3Si)_2NV[CH_2(SiMe_2)N(SiMe_3)]]_2\}$ with PMe_3 yields $\{[(Me_3Si)_2NV[CH_2(SiMe_2)_2N(SiMe_3)](PMe_3)]\}$. Hydrogenolysis of the

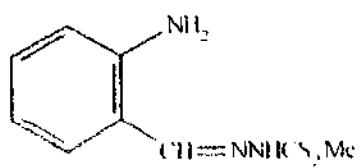


(161)



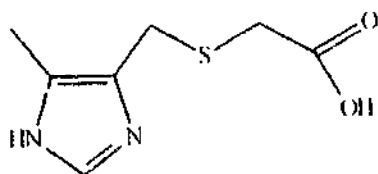
Taz

(162)



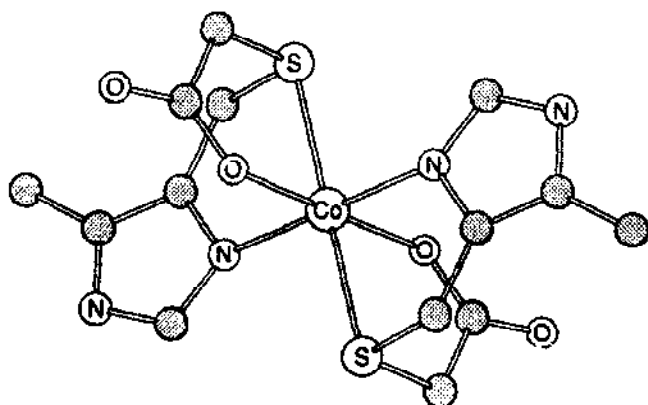
HNNS

(163)



Hiba

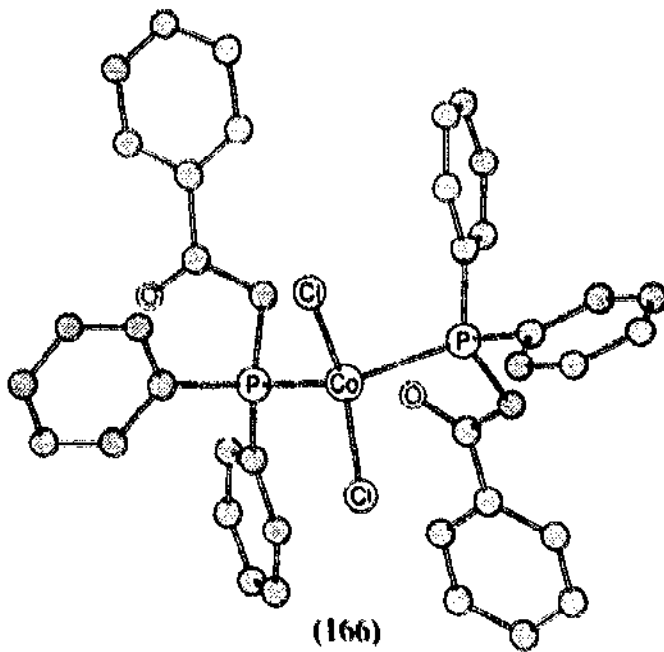
(164)



(165)

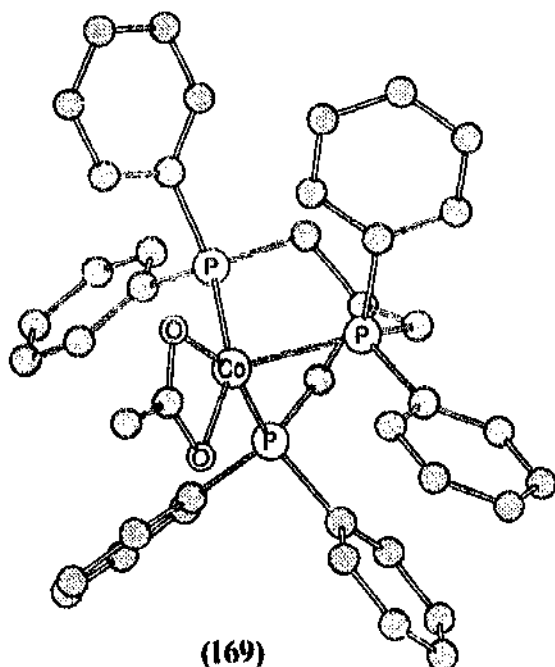
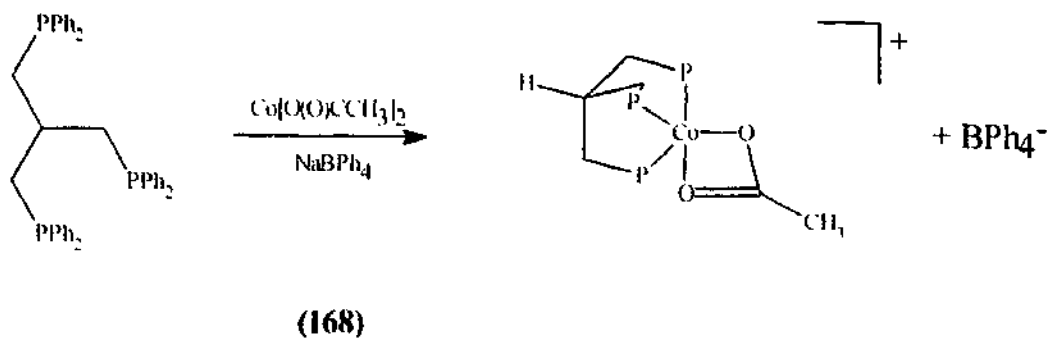
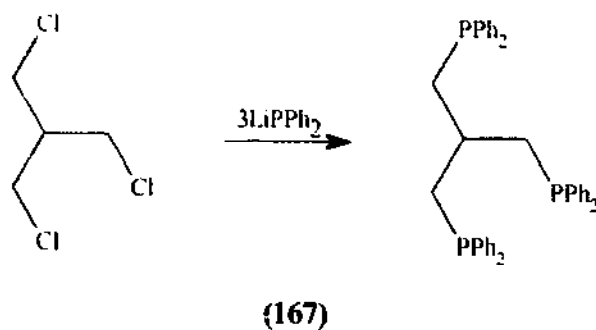
3.8. Complexes with phosphorus donor ligands

A range of Co(II) ketophosphine complexes of the type $[\text{CoX}_2\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}\}_2]$, in which $\text{X} = \text{Cl}, \text{Br}$ and I , have been prepared and the chemistry in solution compared with that of the corresponding complex $[\text{CoX}_2(\text{PPh}_3)_2]$ [294]. These complexes show tetrahedral-octahedral equilibria in solution in methanol and a feature of these equilibria is that it is the solvent molecules which are involved in the process rather than the carbonyls. The crystal structures of several complexes have been determined including that of $[\text{CoCl}_2\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}\}_2]$ (166).



(166)

The ligand 1,1,1-tris[(diphenylphosphanyl)methyl]methane has been prepared by the reaction shown in (167) [295]. The ligand forms a Co(II) complex by the reaction shown in (168) and the X-ray crystal structure of the cobalt(II) complex confirms that for the cation shown in (169).



3.9. Complexes with halide and pseudohalide donor ligands

Data from a spectrophotometric and conductivity study of CoCl_2 and CoBr_2 in solution in acetone show that they are present as the electrically neutral pseudotetrahedral complexes $[\text{CoX}_2(\text{acetone})_2]$ [296] and the stability constants have been

obtained. Similar experiments with $\text{Co}(\text{SCN})_2$ in aqueous DMSO showed the presence of $[\text{Co}(\text{SCN})]^+$ and again association constants were obtained [297].

When anaerobic solutions of pentacyanocobaltate(II) in aqueous ethanol were irradiated by a high pressure Hg lamp it was found that hydrogen and acetaldehyde were produced in a 1:1 ratio [298]. Similar behaviour resulted when pentacyanocobaltate(II) was replaced by $\text{Co}(\text{II})$ –mixed complexes to which CN^- and en had been added, although in the presence of en the yield of acetaldehyde was lowered.

