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# Vanadium 1995

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Contents

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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].

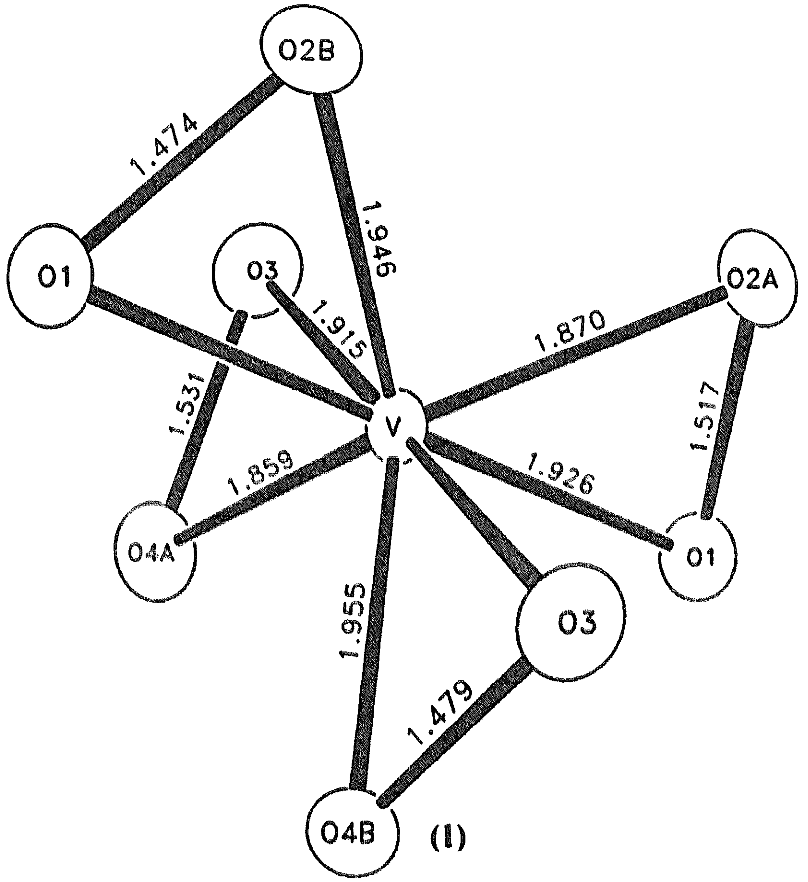
An article on metal ion chelation with reference to marine metabolites discusses the possible form of vanadium in tunichromes [5].

## 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. $Na_3[V(O{-}O)_4]\cdot H_2O_2\cdot 10.5H_2O$ and $Na_3[V(O{-}O)_4]\cdot 14H_2O$ crystallise in the triclinic system with peroxo O–O and $V{-}O_{peroxo}$ bond distances in the normal range. The tetraperoxovanadate ions, $V(O{-}O)_4^{3-}$, (**1**), have approximately dodecahedral symmetry with peroxo ligands bound in an $\eta^2$-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].



(**1**)

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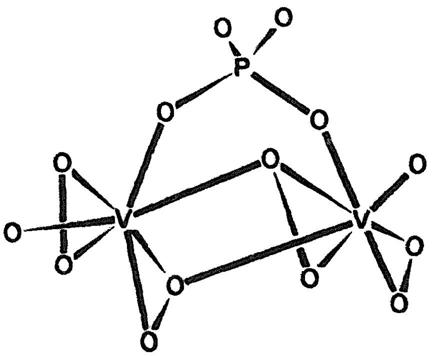
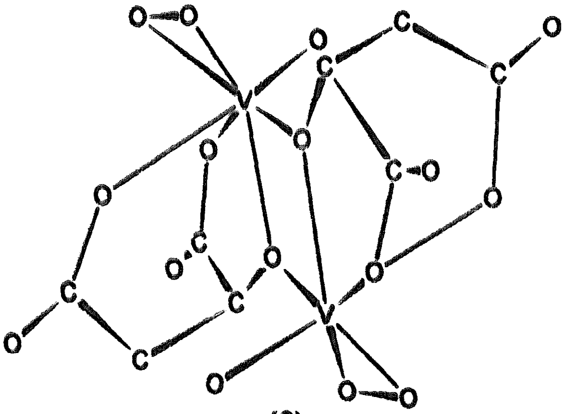
The tetraperoxo phosphato complex $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$ has been obtained from the reaction between $NH_4H_2PO_4$ and $NH_4VO_3$ in $H_2O_2$. The structure, (**2**), was found to consist of $[V_2O_2(O_2)_4PO_4]^{5-}$ anions, $NH_4^+$ cations and water molecules held together by extensive hydrogen bonding and electrostatic forces. Within the structure are 22 strong H bonds ($d < 2.9$ Å) [7].



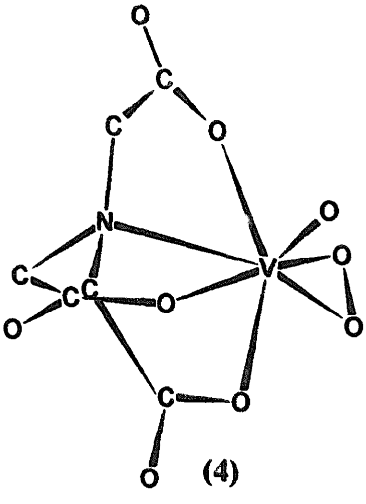
$[V_2O_2(O_2)_4PO_4]^{5-}$
(2)

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].



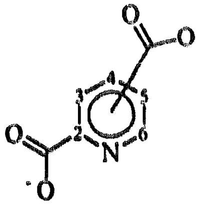
(3)
Reproduced from ref. [8] with permission.

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].

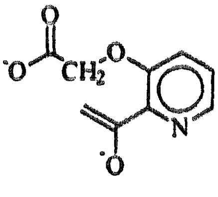


(4)

A series of bisperoxovanadium complexes of general formula $K_3[VO(O_2)_2(L\text{-}L')]$, ($L\text{-}L'$ = 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 $K_3[VO(O_2)_2(2,4\text{-pdc})]$, (**7**), and $K_3[VO(O_2)_2(3\text{-acetpic})]$, (**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].

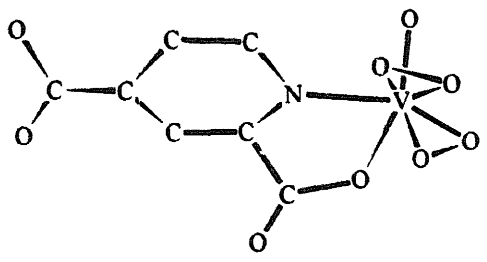


**pdc**
**(5)**



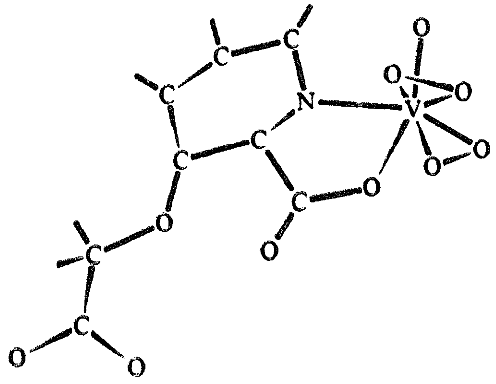
**3-acetpic**
**(6)**

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 Ade*n* (Ade*n* is an adenosine derivative



$[VO(O_2)_2(2,4\text{-pdc})]^{3-}$

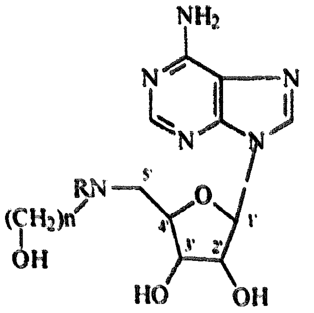
(7)



$[VO(O_2)_2(3\text{-acetpic})]^{3-}$

(8)

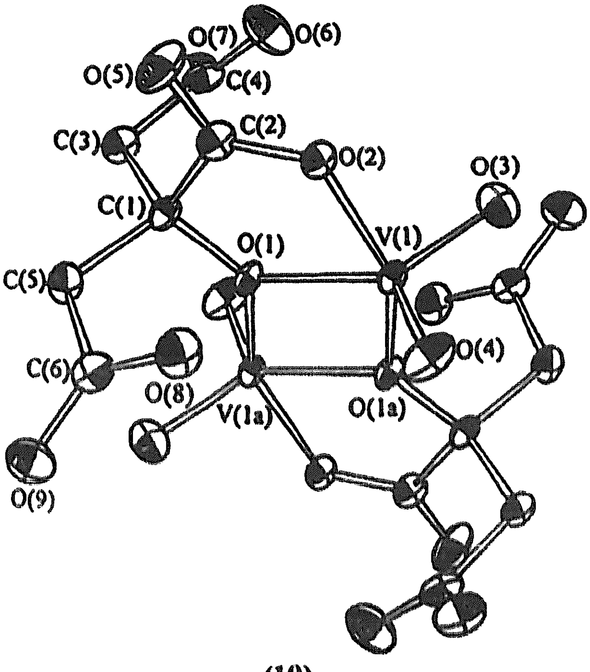
with O5′ replaced by a secondary amine nitrogen tailed by *n* $CH_2$ groups and a terminal OH; *n* = 2, 3, 5; (**9**)). Complex formation constants were reported for the dinuclear biligate complexes formed and possible structures for the products proposed [12].



R = H, n = 2 Ade2
3 Ade3
5 Ade5
R = Et, n = 2 Ade2a

(9)

There is currently considerable interest in citrato complexes of vanadium. The complex $K_2[V(O)_2(C_6H_6O_7)]_2 \cdot 4H_2O$ has been isolated and characterised both spectroscopically and by X-ray diffraction. The citrate ligand ($cit^{2-}$) 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 $\alpha$-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 $\alpha$-carboxylato oxygens to one vanadium and *via* two acetato branches to the two vanadium atoms, making each metal atom 6-coordinate [14].



**(10)**

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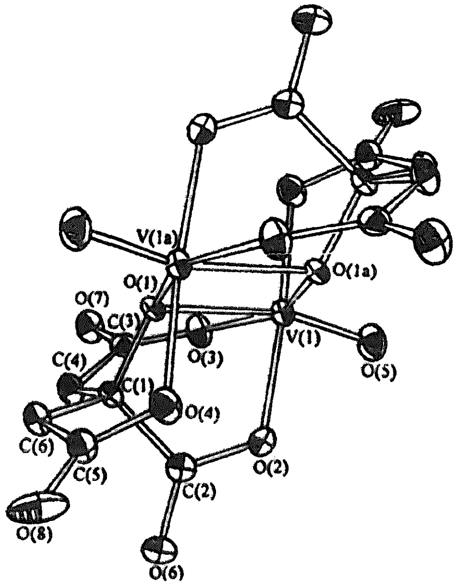
$^{13}C$ NMR spectroscopy has been used to study the reactions of vanadate, $H_2VO_4^-$, with $^{13}C$ labelled oxalate in aqueous and acetic acid media. Results from the aqueous studies suggest the formation of both mono(oxalato)-, $[VO_2(ox)(OH_2)]^-$ and bis-oxalato *cis*-$[VO_2(ox)_2]^{3-}$ V(V) 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($\mu$-acetato $\mu$-oxo oxovanadium) crown with all four vanadium atoms linked to one oxygen of the nitrate ion. The compound is thought to be the



**(11)**

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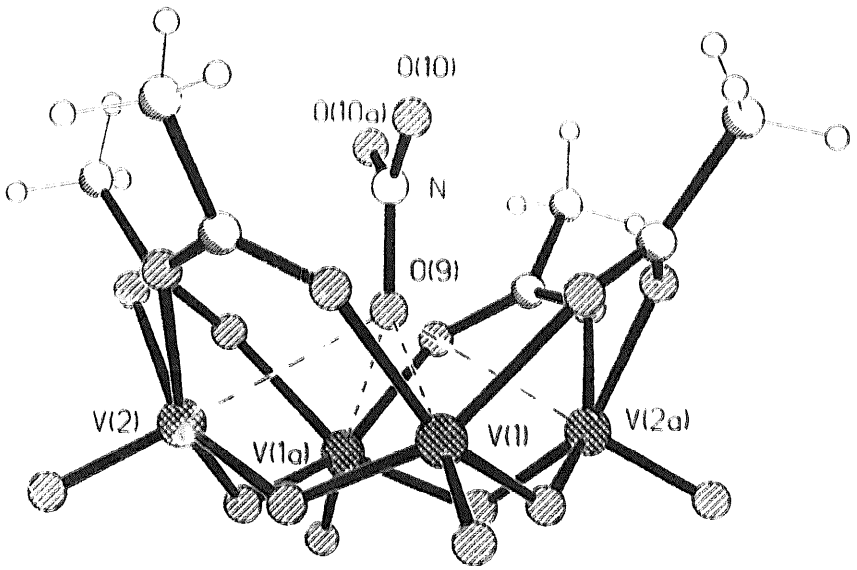
first example of a neutral polynuclear vanadium carboxylate to accommodate a guest anionic species inside the cavity [16].



**(12)**

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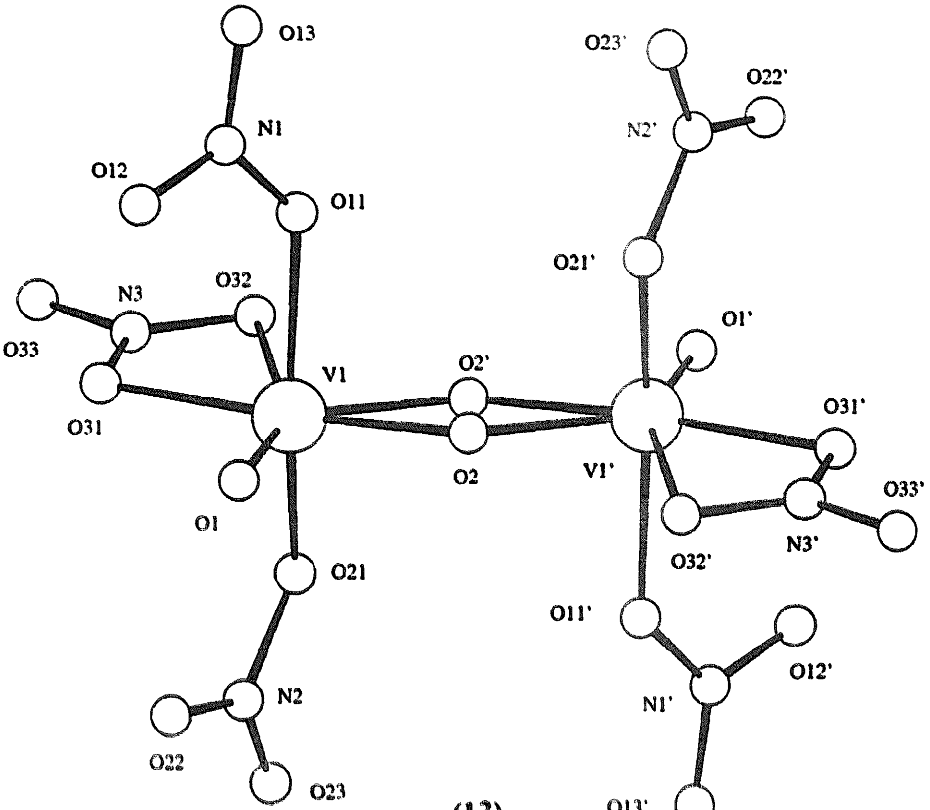
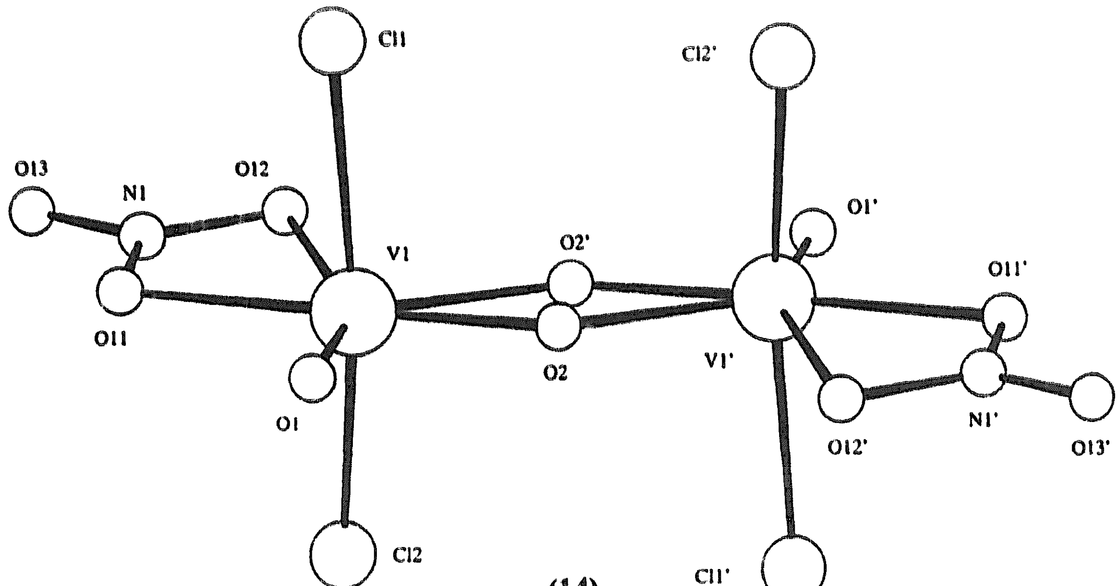
Two dinuclear vanadium species containing the $(V_2O_3)^{4+}$ central core have been obtained from the reactions of tetraphenylarsonium nitrate with $VO(NO_3)_3$ and $VOCl_3$. The compounds, $[Ph_4As]_2[V_2O_3(NO_3)_6]$, **(13)**, and $[Ph_4As]_2[V_2O_3Cl_4(NO_3)_2]$, **(14)**, are structurally related, 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. $[Ph_4As]_2[V_2O_3Cl_4(NO_3)_2]$ is the first example of a halonitrato species to be isolated [17].



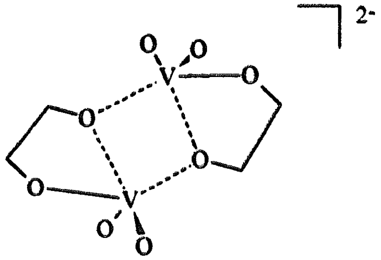
**(13)**



**(14)**

(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]



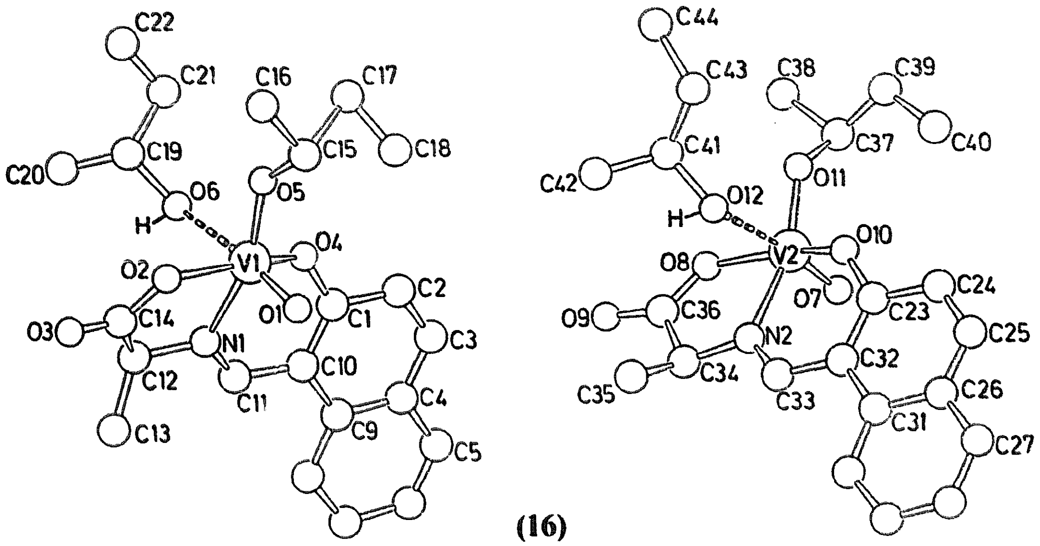
(15)

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-ala} $O^sBu$ ($HO^sBu$)], (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-



**(16)**

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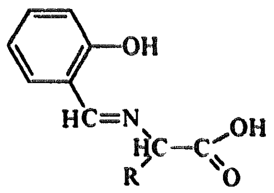


| R | |
|---|---|
| H | $H_2L^1$ |
| $CH_2Ph$ | $H_2L^2$ |

**(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 $H_2O_2$ by V(V) and the reaction has been studied spectroscopically [23].

The reaction of KBr with aromatic compounds $C_6H_4XY$ ($X = NHCOMe$, $Y = H$ or 4-Me; $X = CHO$, $Y = 2\text{-}OH$) and 5,5-dimethylcyclohexa-1,3-dione in aqueous media in the presence of $[V_2O_2(O_2)_3(GlyH)_2(H_2O)_2]$ 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, $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ by *cis*-$[VO_2(H_2O)_4]^+$ acting as a one-equivalent oxidant [25]. Reaction of $VOCl_3$ with equimolar and bimolar amount of 4-$^tBuC_6H_4OSiMe_3$ led to the isolation of $[VOCl_2(OC_6H_4^tBu_4)]$ and $[VOCl(OC_6H_4^tBu_4)_2]$ 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, $[(pz)_4VOCl]Cl\cdot H_2O$, $(3,5\text{-}Me_2pz)_2VOCl_2(H_2O)$, $(^tBupz)_2VOCl_2$, $[(^tBupz)_4VO(H_2O)]Cl_2\cdot 4CH_3CN$, $(^tBupz)_2VOCl_2(F)VOCl(^tBupz)_3$ and $(^tBupz)_2VO_2F$ have all been characterised by X-ray crystallography and were found to contain six-coordinate vanadium with a terminal V=O bond [27].

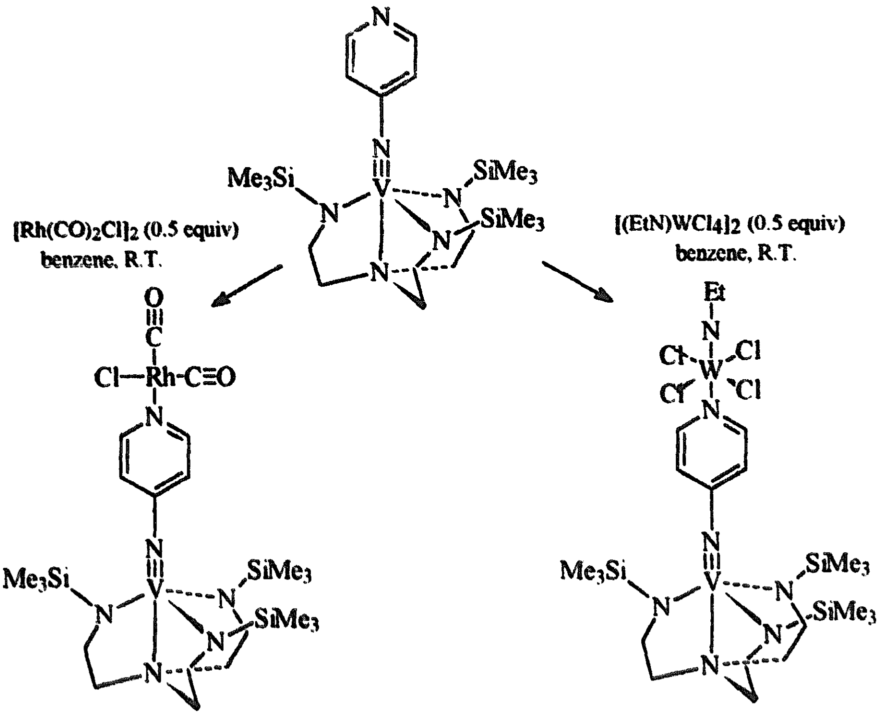
### 3.2. Complexes having V–N bonds

Reaction of $[(N_3N)V^{III}]$ ($N_3N=[Me_3SiNCH_2CH_2)_3N]^{3-}$) with 4-azidopyridine in pentane yields $[(N_3N)V{\equiv}N\text{-}C_5H_4N]$. 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 V≡N(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].

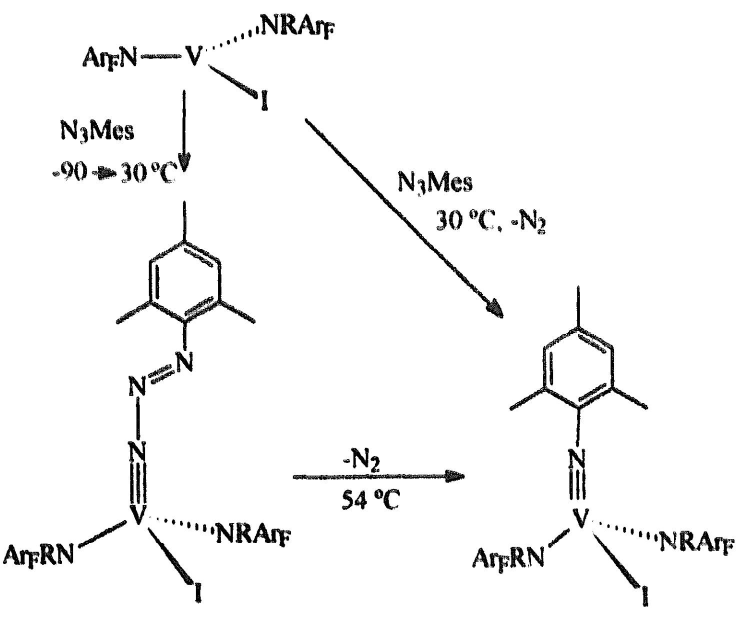
The V(III) complex $V(I)(NRAr_F)_2$ has been synthesised in a three step reaction starting from $VCl_3(THF)_3$ and $Li(NRAr_F)(OEt_2)$, ($R=C(CD_3)_2CH_3$). Reaction of $V(I)(NRAr_F)_2$ with mesityl azide at −100°C yielded $V(N_3Mes)(I)(NRAr_F)_2$ whose structure was determined by X-ray crystallography. At 54°C the azide complex loses $N_2$ in a reaction with second order kinetics to give the imido complex $V(NMes)(I)(NAr_F)_2$ as shown in Scheme 2. The compound $V(NMes)(I)(NAr_F)_2$ can also be prepared directly from $V(I)(NRAr_F)_2$ by dropwise addition of mesityl azide to an ether solution of $V(NMes)(I)(NAr_F)_2$ [29].

Treatment of $VOCl_3$ with 1 equivalent of $^tBuNCO$ or ArNCO ($Ar=2,6\text{-}^iPr_2\text{-}C_6H_3$) yields $V(N\text{-}^tBu)Cl_3$ and $V(NAr)Cl_3$ respectively which, when treated with 1 equivalent KTp or KTp* produce the complexes $TpV(N\text{-}^tBu)Cl_2$, $Tp^*V(N\text{-}^tBu)Cl_2$, $TpV(NAr)Cl_2$ and $Tp^*V(NAr)Cl_2$. The X-ray crystal structures of $TpV(N\text{-}^tBu)Cl_2$ and $Tp^*V(NAr)Cl_2$ have been determined and the polymerisation of ethylene and propylene in the presence of $Tp^*V(NAr)Cl_2$ and methylalumoxane investigated [30].