3.10. Complexes with arsenic donor ligands

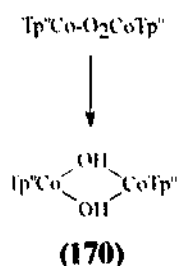
Tetrakis(alkylisocyanide)bis(triarylsarsine)cobalt(II) complexes have been prepared by the reaction of pentakis(alkylisocyanide)cobalt(II) in ethanol with triarylsarsines [299]. Magnetic and solid state spectrophotometric measurements suggest that the structures of these complexes are tetragonal *trans*- $[\text{Co}(\text{CNR})_4(\text{AsR}_3)_2]\text{X}_2$. In a related study [300], the complex $[\text{Co}(\text{CNCHMe}_2)_4(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)_2](\text{ClO}_4)_2$ has been prepared and it is suggested that this too has a tetragonal arrangement around the $\text{Co}(\text{II})$ with the arsenic-containing ligand being monodentate.

4. Reactions of cobalt complexes involving dioxygen

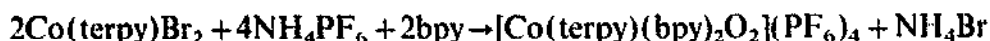
As is usually the case, this area of cobalt chemistry has attracted much interest. The topic has been reviewed in various aspects on a number of occasions. There has been a survey of the chemistry of synthetic heme dioxygen complexes which contains a number of examples involving cobalt [301]. The photochemical reactions of metalloporphyrins which contain dioxygen have been reviewed and the reactivity of various porphyrin complexes compared with $\text{Co}(\text{II})$ tetraphenylporphyrin [302]. The properties of transition metal dioxygen complexes have been reviewed from the point of view of using them industrially in the future as an alternative method to cryogenics for separating dioxygen from the other gases in the atmosphere in a more efficient and cost-effective manner [303]. The effect of pH and the nature of the ligand on the uptake of dioxygen by a number of $\text{Co}(\text{II})$ complexes has been investigated for a wide variety of dipeptide complexes [304]. The dipeptides studied were glycylglycine, alanylglycine, leucylglycine, tyrosylglycine, phenylalanineglycine, glycylalanine, glycylleucine, glycyltyrosine and glycylphenylalanine. The method of comparison was to measure the rate of uptake of dioxygen by a solution of $\text{Co}(\text{ClO}_4)_2$ in the presence of an excess of the appropriate dipeptide. Below pH 6.5, dioxygen adducts were not formed and this is believed to be a function of the deprotonation of the dipeptide amine groups. The rate of uptake of dioxygen was also related to the occurrence of steric hindrance by side chains in the dipeptides, with the rate increasing when there is substitution on the *N*-terminal amino acid and decreasing when there is substitution on the terminal C atom. Histidine and moniodohistidine complexes of $\text{Co}(\text{II})$ have been found to bind dioxygen, whereas

diiodohistidine complexes do not [305]. The formation of dioxygen complexes with Co(II) asparagine compounds is found to be enhanced at pH higher than 13 as a result of the formation of a tridentate complex between the asparagine and the Co(II) [306]. This in contrast to the behaviour of other similar amino acids.

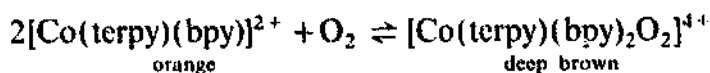
Reaction of the complex $\text{Tp}''\text{Co}(\text{O}_2)$ with 0.5 equiv of $\text{Tp}''\text{Co}-\text{N}_2-\text{CoTp}''$ yields the species $\text{Tp}''\text{Co}-\text{O}_2-\text{CoTp}''$, where Tp'' = hydridotris(3-isopropyl-5-methylpyrazoyl)borate [307]. The kinetics of the decomposition of this complex (170) in CD_2Cl_2 , followed by ^1H NMR spectroscopic studies showed that the reaction was first order and $k = 2.27 \times 10^{-3} \text{ s}^{-1}$ at 281 K with $\Delta H^\ddagger = 16.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -12 \text{ eu}$. It was further shown that there was a very significant isotope effect with $k_{\text{H}}/k_{\text{D}} = 22$. It is concluded that C–H bond breaking is the rate determining step in the reaction with the probability of tunnelling being a factor in the H transfer. The scheme proposed by the authors for the activation of the dioxygen molecule is shown in scheme (171).



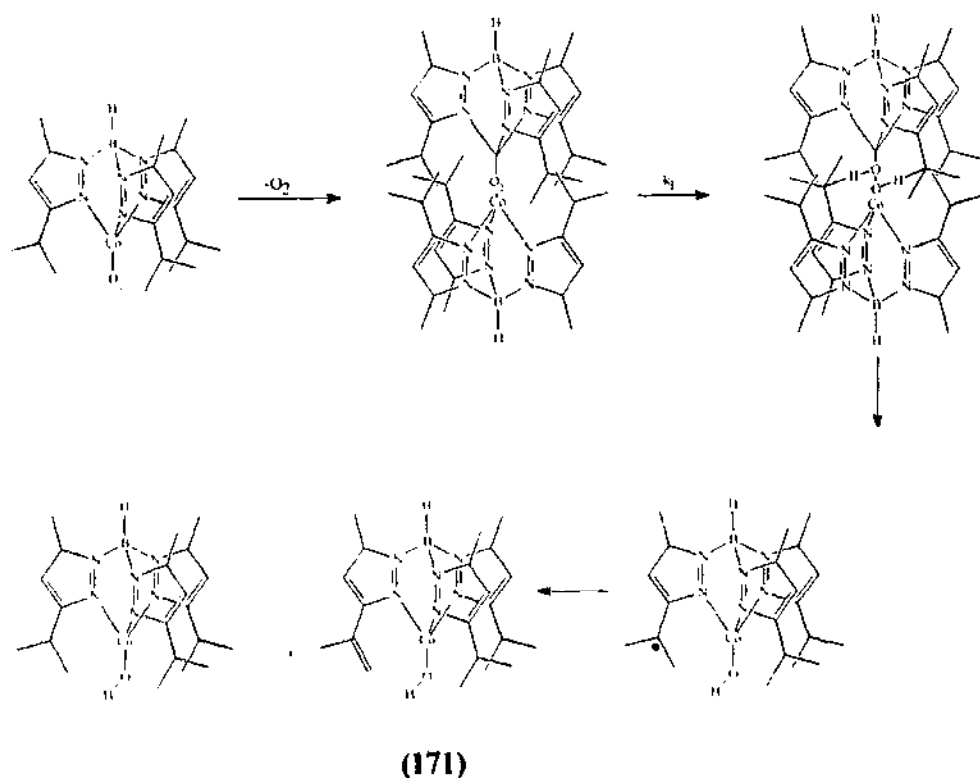
A number of complexes of the form $[\text{Co}(\text{terpy})(\text{L})\text{X}]$ in which L = 2,2'-bipyridine or 1,10-phenanthroline or one of a number of substituted 1,10-phenanthrolines, X is a weakly binding species such as triflate, have been prepared and characterized [308]. These reversibly bind dioxygen and this process has been studied by a variety of techniques. A typical example is the complex $[\text{Co}(\text{terpy})(\text{bpy})]^{2+}$. When an attempt is made to prepare this complex in acetonitrile under an inert atmosphere it is found that the product does not reversibly take up dioxygen. When, however the same preparation is carried out in air and the resulting solid is dissolved in acetonitrile, it reversibly took up O_2 . During experiments to elucidate the nature of these reactions the authors prepared the peroxo species:



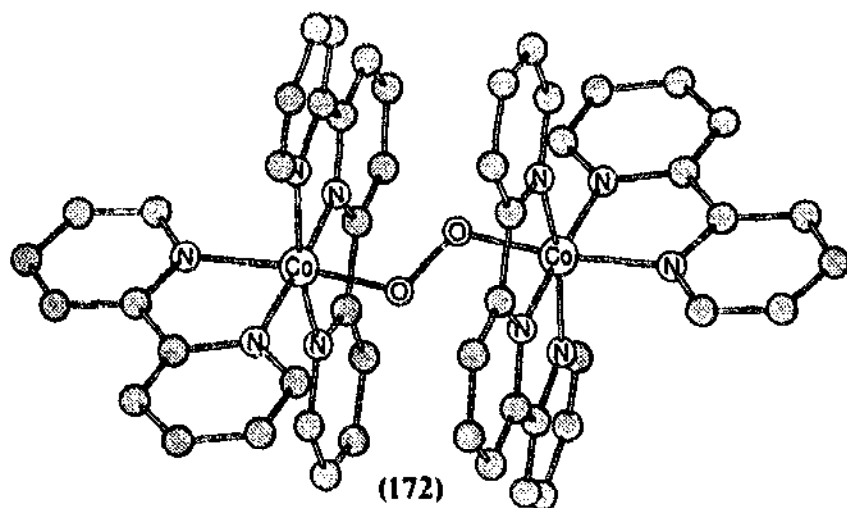
The X-ray structure determination on this complex confirms that it is the peroxo complex. When solutions of this compound were saturated with N_2 , the complex $[\text{Co}(\text{terpy})(\text{bpy})](\text{PF}_6)_2$ was formed quantitatively:



The presence of a band at 824 cm^{-1} in the Raman spectrum confirms the presence of the peroxo moiety and at 25°C $\log K_{\text{O}_2}$ for the formation of $[\text{Co}(\text{terpy})(\text{bpy})_2\text{O}_2]^{4+}$ in acetonitrile is $4.4 \text{ M}^{-1} \text{ atm}^{-1}$. Various coordinated solvents were investigated to examine their effect on dioxygen binding. Thus, in



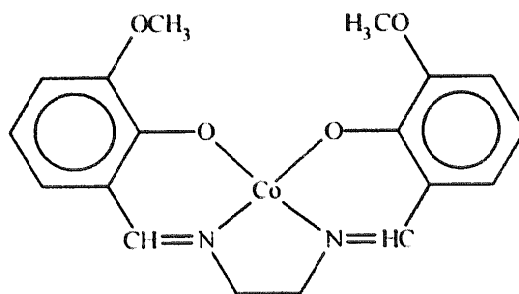
nitrobenzene the binding was extremely tight. By judicious choice of added weak ligands such as triflate, reversible binding could readily be achieved. The X-ray structure of solvated $[\{\text{Co}(\text{terpy})(\text{bpy})\}_2\text{O}_2](\text{PF}_6)_4$, [(172)] $(\text{PF}_6)_4$, has been determined.



The complex $[\text{Co}(\text{nbsal})_2]$, where $\text{nbsal} = N$ -*n*-butylsalicylideneimine, reacts readily with both nitric oxide and dioxygen [309]. However, the complex $[\text{Co}(\text{tbsal})_2]$, where $\text{tbsal} = N$ -*tert*-butylsalicylideneimine shows no reactivity to either NO or O_2 . The crystal structures of both these complexes have been determined

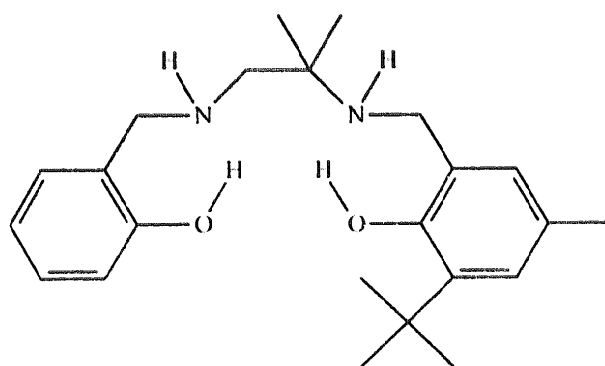
and both are found to have a distorted tetrahedral arrangement around the Co. However, there is much greater distortion of the tetrahedral arrangement when there are *tert*-butyl groups present.

The response to dioxygen by CdSe coated with [Co(3-MeO-salen)] (173) raises the possibility of using this system as a sensor [310]. It has been found that band gap photoluminescence excited by light of wavelength 633 nm of etched single crystal of n-CdSe is significantly enhanced in MeCl solution in anaerobic conditions by the presence of [Co(3-MeO-salen)]. This effect depends on the concentration of the complex. Using the Langmuir isotherm model, an equilibrium constant between 10^4 and 10^5 was obtained. The photoluminescence is quenched by the presence of dioxygen in a way which depended on the dioxygen pressure.



(173)

The complex [Co(II)L], where H_2L is (174) has been prepared and characterized and its X-ray structure determined [311]. The crystal structure shows that it is monoclinic $C2/c$ and $a=25.389$, $b=18.139$, $c=10.179$ Å, $\beta=112.227^\circ$ and $Z=8$. The complex has a square planar N_2O_2 arrangement around the Co. In the presence of dioxygen the species [Co(H_4)L] and [Co(H_2)L] in acetone are easily oxidized to [CoL].

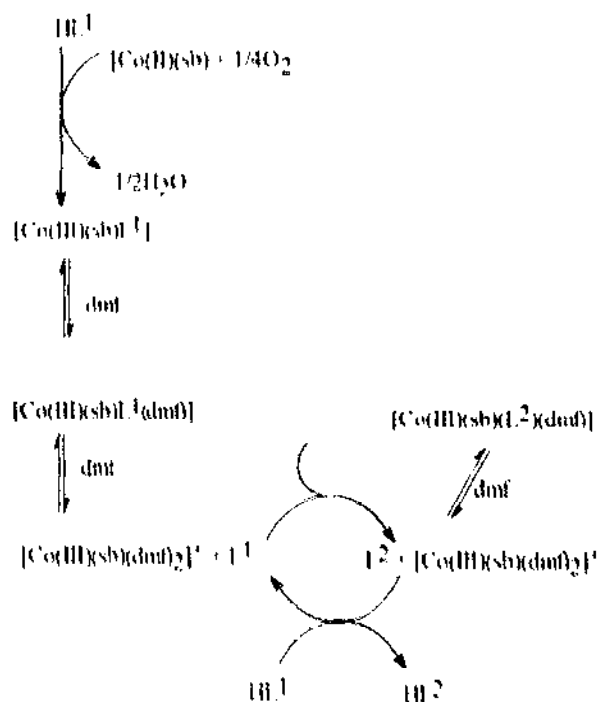
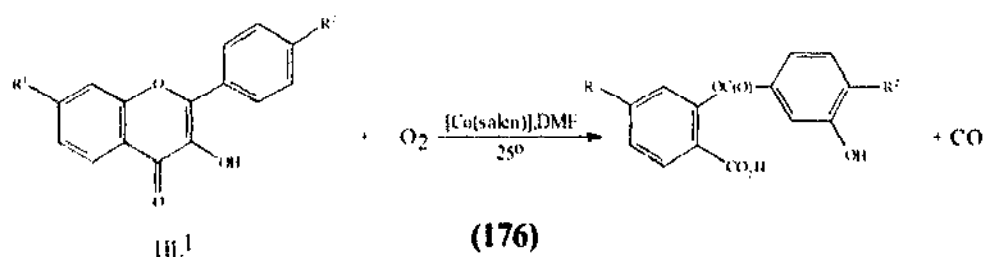
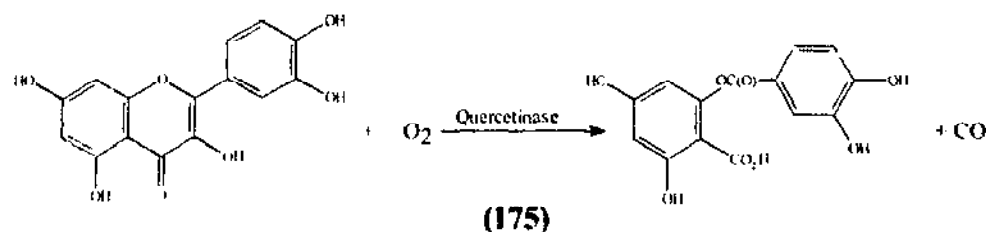
 H_2L

(174)

The dioxygenase, quercetinase, produced by *Aspergillus flavus*, catalyses reaction (175) [312] which results in the production of depsides and CO. This behaviour can

to some extent be mimicked using [Co(salen)] in DMF as shown in scheme (176). This work involves a study of the mechanism of the reactions involving [Co(salen)] using cyclic voltammetry. The proposed mechanism is shown in scheme (177).