The reactions of $^tBuNVCl_3$ with cyclic ethers, ethylene carbonate and thiethane have been studied. The reactions of $^tBuNVCl_3$ with 2-chloroethanol, 3-chloropropanol and 5-chloropentanol yield the complexes $^tBuN{:}V(OR)Cl_2$ ($R=(CH_2)_nCl$, n=2,3,5) and $^tBuN{:}V(OR)Cl_2\cdot ROH$. In the presence of triethylamine the disubstituted compounds $^tBuN{:}V(OR)_2Cl$ are formed. The



Scheme 1.



Scheme 2.

crystal structures of ${}^tBuN{:}VCl_3\cdot dme$ and ${}^tBuN{:}V(OCH_2CH_2Cl)Cl_2\cdot OHCH_2CH_2Cl$ have been determined [31].

Reaction of $ArNVCl_3$ ($Ar = 2,6\text{-}C_6H_3\text{-}({}^iPr)_2$) with $CpSiMe_3$ results in the formation of the half sandwich imido vanadium complex $CpV(NAr)Cl_2$. Attempts at alkylation of CpV(NAr)Cl$_2$ and CpV(N-*p*-tolyl)Cl$_2$ led to extensive reduction of the vanadium. Reaction of CpV(N-*p*-tolyl)Cl$_2$ with AlMe$_3$ led to a mixture of diamagnetic dimeric, imido-bridged complexes (CpV)$_2$($\mu$-N-*p*-tolyl)$_2$MeR (R = Me or Cl) which were converted to the pure chloro compound [CpV($\mu$-N-*p*-tolyl)Cl]$_2$ by reaction with HCl. Alkylation of [CpV($\mu$-N-*p*-tolyl)Cl]$_2$ with MeLi gives [CpV($\mu$-N-*p*-tolyl)Me]$_2$. The structures of [CpV($\mu$-N-*p*-tolyl)Cl]$_2$ and [CpV($\mu$-N-*p*-tolyl)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*

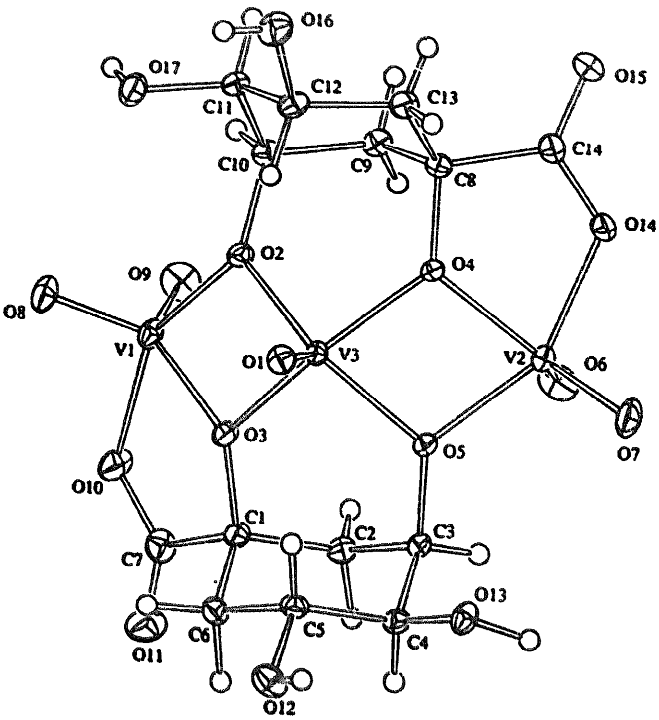
The compounds [VS$_4$(CuPPh$_3$)$_5$Br$_2$CuX] and [VS$_4$(CuPPh$_3$)$_5$Br$_2$CuX]·CH$_2$Cl$_2$ (X = 0.5 Br and 0.5 Cl), prepared by heating a mixture of (NH$_4$)$_3$VS$_4$, CuCl, PPh$_3$ and Et$_4$NBr, have been characterised by single crystal X-ray diffraction. The clusters were found to consist of 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)

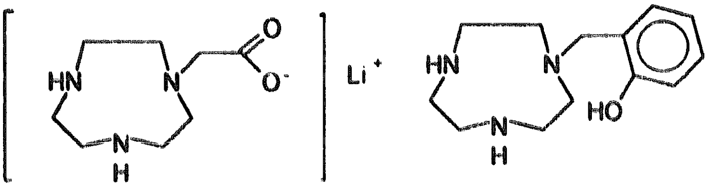
The mixed valence V(V)-V(IV)-V(V) trinuclear complex (NH$_4$)$_2${[V$^{\text{V}}$(O)$_2$]$_2$[V$^{\text{IV}}$(O)]($\mu$-(-)-quinato(3-))$_2$}·H$_2$O has been prepared by two different routes each involving quinic acid and V$_2$O$_5$. In the molecule each quinic acid trianion coordinates to all three 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 Li[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: [L$^1$V$^{\text{IV}}$O(NCS)], [L$^1$VO$_2$]·H$_2$O, [L$^2$VO(NCS)], [L$^2$VO(NCS)]Cl and [L$^2$VO$_2$] along with those of the dinuclear, mixed valence compounds [L$^1_2$V$_2$O$_3$]Br and [L$^2_2$V$_2$O$_3$](ClO$_4$)·0.5acetone. The latter two complexes contain the [OV–O–VO]$^{3+}$ core. In [L$^1_2$V$_2$O$_3$]Br, the bridging O atom lies on a crystallographic two-fold axis and the two L$^1$V=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 [L$^2_2$V$_2$O$_3$](ClO$_4$)·0.5acetone again contains two L$^2$VO 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$_2$L$^2$) (**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 [L$^2$]$^{2-}$ anion on reaction with VO(acac)$_2$. The mixture reacts with nickel(II) perchlorate yielding three compounds of composition



**(18)**

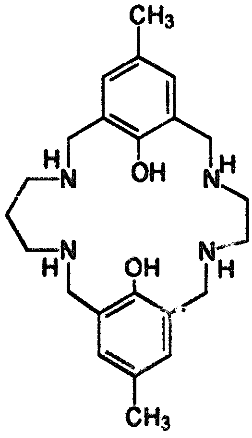


$Li[L^1]$ $HL^2$

**(19)**

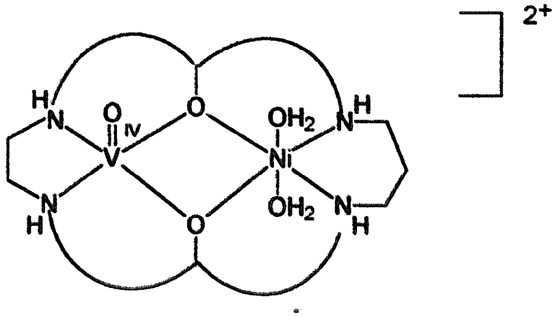
$[(V^{IV}O)L^2Ni(H_2O)_2](ClO_4)_2$ (**21**), $[\{(V^{IV}O)L^2Ni(H_2O)\}\{(V^{V}O_2)(HL^2)\}(ClO_4)_2 \cdot 3H_2O \cdot 2.5CH_3OH$ (**22**) and $[NiL^2(V^{IV}O)](ClO_4)_2$ (**23**). Complex (**23**) reacts with pyridine to produce $[(V^{IV}O)L^2Ni(py)](ClO_4)_2 \cdot H_2O$ (**24**). Reaction of $VO(SO_4)$ 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 $\text{-NH(CH}_2)_2\text{NH-}$ moiety are protonated [36].

The synthesis and X-ray structure of the mixed valence complex $[V^{IV}V^{V}_2O_7(phen)]$ have been described. The compound was obtained by heating a mixture of $V_2O_5$, and phenanthroline at 180°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].



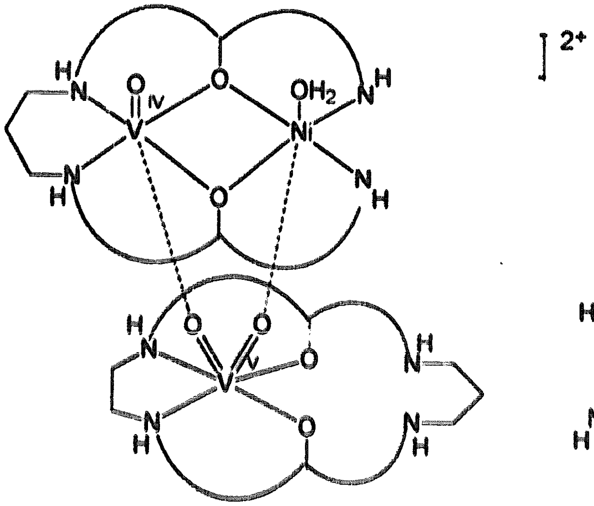
$H_2L^2$

**(20)**



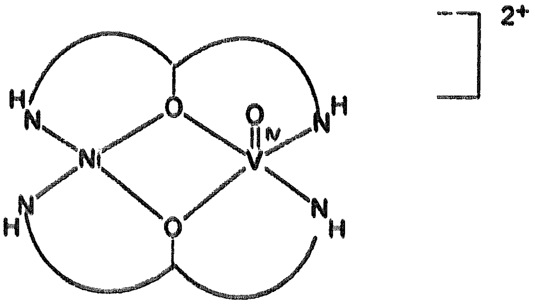
$[(V^{IV}O)L^2Ni(H_2O)_2](ClO_4)_2$

**(21)**



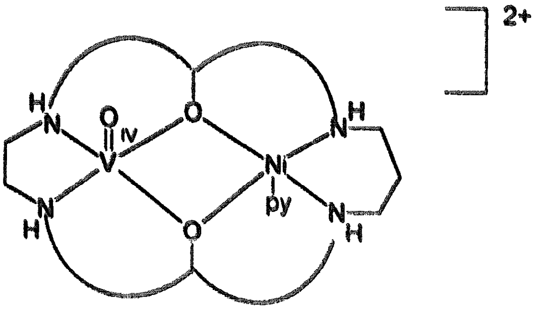
$[(V^{IV}O)L^2Ni(H_2O)][(V^VO_2)(HL^2)]^{2+}$

**(22)**



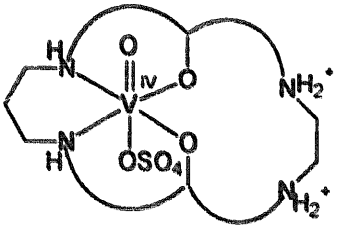
$[NiL^2(V^{IV}O)]^{2+}$

**(23)**



$[(V^{IV}O)L^2Ni(py)]^{2+}$

**(24)**



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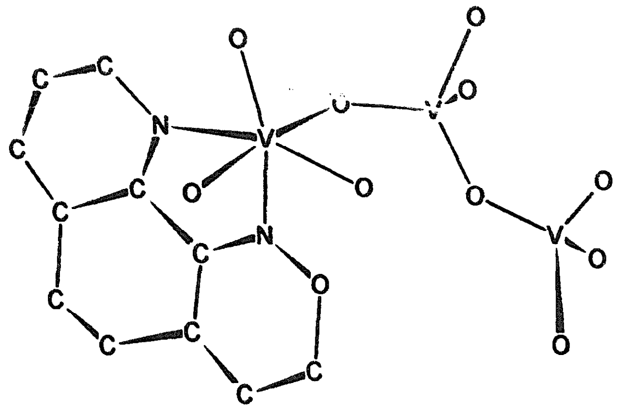


$V^{IV}V_2O_7$(phen)

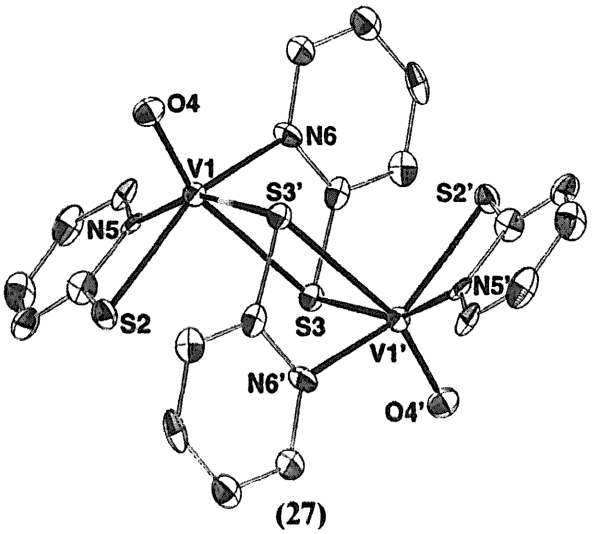
**(26)**

## 5. Vanadium(IV)

### *5.1. Complexes having V-Cl bonds*

The chloride $VCl_4$ undergoes reaction with $Me_3SiNPMe_3$ in $CCl_4$ solution to form the donor acceptor complex $[VCl_4(Me_3SiNPMe_3)]$ which goes on to react with excess $Me_3SiNPMe_3$ to yield $[V_3Cl_6(NPMe_3)_5]Cl$. Partial hydrolysis of this complex resulted in $[V_3Cl_6(NPMe_3)_5]_2[V_4O_4Cl_8(NPMe_3)_2]\cdot 6CH_3CN$ whose structure was determined. In the cation $[V_3Cl_6(NPMe_3)_5]^+$ the three V atoms form a trigonal bipyramid with two $\mu_3$-$NPMe_3$ groups and the remaining $NPMe_3^-$ groups and Cl atoms are terminally bonded. In the $[V_4O_4Cl_8(NPMe_3)_2]^{2-}$ anion the V atoms are linked by $\mu_2$-O atoms to form a rectangle [38]. A study by EPR spectroscopy of $VCl_4$ solutions and alkyl phosphines showed no evidence for species such as $VCl_4(PR_3)_2$. The main reactions taking place lead to V(III) species such as $[VCl_4(PR_3)_2]^{2-}$ and varying amounts of $VOCl_2(PR_3)_2$ which give rise to the observed EPR spectra. In the absence of air, *trans*-$VCl_4(PEt_3)_2$ is stable and no EPR signal is observed. The structures of $VOCl_2(PPh_3)_2$ and $[HPMe_2Ph][VCl_4(PMe_2Ph)(OPMe_2Ph)]$ were determined [39].