A study of the effectiveness of Co(II) Schiff base chelates incorporated into

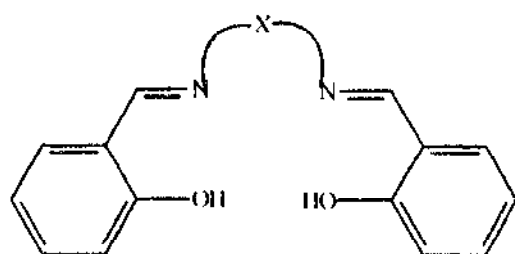


Fl.1 = flavonol substrate

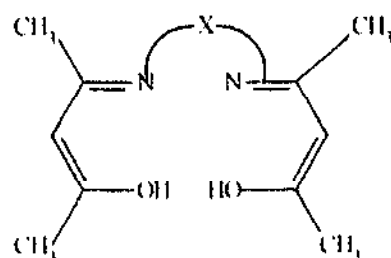
Fl.2 = deprode product

sb = Schiff base dianion

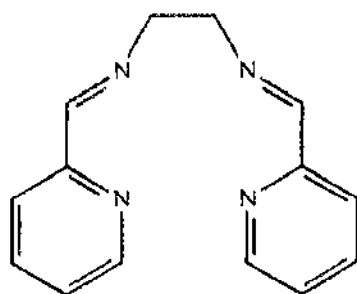
faujasite-type zeolites has focussed on the ligands shown in (178) [313]. The tetradentate ligand, acacen and salen in zeolite Y were rather poor in producing active oxygen binding Co(II). The pentadentate ligands, smpt = bis(salicylaldehyde)methylnitrilodipropylenediimine and amdpt = bis(acetylaceton)methylnitrilodipropylenediimine, on the other hand greatly improved the amount of Co(II) which was active in oxygen binding. Another Co(II)-zeolite interaction which has been examined this year for dioxygen affinity is the tetramethylporphyrinatocobalt complex with zeolite Y [314]. The dioxygen affinity has been studied as a function of partial pressure and temperature. The dioxygenation reaction is reversible and the kinetics show the process to be pseudo first order with $k = 2.7 \times 10^{-5} \text{ s}^{-1}$ at 25°C . The kinetics of dioxygen binding reactions have been examined as a function of the structure of the porphyrins in a polymer membrane [315]. The new porphyrins were derivatives of *meso*- $\alpha,\alpha,\alpha,\alpha$ -tetrakis(*o*-pivalamidophenyl)porphyrinatocobalt. Very significant differences in rate for dioxygen binding were obtained for the different structures (179a) and (179b). There was a linear correlation between the logarithms of the dioxygen dissociation constant and the diffusion constant for the dioxygen via the porphyrin complexes in the membranes.



1,3

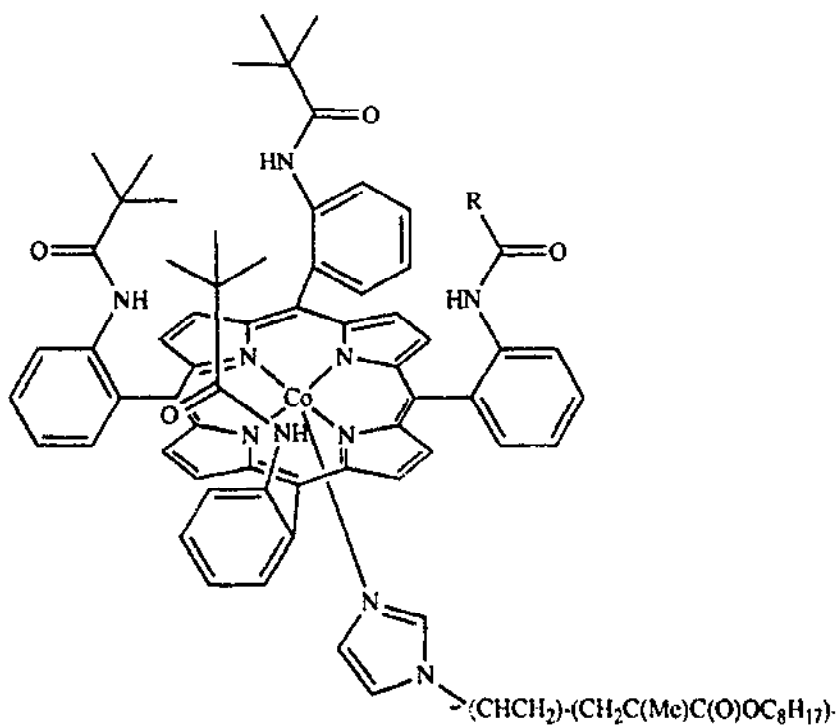


2,4

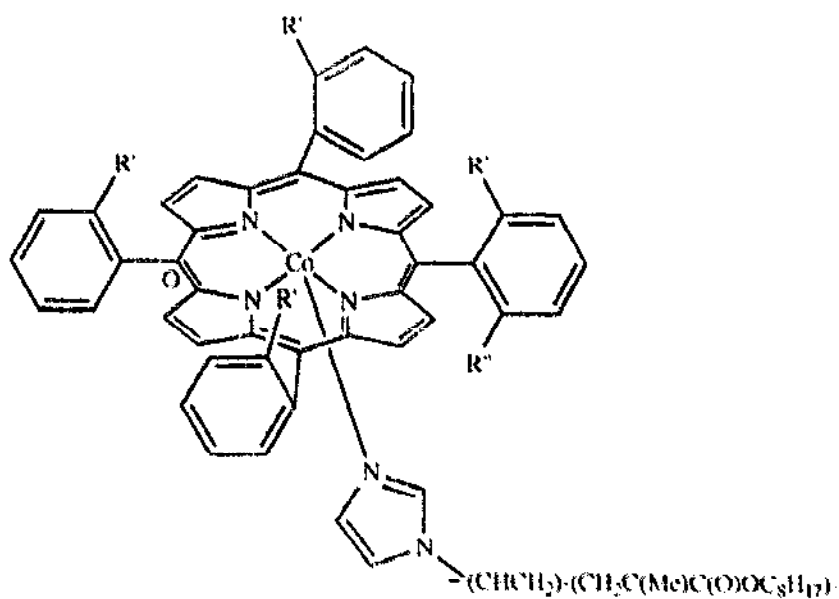
X = $-\text{CH}_2\text{CH}_2-$ (1,2)X = $-(\text{CH}_2)_3\text{N}(\text{CH}_2)_3-$ (3,4)

(178)

A series of porphyrin complexes of Co(II) which had on the periphery of their structure either cyanophenyl groups or *N*-CH₃py structures have been prepared [316]. These porphyrins were mixed with a dilute alcoholic solution of Nafion and



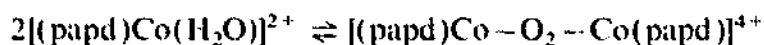
(179a)



(179b)

the mixture applied to the surface of a graphite electrode and then reacted *in situ* with $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$. This resulted in electrodes which had coatings containing 0, 1, 2 or 3 Ru atoms per porphyrin molecule (180). These systems were then examined for activity in reducing O_2 to H_2O via a 4-electron reduction. It was found that the species containing the 3 Ru atoms was the only one which exhibited significant 4-electron reduction. The 2 Ru species showed some tendency for 4-electron reduction, while the one-Ru atom complex only exhibited a 2-electron reduction of O_2 to H_2O_2 .