A series of vanadium complexes with pyridine-2-thiolate (pyt$^-$) having the metal in oxidation states II, III, and IV has been prepared. Reaction of $VOCl_2(thf)_2$ with 2 equivalents of Na(pyt) in thf leads to the formation of $[V_2O_2(pyt)_4]$. The structure of the core of the molecule, (**27**), consists of two $VO(pyt)_2$ units joined by two monatomic bridges provided by the S atoms of two pyt$^-$ groups. The reaction of $VCl_3(thf)_3$ with four equivalents of Na(pyt) in thf gives $[VNa(pyt)_4(thf)_2]$, (**28**), a heterodinuclear complex having the metals bridged by S atoms from three pyt$^-$ groups. The vanadium atom is 7-coordinate and the sodium centre is 6-coordinate. The V(II) complex, $[V(pyt)_2(tmeda)]$ (**29**) was obtained from the reaction between $VCl_2(tmeda)_2$ with two equivalents of Na(pyt) in thf or $CH_2Cl_2$ [40].



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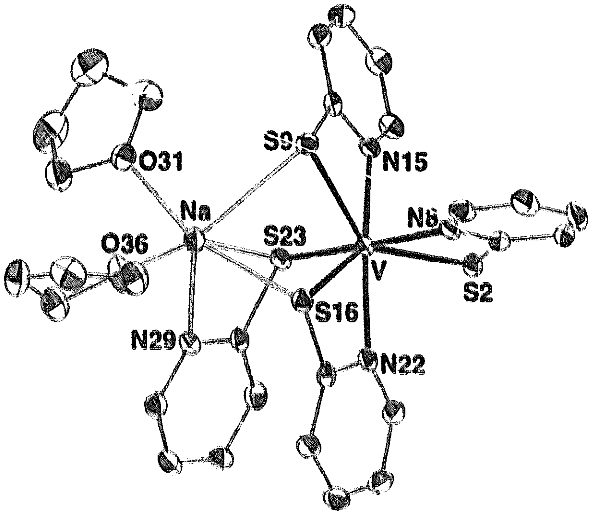

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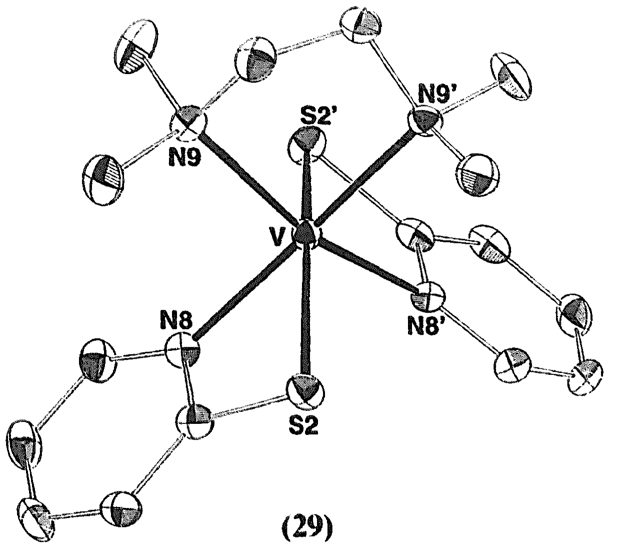
## 5.2. *Vanadyl complexes*

A series of V(IV) and V(V) complexes having hydrazine derivatives as ligands has been prepared from the reactions between $VCl_2(acac)_2$ and $VCl_2(acpn)$ (acpn = propylenediiminobis(acetylacetonato(2−)) and benzoylhydrazine. The complexes, ($\mu$-PhCONNCOPh){VOCl(NHNHCOPh)}$_2 \cdot 5CH_3CN$ and ($\mu$-PhCONNCOPh){V(dbh)}$_2 \cdot 2CH_3CN$ both contain doubly deprotonated *N,N'*-dibenzoylhydrazine (dbh) as a bridging, doubly *N,O*-chelating ligand. In ($\mu$-PhCONNCOPh){VOCl(NHNHCOPh)}$_2 \cdot 5CH_3CN$ the two remaining coordination sites at the VOCl group are occupied by the hydrazido(1−) ligand $[NHNHCOPh]^-$. In the non-oxo V(IV) complex ($\mu$-PhCONNCOPh){V(dbh)}$_2 \cdot 2CH_3CN$ the coordination geometry at the V atom is approximately trigonal prismatic. Back donation from



**(29)**

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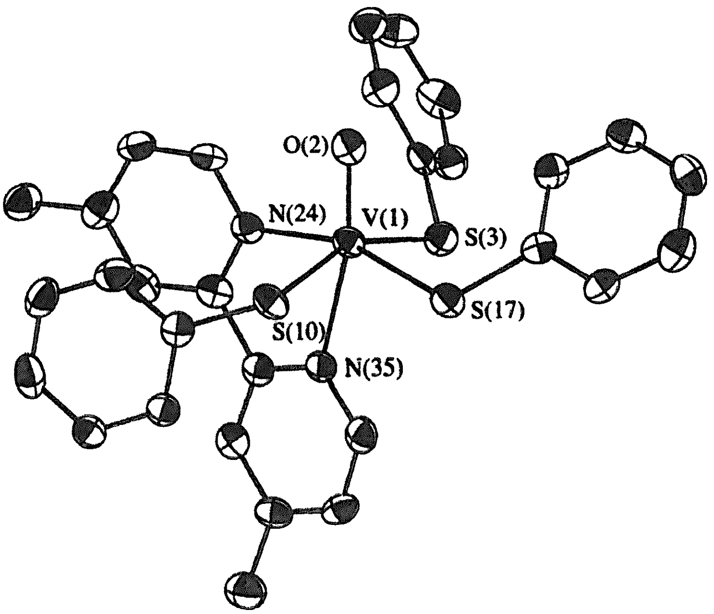
three negatively charged enolic oxygen atoms compensates for the lack of π-back donation from the vanadyl oxygen atom. The third complex, $[\{VO\}_2(tbh)]$, contains a highly symmetrical octadentate ligand formed during the synthesis. The ligand is coordinated to two VO(IV) centres by *N,O*-chelation 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 $[VO(SPh)_3(Me_2\text{-bpy})]^-$ 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 $[V(SPh)_4(Me_2\text{-bpy})]^-$ leads to $V_2O(SPh)_4(Me_2\text{-bpy})_2$ (**31**) which has a $[V_2(\mu\text{-}O)(\mu\text{-}SPh)_2]^{2+}$ 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 (Na*SNNS*Na) led to the tetranuclear V(IV) complex $\{V({}^-SNNS^-)\}_4(\mu\text{-}O)_4$, (**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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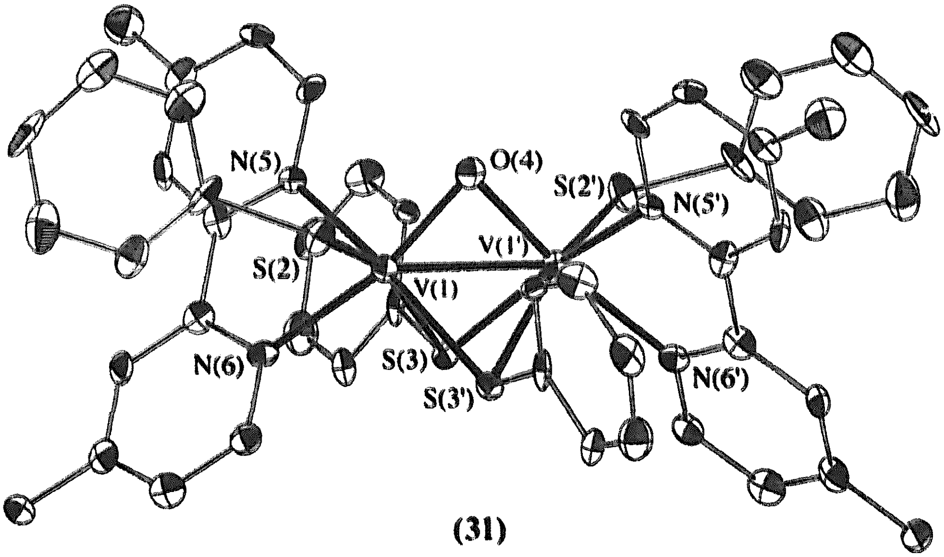

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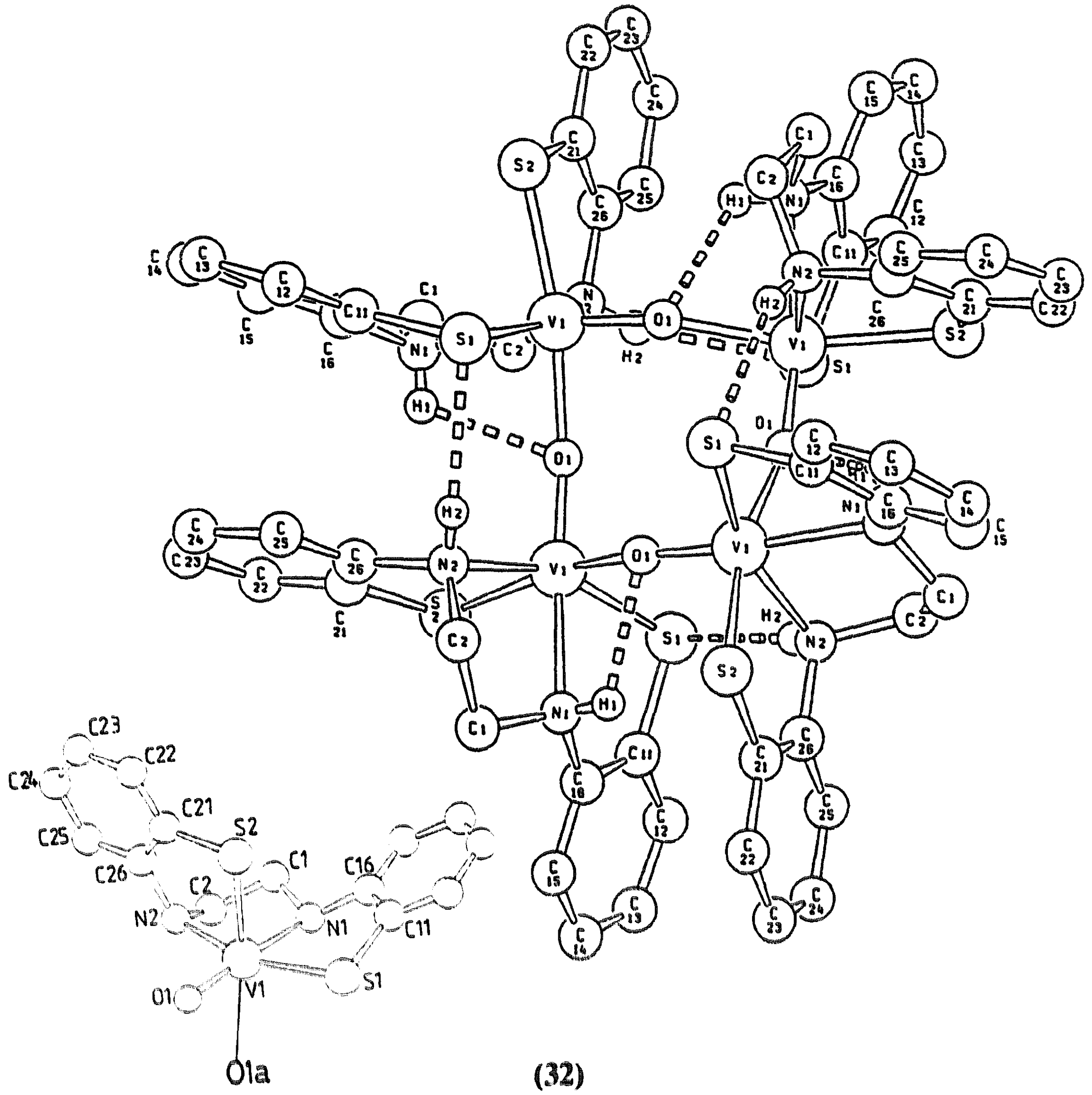
Reaction of colourless $V^{V}(O)(O\text{-}^{i}Pr)_3$ with $Ti(NRAr)_3$ in ether is accompanied by a colour change to yellow and marked shifts in the $^2H$ NMR spectroscopic signal of the Ti complex consistent with the formation of a heterodinuclear $\mu$-oxo complex, $(^{i}PrO)_3V^{IV}OTi^{IV}(NRAr)_3$ 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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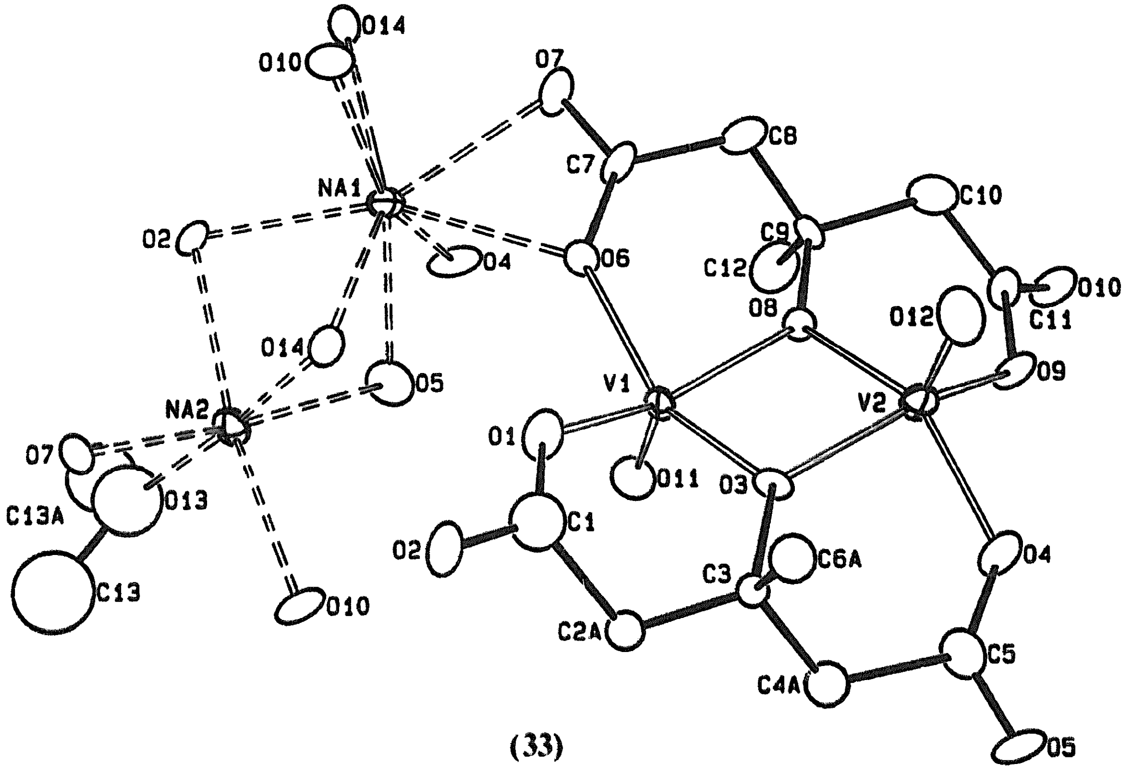
dine, the six-coordinate VO(ma)$_2$py can be formed which undergoes aerial oxidation much more slowly indicating that a vacant site is required for $O_2$ coordination. A complete study by $^{51}$V NMR spectroscopy and electrochemistry was made of the aqueous chemistry of VO(ma)$_2$ and [VO$_2$(ma)$_2$]$^-$. The X-ray crystal structures of VO(ma)$_2$ and [*cis*-VO$_2$(ma)$_2$]$^-$ were determined [45].

The V(IV) dimer Na$_2$[(VO)(3-hydroxy-3-methylglutarate)]$_2$·3H$_2$O·CH$_3$OH, (**33**), has been obtained by reaction of 3-hydroxy-3-methylglutarate with VO(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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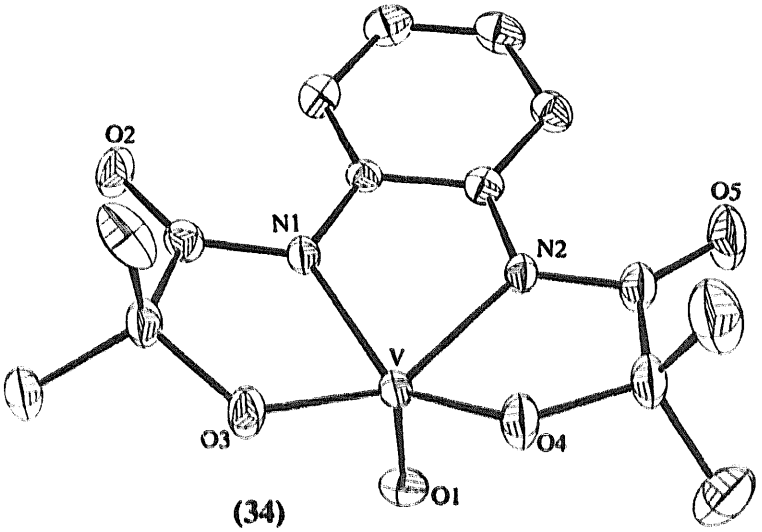
The structure of oxobis(pentane-2,4-dionato)vanadium(IV), $[VO(C_5H_7O_2)_2]$, has been redetermined using high resolution Mo data but no significant differences from those previously reported were found in the geometrical parameters [47].

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*-(salicylideneamine)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 $A_{//}$ 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].



**(34)**

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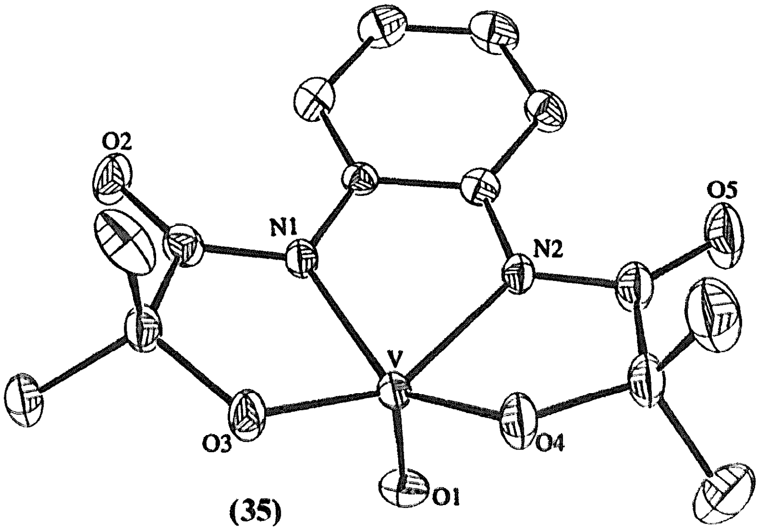
The complex $VO(sal\text{-}glygly)(H_2O)_n$, (**36**), (sal-glygly = *N*-salicylideneglycylglycinate; n = 1.5-3.0), has been isolated from concentrated solutions containing $VO^{2+}$, glycylglycine and salicylaldehyde. Dilute solutions used in the preparation of (**36**) on standing, yielded the decavanadate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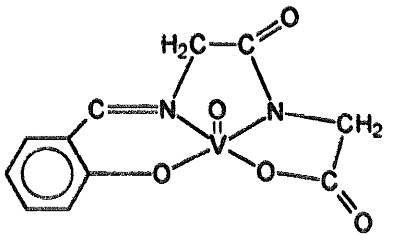
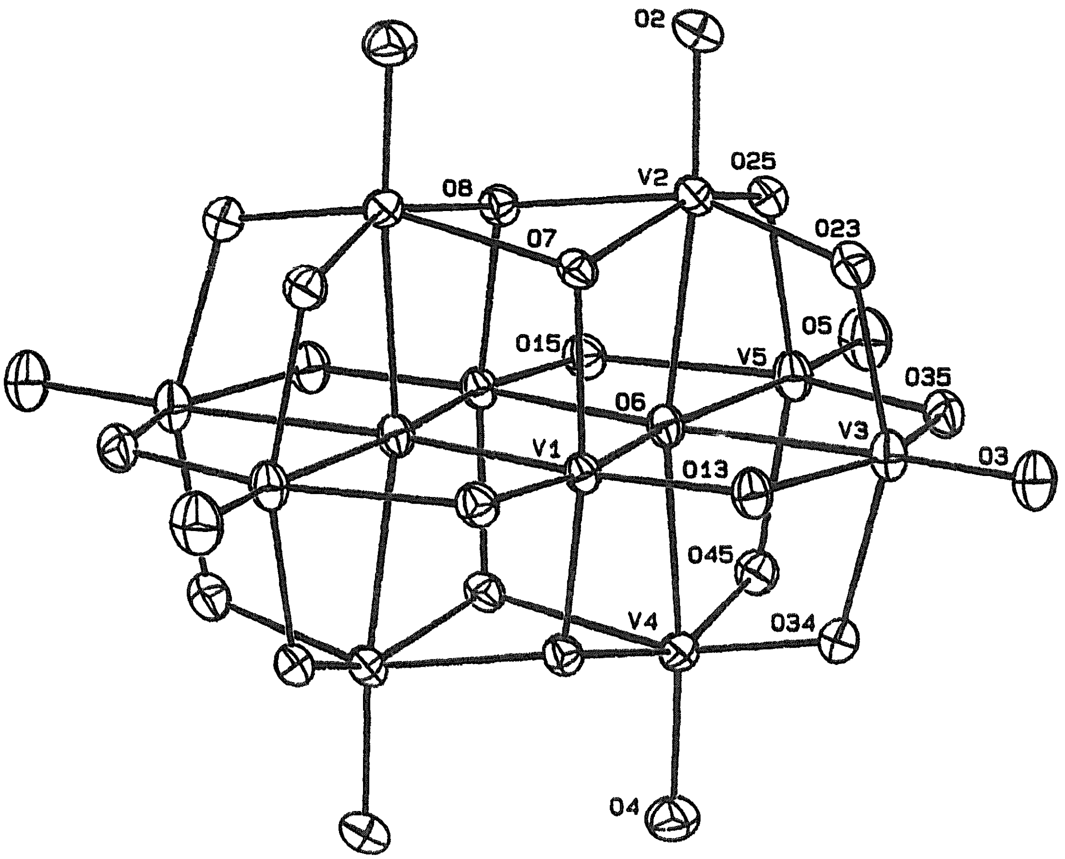


VO(sal-glygly)

**(36)**

Vanadyl complexes of the peptides VHCGAG-NH$_2$, VHMxurSAG-NH$_2$ and VFCSAG-NH$_2$ (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 VO$^{2+}$ 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 $^{15}$N enriched ligands showed that the coordinated and remote ring N atoms in the [$^{15}$N]imidazole complex have very different isotropic hyperfine coupling whereas in the [$^{15}$N]histidine complex equatorial coordination by both imine and amine nitrogen takes place. As such it was concluded that the VO$^{2+}$-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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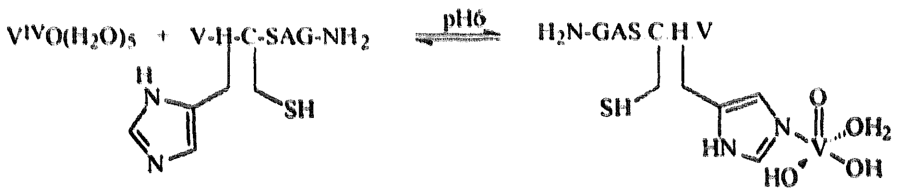
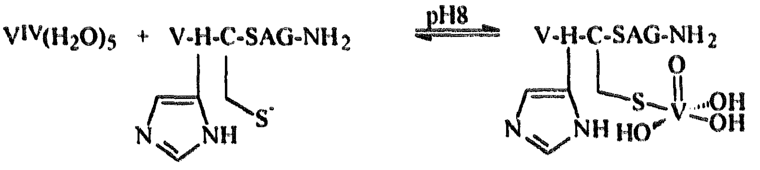


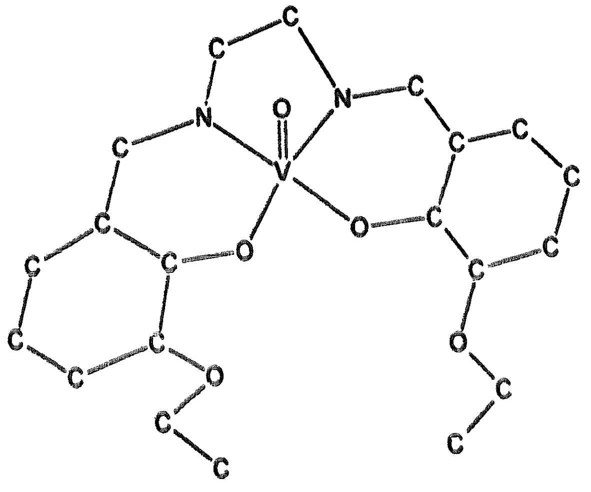
(Eq.1)



(Eq.2)

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 $\beta$-alkylcorrolate has been synthesised by the reaction of the corrole, $H_3L$ = 2,3,7,8,12,13,17,18-octaalkylcorrole) with VO(acac). The complex retains the aromatic $\pi$-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-ethoxysalicylideneaminate)) 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].

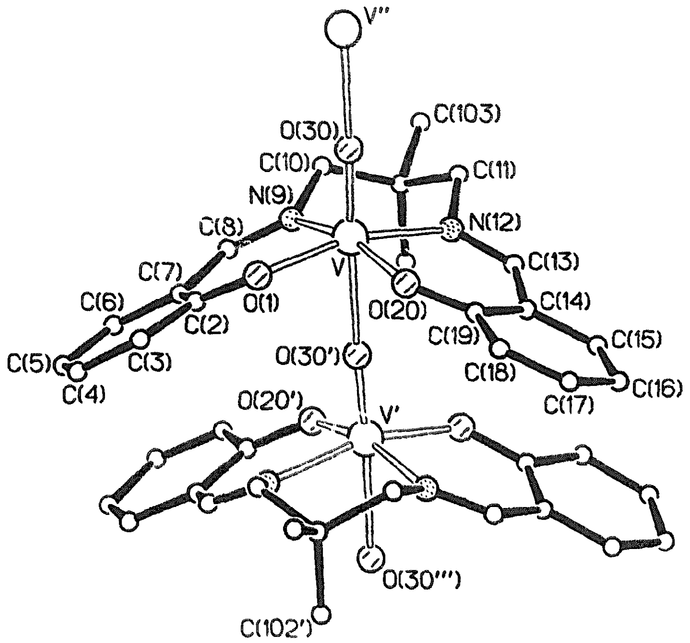


[V(IV)O(3-EtOsalen)]

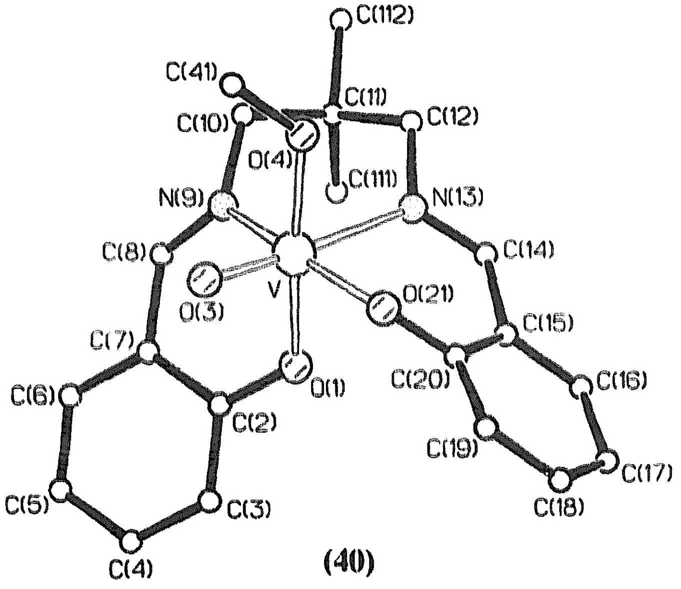
(**38**)

The structure of [VO(salnptn)] (salnptn = *N,N'*-2,2-dimethyltrimethylenebis-[salicylideneiminate(2-)]) has been determined and was found to be polymeric in the solid state having...V=O→=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).n$X_2$ (X = Cl, Br, I, NCS or $NO_3$, n = 1; X = $ClO_4$, n =



**(39)**



**(40)**

(**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 complexes on the basis of spectral data and conductivity measurements [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 $[V(hida)_2]^-$ ($H_3$hida = *N*-hydroxyiminodiacetic acid) and $[V(hidpa)_2]^{2-}$ and $[V(hidpa)_2]^-$ ($H_3$hidpa = (*S*,*S*)-*N*-hydroxy-2,2′-iminodipropionic acid). Vanadium is concentrated by fungi of the *Amanita* genus as amavadin, a complex of $H_3$hidpa, which has not hitherto been fully characterised. The studies reported here suggest that amavadin consists of an approximately equal mixture of $[\Delta\text{–V}\{(S,S)\text{-hidpa}\}_2]^{2-}$ and $[\Lambda\text{-V}\{(S,S)\text{-hidpa}\}_2]^{2-}$, 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].