New peroxo complexes of Co(II) have been synthesized [317]. The ligand used was 1,4-bis[bis2-pyridylmethyl]amino]-3-propanol, Htpdb (181). The parent complexes were of the form $[\text{Co}_2(\text{tpdb})(\text{RCOO})](\text{ClO}_4) \cdot n\text{H}_2\text{O}$, $\text{R} = \text{CH}_3$ or C_6H_5 . These reacted with dioxygen in acetonitrile to produce the dioxygen complexes $[\text{Co}_2(\text{tpdb})(\text{RCOO})(\text{O}_2)]^{2+}$ (182) ($\text{R} = \text{Me}$). The X-ray crystal structure of the species $[\text{Co}_2(\text{tpdb})(\text{CH}_3\text{COO})(\text{O}_2)](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ was determined, but there was a disorder in the backbone of the tpdb[−] ligand and the carbon atoms have been omitted from diagram (182). The bridging mode between the two Co atoms involves acetate, alkoxy and dioxygen. Single dioxygen bridging is a feature of reactions involving the complex $[(\text{papd})\text{Co}(\text{II})(\text{H}_2\text{O})]^{2+}$, in which papd = 1,5,8,11,15-pentazapentadecane [318]. The overall reaction with dioxygen is:

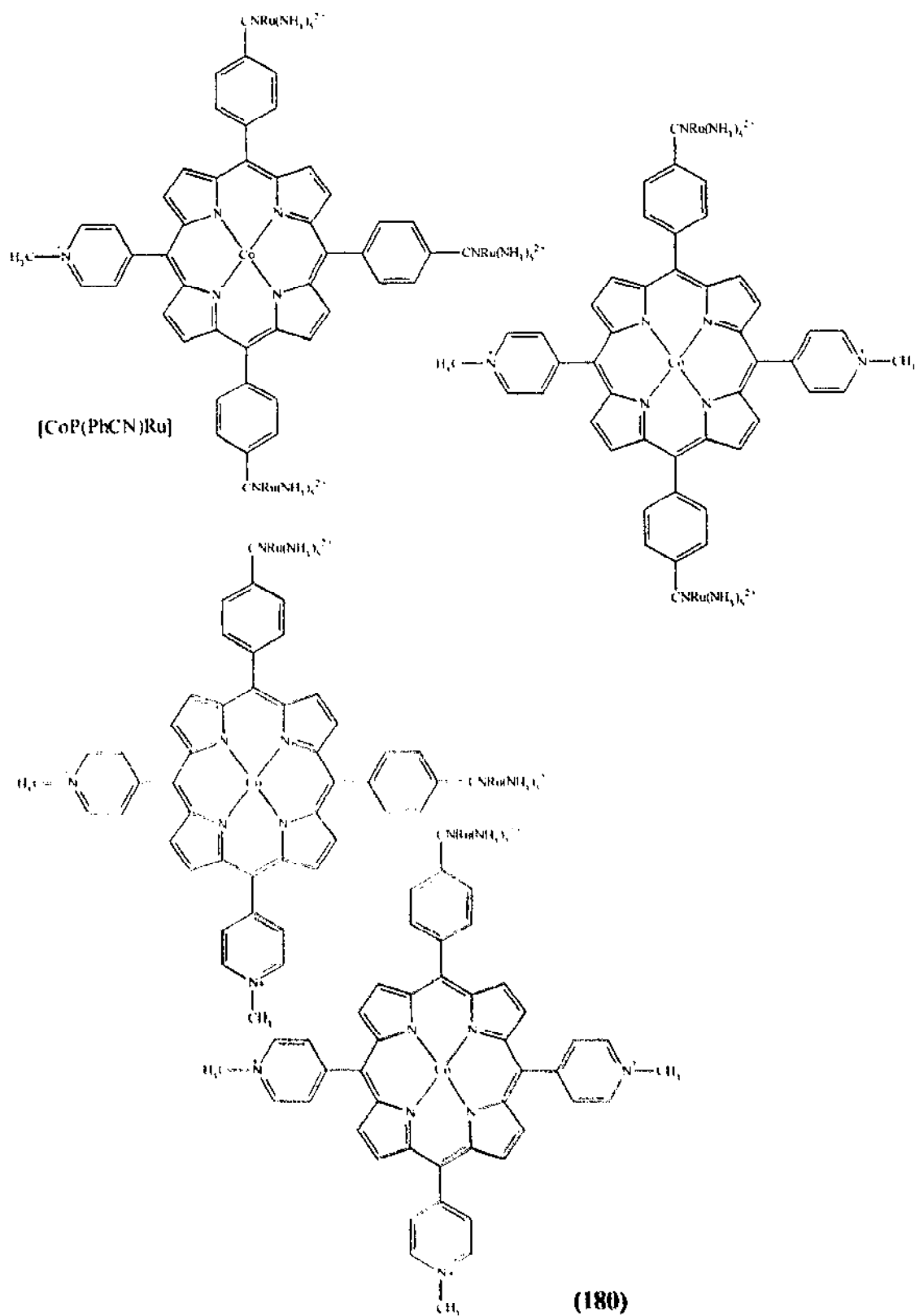


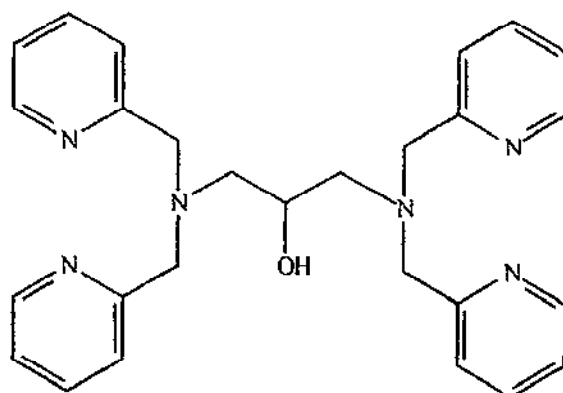
Early in the study, the authors found that when the dioxygen uptake by $[(\text{papd})\text{Co}(\text{II})(\text{H}_2\text{O})]^{2+}$ monitored by an oxygen sensitive electrode with $[\text{O}_2] > [\text{complex}]$ that there was a rapid decrease in O_2 producing a short-lived minimum and that this was followed by a release of oxygen. Under these conditions there was also observed a build-up of the superoxo complex and a clear separation of the steps in the process:

- i) the formation of a mononuclear intermediate, $[(\text{papd})\text{CoO}_2]^{2+}$, and
- ii) the formation of the product dinuclear complex $[(\text{papd})\text{Co}-\text{O}_2-\text{Co}(\text{papd})]^{4+}$.

The kinetics of each of these steps were investigated and the respective rate constants at 25°C were $k_1 = 1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. During these processes the first consists of the replacement of water in $[(\text{papd})\text{Co}(\text{II})(\text{H}_2\text{O})]^{2+}$ followed by electron transfer to produce superoxide ion and the second replacement of water in $[(\text{papd})\text{Co}(\text{II})(\text{H}_2\text{O})]^{2+}$ by $[(\text{papd})\text{CoO}_2]^{2+}$ followed by electron transfer to produce the peroxide ion. In both cases the electron transfer process was fast and the water exchange the rate determining step.

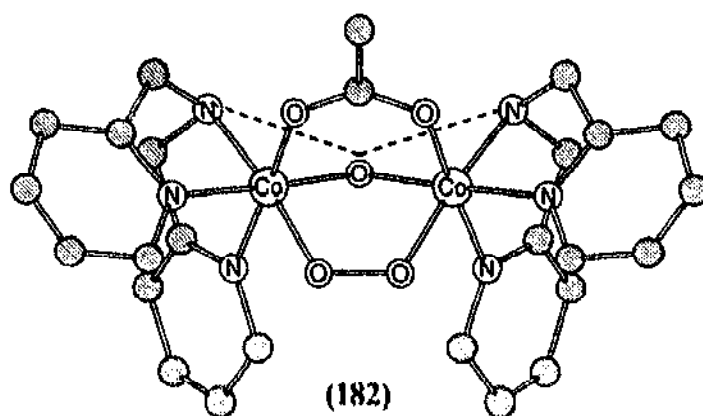
It is reported that the Co(II) complexes of Obistren and Obisdien behave as very good dioxygen carriers because the ligands remain intact and the dioxygen in the complex may be removed or added readily according to conditions such as temperature and pressure [319]. Detailed studies have been made of the equilibria involving Obisdien (Bd = Free base), Co^{2+} and phosphite (Ps) and also similar equilibria involving Bd, Co^{2+} and phosphate [320]. In the former series of equilibria, there





Htpdp

(181)



(182)

were two reactions involving the formation of Co_2 dinuclear complexes:



and only one in the case of phosphate:



The complex Co_2 -Obisdien-phosphite-dioxygen reacts at temperatures above 60°C such that the phosphite is oxidized to phosphate and the dioxygen in the complex is reduced to water. The kinetics of this internal redox reaction were studied and a typical pseudo first order rate constant was at pH 9 and $\text{Bd}/\text{HPO}_3^{2-}$ 1:1 $5.3 \times 10^{-9} \text{ s}^{-1}$. By substituting $^{18}\text{O}_2$ for $^{16}\text{O}_2$ in the Co_2 -Obisdien-phosphite-dioxygen system and examining the isotope distribution in the product, it was shown that the O which was in the phosphate derived from the oxidation of

phosphite came from the original molecular dioxygen which produced the dioxygen adduct.

There is a delicate balance between the redox behaviour of the metal ion, the nature of the ligand and the structure of any given ligand on the uptake and retention of dioxygen. The effects of a series of lacunar cobalt(II) cyclidene ligands which are structurally altered in a systematic way on the affinity of complexes has been investigated [321,322]. The structures of the lacunar Co(II) cyclidenes are shown in (183) and the modifications carried out were by changing R^1 , R^2 , R^3 . A key feature of the structural effect examined was the presence and variation of the polyethylene bridging ligand R^1 . A total of 20 cyclidene complexes were prepared and it was found that there is a systematic decrease in the binding of dioxygen as the length of the chain in the bridge is decreased from the octamethylene complex to the tetramethylene species, (e.g. for $[\text{MeMeC4[16]cyclidene}(\text{MeIm})]^{2+}$ $K_{\text{O}_2} = 0.005$ at -40°C and $[\text{MeMeC8[16]cyclidene}(\text{MeIm})]^{2+}$ $K_{\text{O}_2} = 0.45$ at 25°C) becoming zero for the trimethylene-and-below complexes. The X-ray crystal structure of one of the O_2 adducts was determined and the position of the end-on bonded O_2 in relation to the cyclidene ligand can be clearly seen in (184). It is pointed out by the authors that the factor associated with the structure that most affects the dioxygen uptake is the cavity width controlled by the length of the polymethylene chain. In the case of the variation of the other substituents on the cyclidine ligand, i.e. R^1 and R^2 , any changes in dioxygen affinity are attributed to the electron donating properties of the groups. The X-ray structure of the Co(III) complex $[\text{Co}\{\text{MeMeC8[16]cyclidene}\}(\text{SCN})_2](\text{PF}_6)_3$ was also determined in order to examine the conformational changes which occur due to the presence of a small molecule in the cyclidine cavity.

The rate constants for the uptake and release of dioxygen by the Co(II) complexes of cyclam (L^1) and hexamethylecyclam (L^2) have been measured as a function of pressure [323]. The method used was laser flash photolysis by using the reaction:

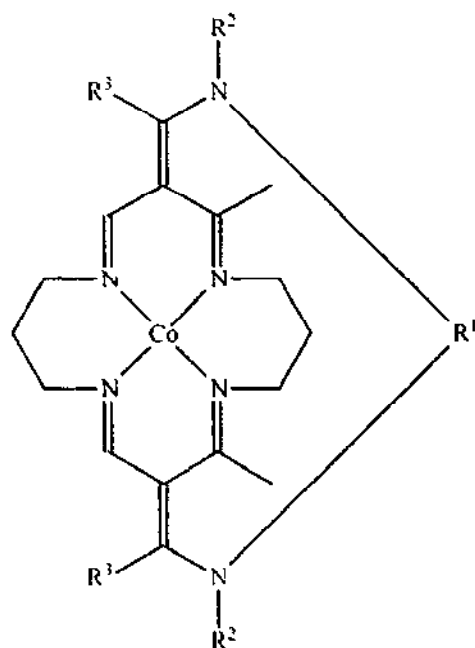


The flash produces the right hand side products which then re-form the starting material, and this reaction may be kinetically followed. The rate law for the process involving $[\text{L}^2\text{Co}(\text{H}_2\text{O})_2]^{2+}$ is:

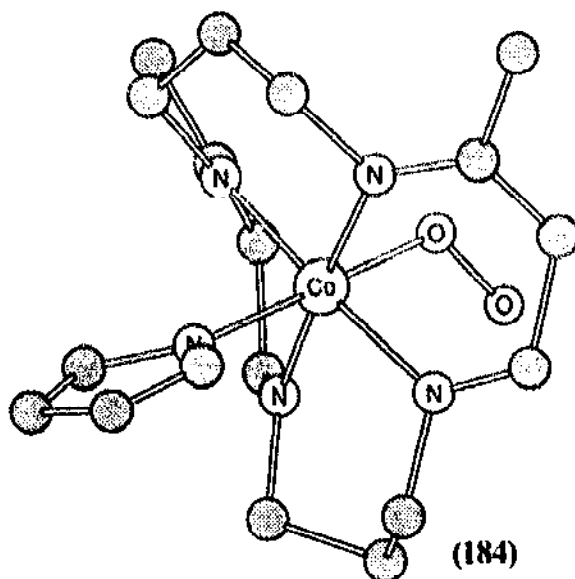
$$k_{\text{e}} = k_1[\text{O}_2]_{\text{e}} + [\text{L}^2\text{Co}^{2+}]_{\text{e}} + k_{-1}$$

The pressure dependence was determined for k_1 and k_{-1} . For the L^1 complex the equilibrium lies towards the dioxygen species and a more straightforward approach is therefore possible. The pressure dependence of the equilibrium constants for the L^2 ligand is also studied. It is proposed that the reaction of the L^2 complex has an interchange mechanism.

A range of Schiff bases made from 2-hydroxy-3-methoxy-5-methylbenzaldehyde and en, 1,3-propylenediamine, 2,3-dimethyl-2,3-butylenediamine, 1,3-propylene-



(183)



(184)

diamine or 1,2-phenylenediamine and having 4-methylpyridine in the axial position have been prepared and their dioxygen affinities measured in diglyme solution [324].

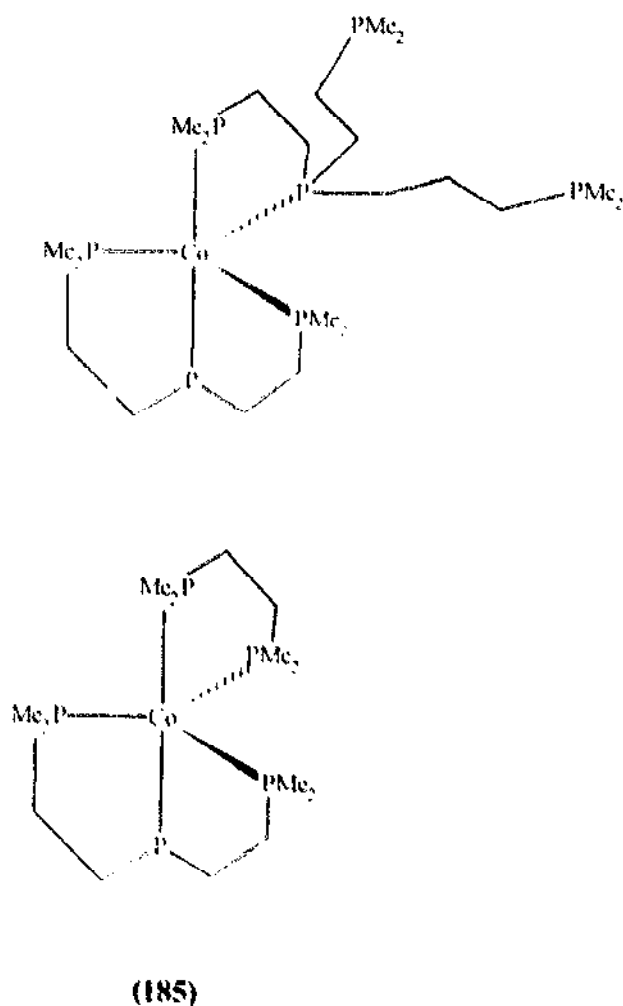
The use of Co-PMA complexes as models for the corresponding bleomycin complexes has been discussed in 2.1.1. Mascharak and coworkers have also examined the reaction of $[\text{Co(II)}(\text{PMA})]$ with O_2 and found that the product is