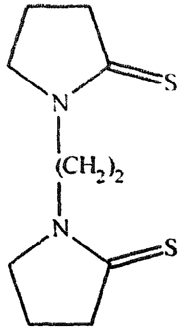
Reaction of tris(acetylacetonato)vanadium(III) with salicylaldehyde-2-hydroxyanil yielded the non-oxo compound bis{salicylaldehyde-2-hydroxyanilato(2−)vanadium}(IV) whose crystal structure was determined [66]. Similarly reaction of $V(acac)_3$ with tridentate diacidic ligands led to non-oxo V(IV) complexes 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]·$1.5CH_2Cl_2$. 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 $\sigma$ 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



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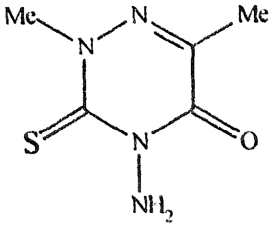
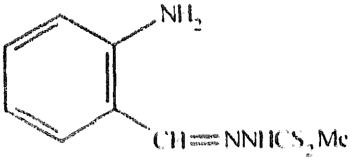


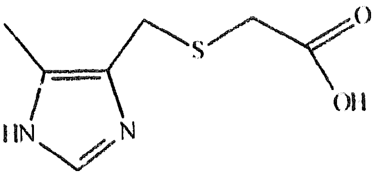
Taz

**(162)**



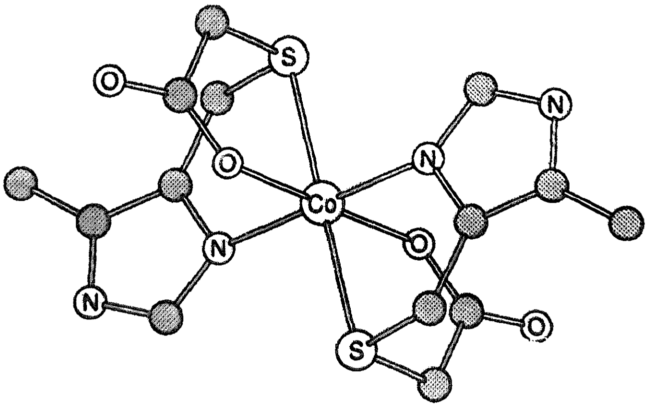
HNNS

**(163)**



Hitba

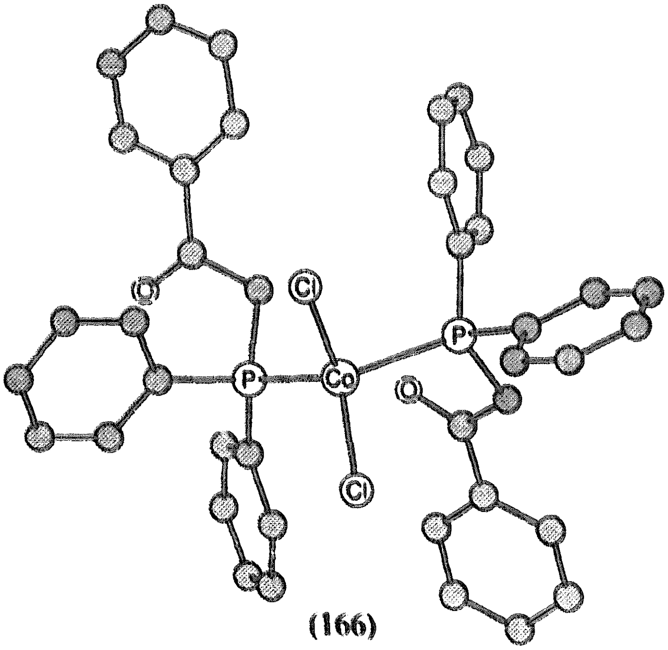
**(164)**



**(165)**

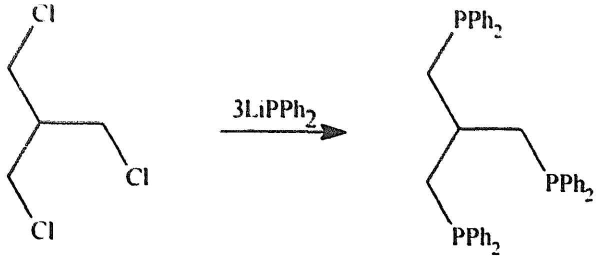
### 3.8. Complexes with phosphorus donor ligands

A range of Co(II) ketophosphine complexes of the type [$CoX_2\{Ph_2PCH_2C(O)Ph\}_2$], in which X = Cl, Br and I, have been prepared and the chemistry in solution compared with that of the corresponding complex [$CoX_2(PPh_3)_2$] [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 [$CoCl_2\{Ph_2PCH_2C(O)Ph\}_2$] (**166**).

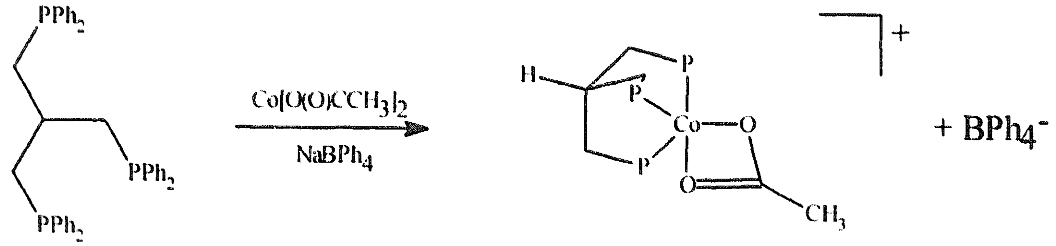


**(166)**

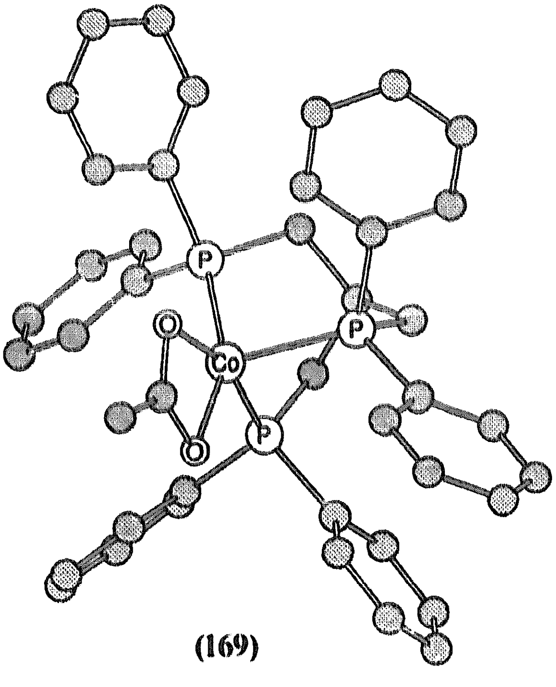
The ligand 1,1,1-tris[(diphenylphosphanyl)methyl]methane has been prepared by the reaction shown in (**167**) [295]. The ligand forms a Co(II) complex by the reaction shown in (**168**) and the X-ray crystal structure of the cobalt(II) complex confirms that for the cation shown in (**169**).



(167)



(168)



(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 $[CoX_2(acetone)_2]$ [296] and the stability constants have been obtained. Similar experiments with $Co(SCN)_2$ in aqueous DMSO showed the presence of $[Co(SCN)]^+$ 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 Co(II)–mixed complexes to which $CN^-$ and en had been added, although in the presence of en the yield of acetaldehyde was lowered.

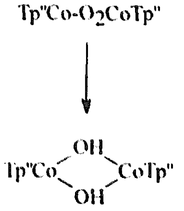
### 3.10. Complexes with arsenic donor ligands

Tetrakis(alkylisocyanide)bis(triarylarsine)cobalt(II) complexes have been prepared by the reaction of pentakis(alkylisocyanide)cobalt(II) in ethanol with triarylarsines [299]. Magnetic and solid state spectrophotometric measurements suggest that the structures of these complexes are tetragonal *trans*-$[Co(CNR)_4(AsR_3)_2]X_2$. In a related study [300], the complex $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ has been prepared and it is suggested that this too has a tetragonal arrangement around the Co(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 Co(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 Co(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 $Co(ClO_4)_2$ 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 monoiodohistidine complexes of Co(II) have been found to bind dioxygen, whereas diiodohistine 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 Tp″Co($O_2$) with 0.5 equiv of Tp″Co–$N_2$–CoTp″ yields the species Tp″Co–$O_2$–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 $k = 2.27 \times 10^{-3}\ s^{-1}$ at 281 K with $\Delta H^{\ddagger} = 16.4\ kcal\ mol^{-1}$ and $\Delta S^{\ddagger} = -12$ eu. It was further shown that there was a very significant isotope effect with $k_H/k_D = 22$. 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**).



**(170)**

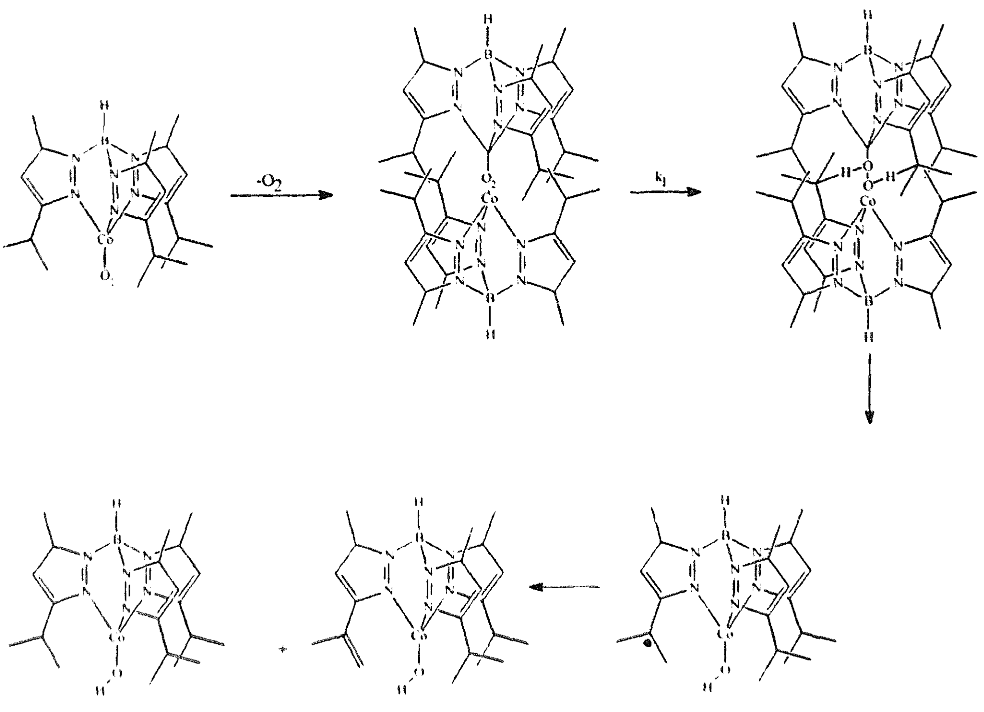
A number of complexes of the form [Co(terpy)(L)X] in which L = 2,2′-bipyridine or 1,10-phenanthroline or one of a number of substituted 1,10-phenanthrolines, X is a weakly binding species such as triflate, have been prepared and characterized [308]. These reversibly bind dioxygen and this process has been studied by a variety of techniques. A typical example is the complex $[Co(terpy)(bpy)]^{2+}$. 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:

$$2Co(terpy)Br_2 + 4NH_4PF_6 + 2bpy \rightarrow [Co(terpy)(bpy)_2O_2](PF_6)_4 + NH_4Br$$

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 $[Co(terpy)(bpy)](PF_6)_2$ was formed quantitatively:

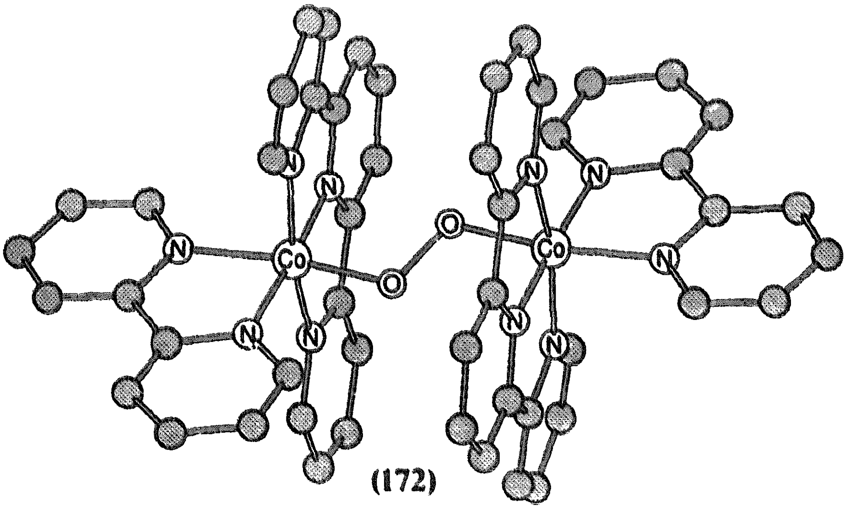
$$\underset{\text{orange}}{2[Co(terpy)(bpy)]^{2+}} + O_2 \rightleftharpoons \underset{\text{deep brown}}{[Co(terpy)(bpy)_2O_2]^{4+}}$$

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 $K_{O2}$ for the formation of $[\{Co(terpy)(bpy)\}_2O_2]^{4+}$ in acetonitrile is 4.4 $M^{-1}\ atm^{-1}$. Various coordinated solvents were investigated to examine their effect on dioxygen binding. Thus, in



**(171)**

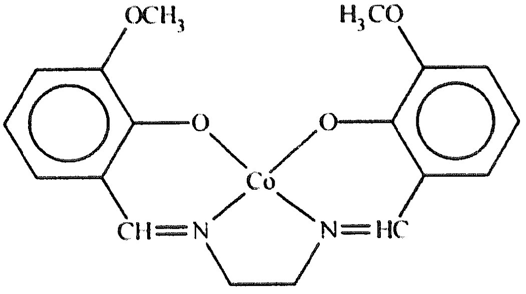
nitrobenzene the binding was extremely tight. By judicious choice of added weak ligands such as triflate, reversible binding could readily be achieved. The X-ray structure of solvated $[\{Co(terpy)(bpy)\}_2O_2](PF_6)_4$, $[(172)](PF_6)_4$, has been determined.



**(172)**

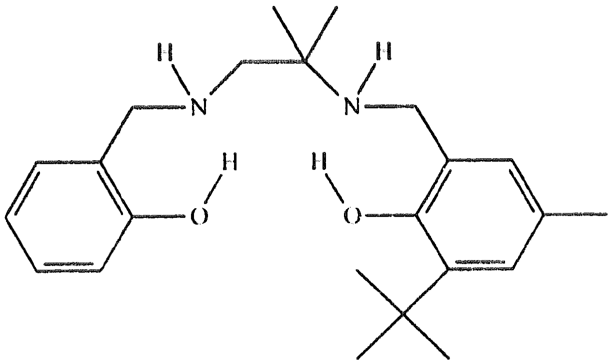
The complex $[Co(nbsal)_2]$, where nbsal = *N*-*n*-butylsalicylideneiminate, reacts readily with both nitric oxide and dioxygen [309]. However, the complex $[Co(tbsal)_2]$, where tbsal = *N*-*tert*-butylsalicylideneiminate shows no reactivity to either NO or $O_2$. The crystal structures of both these 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 it X-ray structure determined [311]. The crystal structure shows that it is monoclinic *C*2/*c* and *a*=25.389, *b*=18.139, *c*=10.179 Å, *β*=112.227° 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].

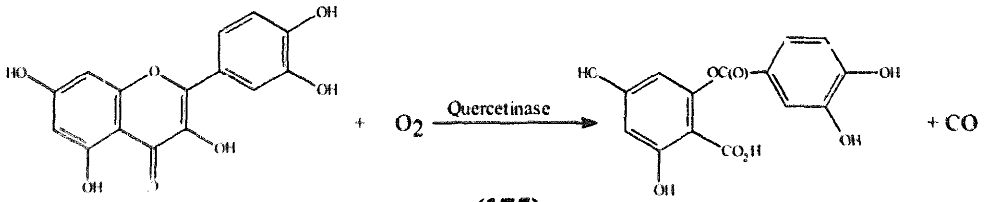


$H_2L$

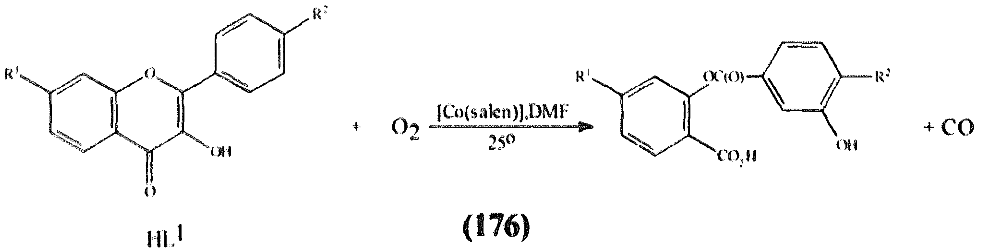
**(174)**

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**).

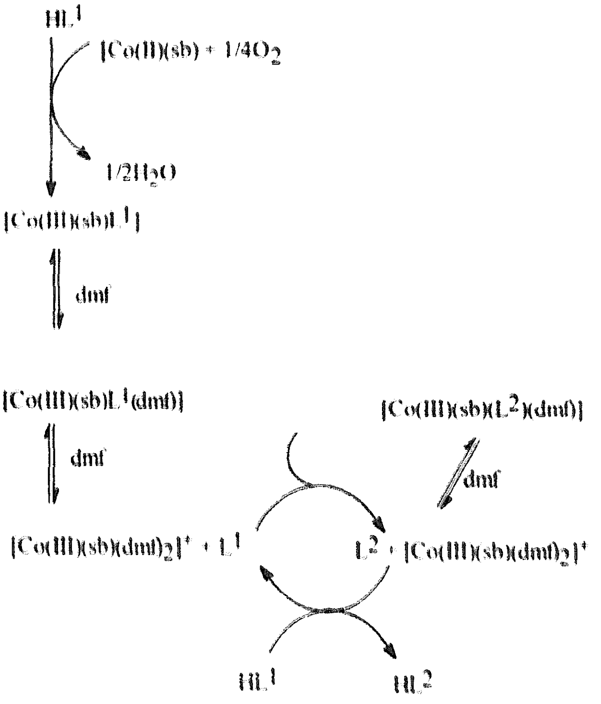
A study of the effectiveness of Co(II) Schiff base chelates incorporated into



**(175)**



**(176)**



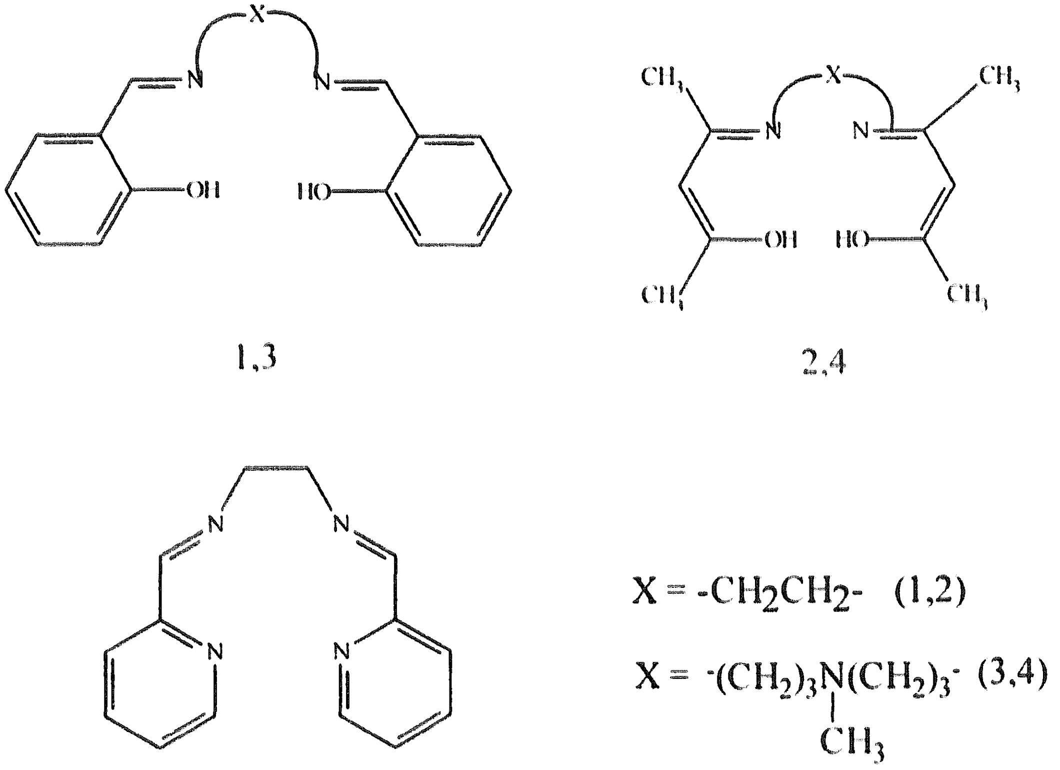
HL¹ = flavonol substrate

HL² = depside product

sb = Schiff base dianion

**(177)**

faujasite-type zeolites has focussed on the ligands shown in (**178**) [313]. The tetradentate ligands, 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(acetylacetone)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 $k = 2.7 \times 10^{-5}\ s^{-1}$ 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*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinatocobalt. 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.

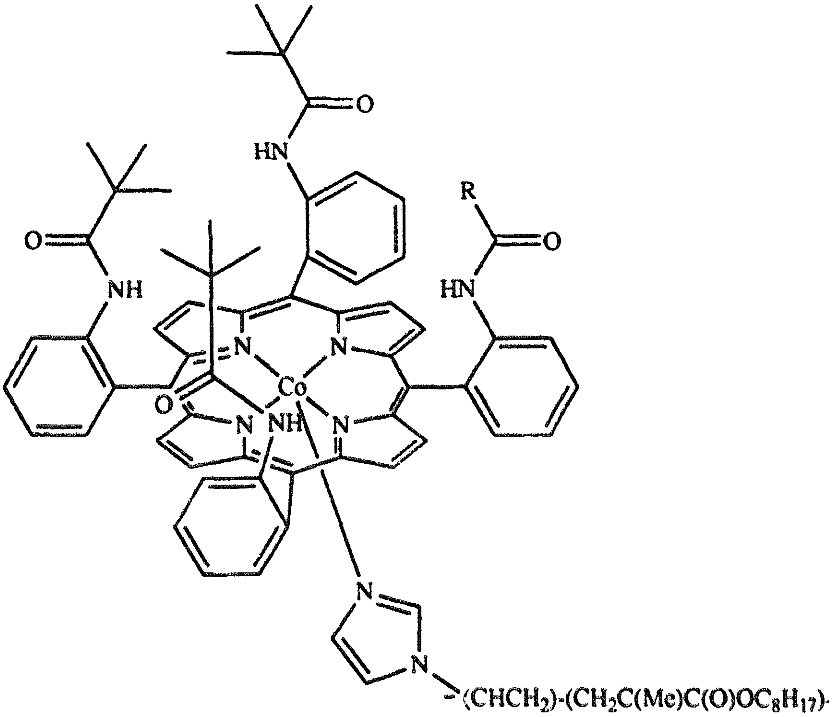


$X = \text{-}CH_2CH_2\text{-}$ (1,2)

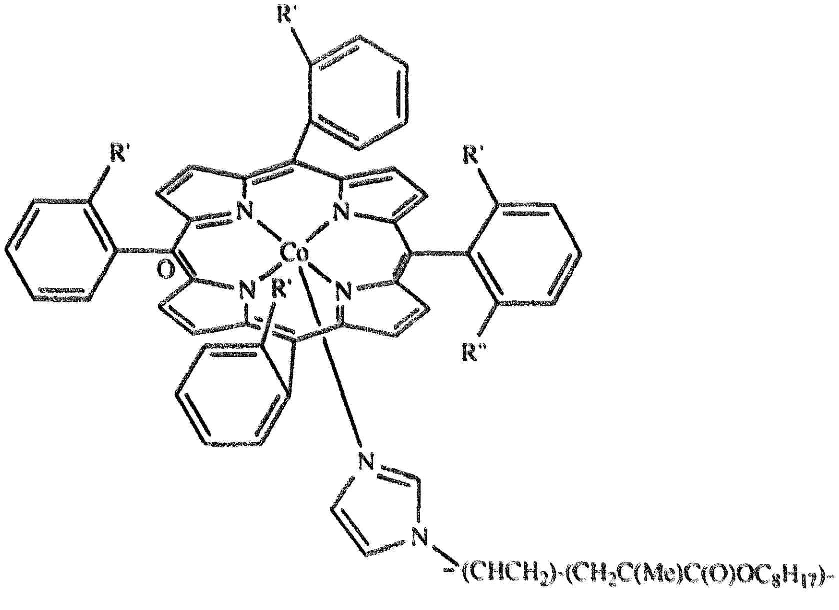
$X = \text{-}(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{N}}(CH_2)_3\text{-}$ (3,4)

**(178)**

A series of porphyrin complexes of Co(II) which had on the periphery of their structure either cyanophenyl groups or *N*-$CH_3$py structures have been prepared [316]. These porphyrins were mixed with a dilute alcoholic solution of Nafion and