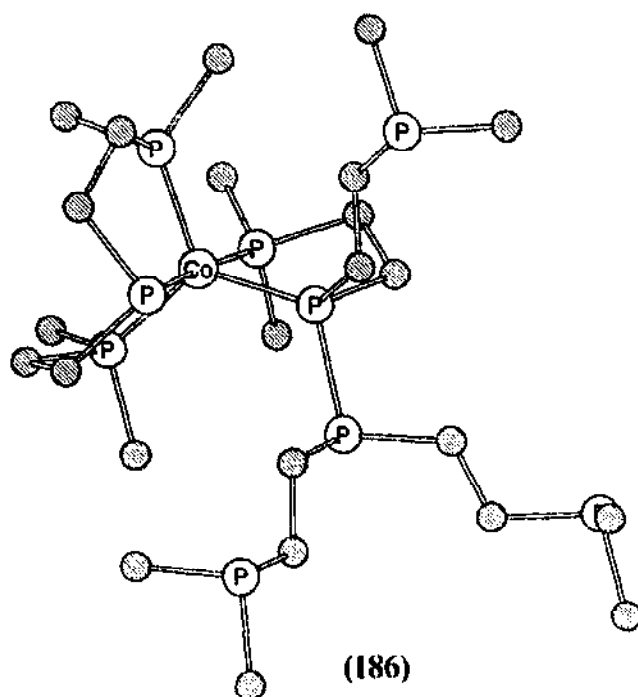
$[\text{Co(III)(PMA)(O}_2^-)]^+$ [324a]. In solution, the superoxide species decomposes to produce $[\text{Co(III)(PMA)(H}_2\text{O)}]^{2+}$.

5. Cobalt(I) complexes

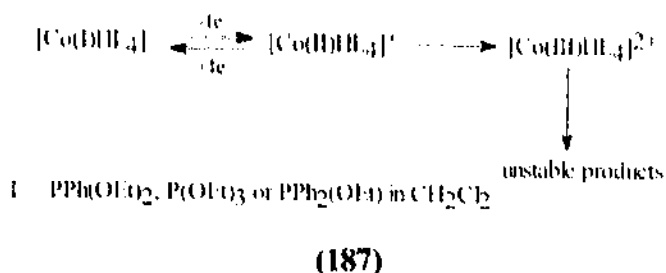
There has been a review of competitive redox reactions in which there is a cobalt(I) intermediate [325].

In a study of Co(I) phosphines, the complexes shown in (185) have been prepared and characterized [326]. The X-ray crystal structure of one, (186), has been determined and NMR spectroscopic studies carried out on the solution. The structures in the solid and in solution are similar, though variable temperature NMR spectra in the latter show that it is fluxional. The environment around the Co is roughly trigonal bipyramidal. The structure of the second complex was examined using ^{31}P - $\{^1\text{H}\}$ NMR spectroscopy, and the geometry around the Co was similar to that of the first complex.



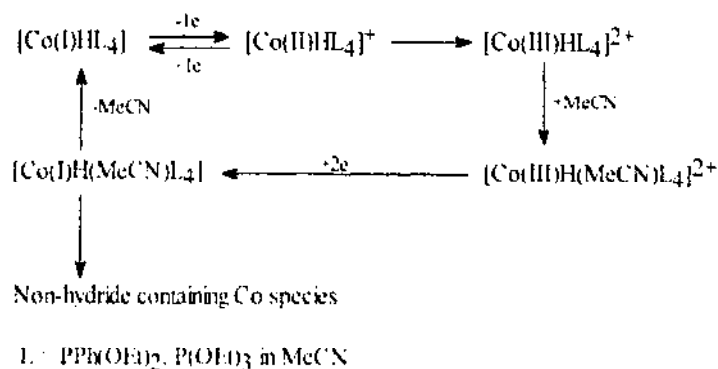


The mechanisms of the oxidation of a range of Co(I) hydride complexes of the form $[\text{CoHL}_4]$, in which $\text{L} = \text{P}(\text{OEt})_3$, $\text{PPh}(\text{OEt})_2$ or $\text{PPh}_2(\text{OEt})$ have been studied using electrochemical methods in CH_2Cl_2 and MeCN [327]. There were significant differences in the redox behaviour in the two solvents. Thus in CH_2Cl_2 there was a clear stepwise progression from Co(I) to Co(II) to Co(III) as shown in scheme (187) and the behaviour was the same for all the complexes studied. In MeCN solution, however the processes are complicated by the formation of MeCN-containing complexes and was not the same for all the complexes as is illustrated in schemes (188) and (189).

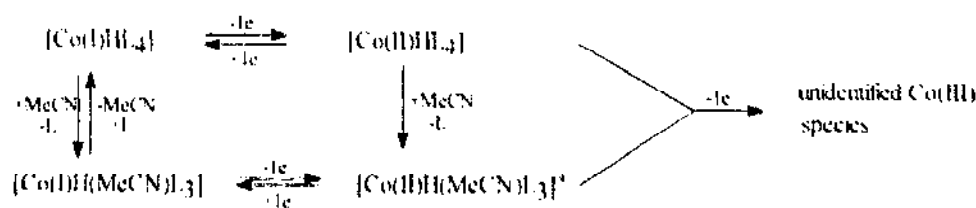


The Raman spectrum of tris(triphenylphosphine)cobalt(I) has been reported for the first time [328]. By comparison with other complexes it has been possible to assign the phosphine ligand vibrations and those of the Co–Cl and Co–P bonds.

The Co(I) state is produced electrochemically in an irreversible process from the complex $[\text{CoLCl}]\text{Cl}$, where $\text{L} = \text{dibenzo}[\text{C},\text{K}][1,6,9,14]\text{tetraone}$ [329]. The question of the nature of the bonding of the hydrogen in the complex $[(\text{PP}_3)\text{Co}(\text{H}_2)]^+$, where

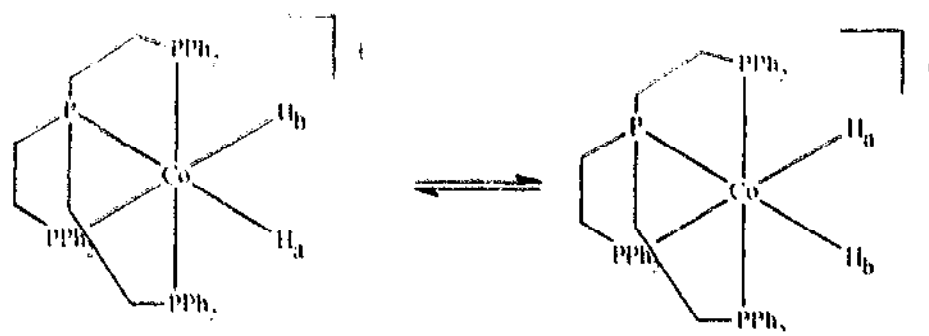


(188)

 $\text{L} = \text{PPh}(\text{OEt})_2 \text{ in MeCN}$

(189)

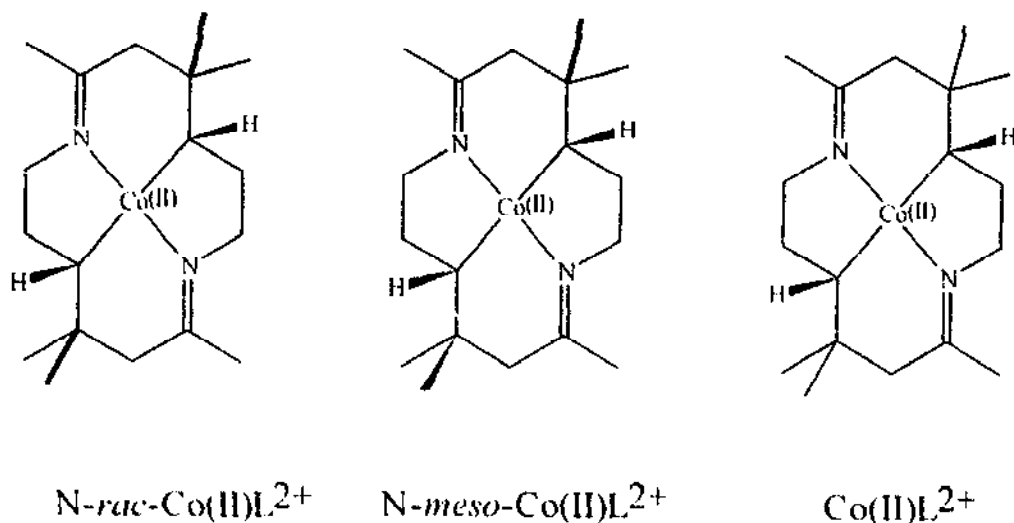
$\text{PP3} = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ has been revisited [330]. It is concluded from ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra that the complex is in fact (190) and involves the equilibrium shown.



(190)

We are accustomed to isotope exchange involving the ^1H in complex ions and ^2H in water, but isotope exchange of this type is very much more unusual in solvents such as acetonitrile. Fujita and Creutz have found that there is a relatively fast proton exchange involving the N-H groups of a Co(I) macrocycle, CoL^+ , where L represents the species shown in structures (191), and CD_3CN with a half life of

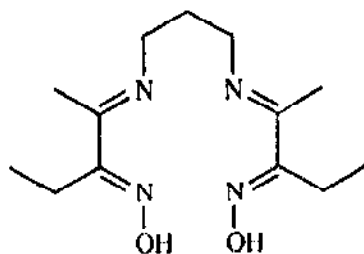
about 20 min [331]. The infrared spectra of $[\text{CoL}]$ prepared from $N\text{-rac-Co(II)L}^{2+}$ show clear changes arising from H/D exchange involving N–H, giving a rate constant of $5 \times 10^{-4} \text{ s}^{-1}$ at 23 °C. This is twice as fast as the exchange of the C–H protons of the macrocycle. Both the *meso* and the octamethyl complexes also show proton exchange, but the latter is about a factor of 20 slower than the former.



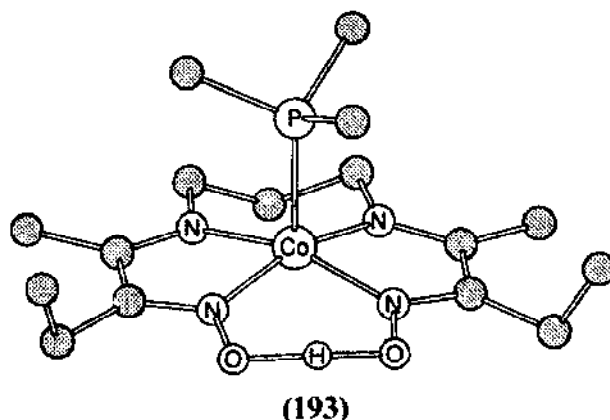
(191)

An insoluble tetrapyrrolineperphyrzincobalt(I) film has been laid down on a highly oriented pyrolytic graphite electrode by electroreduction of N,N',N'',N''' -tetramethyltetra-3,4-pyridinoporphyrazinocobalt(II) in phosphate buffer [332]. When this electrode was then coated with Nafion it could be used as a sensor for S^{2-} and 2-mercaptoethanol.

Complex formation between cobalt(I), PPh_3 and ligand (192) with cobalt(I) gives a complex (193) for which the X-ray crystal structure shows that the arrangement around the Co is square pyramidal [333].



(192)



6. Cobalt(IV) complexes

It is rare to find many studies of coordination compounds involving Co(IV) and in 1994 there appears to have been only one such investigation published [334]. The Co(IV) complex $[\text{Co}(\text{S}_2\text{C}_2\text{R}_2)_2\text{L}]$ ($\text{R}=\text{CN}$, $\text{L}=\text{Et}_3$; $\text{R}=\text{CF}_3$ or Ph , $\text{L}=\text{PPh}_3$ or P(OPh)_3 ; $\text{R}=\text{C}_6\text{H}_4\text{Me}$, $\text{L}=\text{PPh}_3$ or PEt_3 ; $\text{R}=\text{C}_6\text{H}_4\text{OMe}$, $\text{L}=\text{PPh}_3$) has been studied using isotropic and frozen solution ESR spectra in solution in $\text{CH}_2\text{Cl}_2\text{--ClCH}_2\text{CH}_2\text{Cl}$. The spectra confirm that the Co is low spin d^5 and formally Co(IV). The crystal structures of $[\text{Co}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2(\text{P(OPh)}_3)]$ and $[\text{Co}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2(\text{PPh}_3)]$ were also determined. The geometry around the Co was found to be approximately square pyramidal.

7. Reactions involving vitamin B₁₂ and model compounds

Many of the reactions of vitamin B₁₂ are essentially organometallic in nature, involving Co–C bonds and are therefore strictly outside the scope of this review. This section therefore deals only with reactions of vitamin B₁₂ and appropriate related compounds which are confined to cobalamin complexes which do not have Co–C bonds nor involve reactions in which such bonds are formed, the only exception being Co–CN bonds.

In a study of three cobalamin complexes with ligands containing sulfur *viz.* glutathione, sulfite and cysteine, it has been shown using X-ray absorption spectroscopy that the bonding to the Co is via sulfur [335]. The X-ray spectra suggest that there is electron donation from S to Co reducing the charge on the Co to less than 3+.

Equilibrium data for replacement of water in aquacyanocobinamide have been determined for two different groups of compounds; imidazole, 1,2,4-triazole and several other azoles [336] and NH_3 , 4 primary alkylamines, NH_2NH_2 , NH_2OH and four 4-substituted pyridines [337]. In all cases the systems obeyed the linear free energy relationship:

$$\log K = a.pK + b$$

For the azole systems, $a = 0.42$ and $b = 1.3$. For the amines, $a = 0.58$ and $b = -2.6$, while for the azines $a = 0.47$ and $b = 0.18$. NH_2NH_2 and NH_2OH lie above the amine curve and 1,2-diazine pyridazine lies above the azine curve. The higher values are attributed by the authors to the α effect.

The X-ray crystal structure of Co-cyano-(5'-6'-dimethylbenzimidazolyl)cobamide (vitamin B_{12}) has been redetermined at 92 K (original work carried out by Hodgkin and coworkers [338]) and that of Co-cyanoimidazolylcobamide has been determined at 88 K [339]. The lower temperatures were used in order to minimize radiation damage. The interest that the authors had in these structures lay in the need to find out the extent to which the bulk of the nucleotide coordination contributes to the so-called upward folding of the corrin ring system. The crystals of the Co-cyanoimidazolylcobamide showed that it was orthorhombic $P2_12_12_1$ having $Z = 4$ and $a = 15.335$, $b = 21.974$, $c = 25.561$ Å and $V = 8705$ Å³. When the X-ray structure data for this species were compared with the B_{12} data it was found that the bulk of the benzimidazole group in the latter complex contributed to the upward folding of the corrin ring system. Data are also presented in this paper of the application of 2D-HSQC-ROESY (heteronuclear single quantum coherence - rotating frame Overhauser spectroscopy) experiments to the compounds in solution.

The equilibrium constants for the base-on/base-off reactions for a series of alkyl cobalamins, but including cyanocobalamin have been measured [340]. It is becoming increasingly likely that substitution of water in aquacobalamin occurs via a dissociative interchange (I_d) mechanism. Two papers have investigated this situation in 1994. Marques and coworkers [341] have examined the kinetics of the replacement of water in aquacobalamin by a number of anionic ligands (I^- , $\text{S}_2\text{O}_3^{2-}$, NO_2^- , SCN^- , N_3^-) and have found that plots of k_obs vs ligand concentration over a wide range of concentrations exhibit small but significant departures from linearity showing that there is evidence for saturation behaviour and this is interpreted as evidence for the I_d mechanism. Similarly, van Eldik and coworkers have studied the kinetics of the reaction between aquacobalamin and a number of substituted pyridine ligands [342]. They, too, have observed curvature in plots of k_obs vs concentration of entering ligand, though this time the curvature was very much more pronounced. Again this is interpreted as indicating an I_d mechanism but involving an unexpectedly strong precursor complex. This is confirmed by the observed values of V^\ddagger of between $+4$ and $+7$ cm³ mol⁻¹. In terms of the formation of the precursor complexes by this particular set of ligands the strength of the interaction is ascribed to the possibility that it is produced by the interaction of the system of the py ligands with, for example, the corrin ring system.

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