O
HN
R
O
O
NH
HN
N
N
Co
O
N
NH
N
N
N
(CHCH2)-(CH2C(Me)C(O)OC8H17)-

**(179a)**


R'
R'
R'
N
N
Co
O
N
R'
N
R''
N
N
(CHCH2)-(CH2C(Me)C(O)OC8H17)-

**(179b)**

the mixture applied to the surface of a graphite electrode and then reacted *in situ* with $[Ru(NH_3)_5(H_2O)]^{2+}$. 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 $[Co_2(tpdb)(RCOO)](ClO_4) \cdot nH_2O$, $R = CH_3$ or $C_6H_5$. These reacted with dioxygen in acetonitrile to produce the dioxygen complexes $[Co_2(tpdb)(RCOO)(O_2)]^{2+}$ (**182**) (R = Me). The X-ray crystal structure of the species $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2 \cdot CH_3CN \cdot 0.5H_2O$ was determined, but there was a disorder in the backbone of the $tpbd^-$ 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 $[(papd)Co(II)(H_2O]^{2+}$, in which papd = 1,5,8,11,15-pentaazapentadecane [318]. The overall reaction with dioxygen is:

$$2[(papd)Co(H_2O)]^{2+} \rightleftharpoons [(papd)Co-O_2-Co(papd)]^{4+}$$

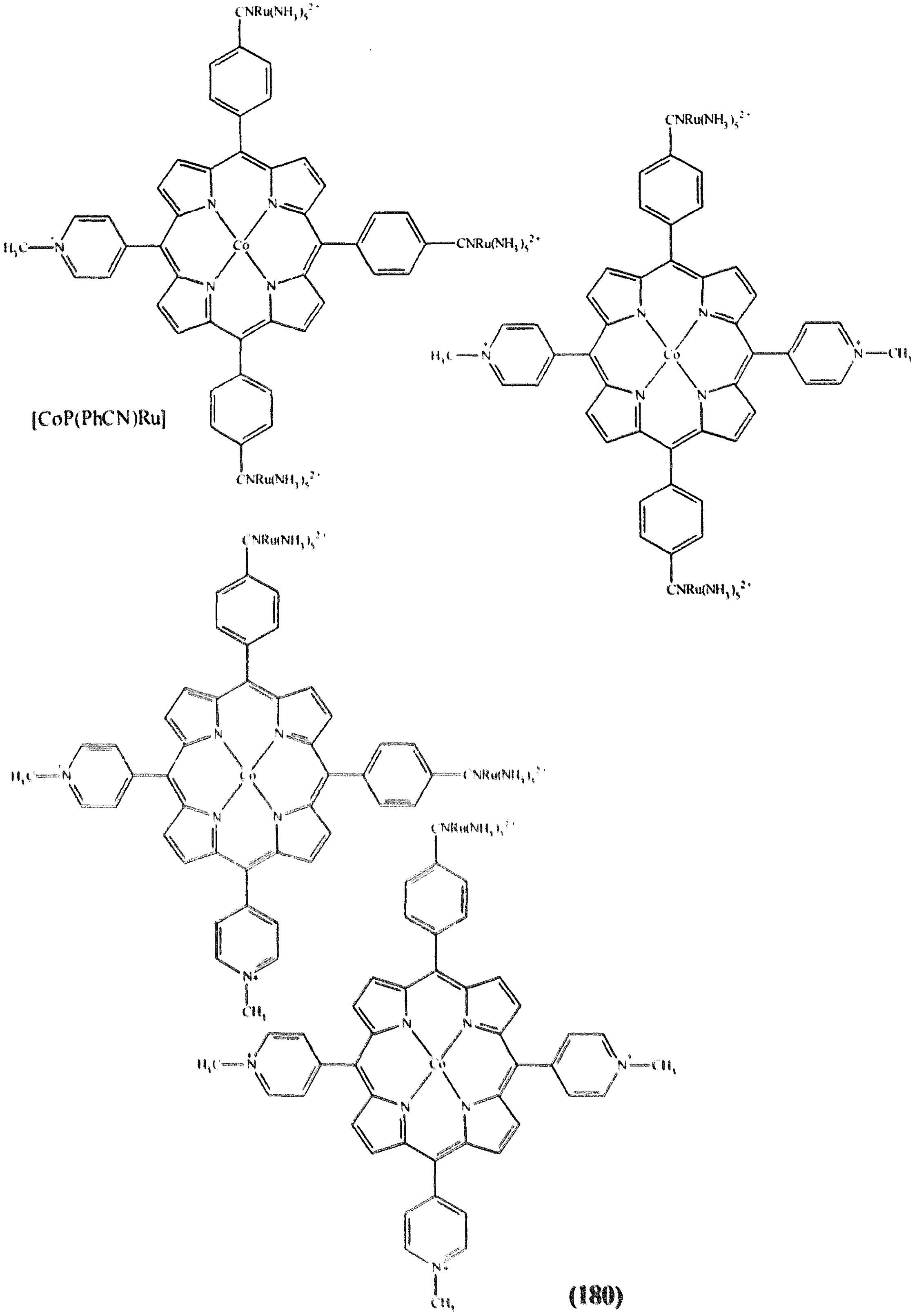
Early in the study, the authors found that when the dioxygen uptake by $[(papd)Co(II)(H_2O]^{2+}$ monitored by an oxygen sensitive electrode with $[O_2] > [complex]$ that there was a rapid decrease in $O_2$ producing a short-lived minimum and that this was followed by a release of oxygen. Under these 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, $[(papd)CoO_2]^{2+}$, and

ii) the formation of the product dinuclear complex $[(papd)Co\text{-}O_2\text{-}Co(papd)]^{4+}$.

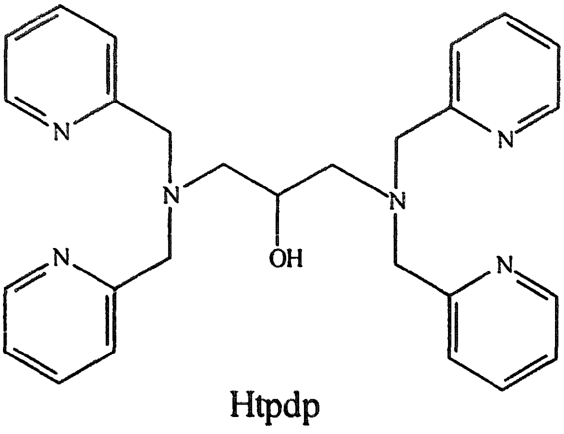
The kinetics of each of these steps were investigated and the respective rate constants at 25°C were $k_1 = 1.4 \times 10^7\ M^{-1}\ s^{-1}$ and $k_2 = 1.2 \times 10^7\ M^{-1}\ s^{-1}$. During these processes the first consists of the replacement of water in $[(papd)Co(II)(H_2O]^{2+}$ followed by electron transfer to produce superoxide ion and the second replacement of water in $[(papd)Co(II)(H_2O]^{2+}$ by $[(papd)CoO_2]^{2+}$ 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

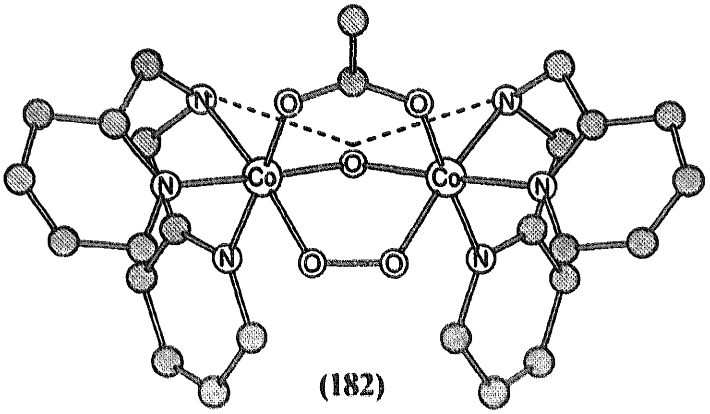


[CoP(PhCN)Ru]

**(180)**



**(181)**



**(182)**

were two reactions involving the formation of $Co_2$ dinuclear complexes:

$$Bd + Ps^{2-} + 2Co^{2+} + H^{+} \rightleftharpoons [BdCo_2PsH]^{3+} \quad \log\beta = 23.00$$

$$Bd + Ps^{2-} + 2Co^{2+} \rightleftharpoons [BdCo_2Ps]^{2+} \quad \log\beta = 15.39$$

and only one in the case of phosphate:

$$Bd + Ps^{3-} + 2Co^{2+} + H^{+} \rightleftharpoons [BdCo_2PsH]^{2+} \quad \log\beta = 27.00(?)$$

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 Bd/$HPO_3^{2-}$ 1:1 $5.3 \times 10^{-9}\ s^{-1}$. By substituting $^{18}O_2$ for $^{16}O_2$ 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 $[\mathrm{MeMeC4[16]cyclidene(MeIm)}]^{2+}$ $K_{O_2}=0.005$ at −40°C and $[\mathrm{MeMeC8[16]cyclidene(MeIm)}]^{2+}$ $K_{O_2}=0.45$ 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 $[\mathrm{Co\{MeMeC8[16]cyclidene\}(SCN)_2}](\mathrm{PF_6})$ 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 hexamethylcyclam ($L^2$) have been measured as a function of pressure [323]. The method used was laser flash photolysis by using the reaction:

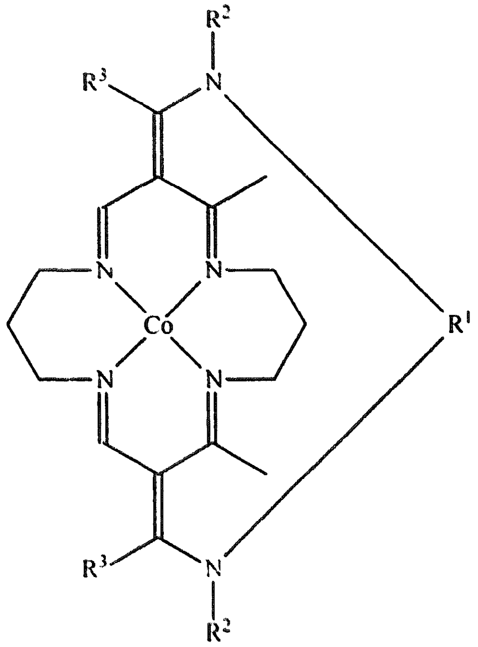
$$[(\mathrm{H_2O})\mathrm{LCoOO}]^{2+} \rightleftharpoons [\mathrm{LCo(H_2O)_2}]^{2+} + \mathrm{O_2}$$

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 $[\mathrm{L^2Co(H_2O)_2}]^{2+}$ is:

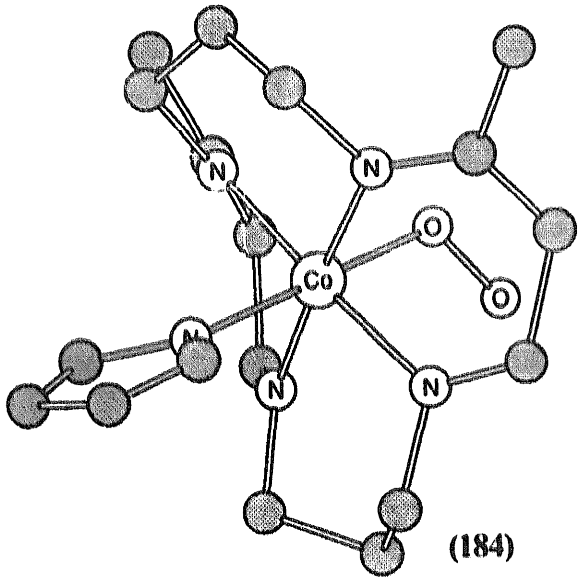
$$k_e = k_1[\mathrm{O_2}]_e + [\mathrm{L^2Co^{2+}}]e + k_{-1}$$

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, 1,2-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].

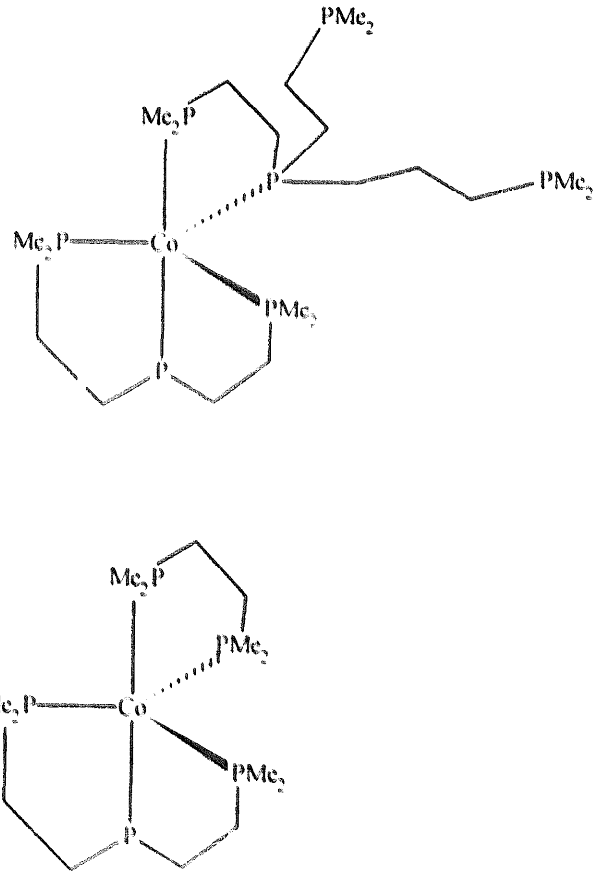
The use of Co–PMA complexes as models for the corresponding bleomycin complexes has been discussed in 2.1.1. Mascharak and coworkers have also examined the reaction of [Co(II)(PMA)] with $O_2$and found that the product is

$[Co(III)(PMA)(O_2^-)]^+$ [324a]. In solution, the superoxide species decomposes to produce $[Co(III)(PMA)(H_2O)]^{2+}$.

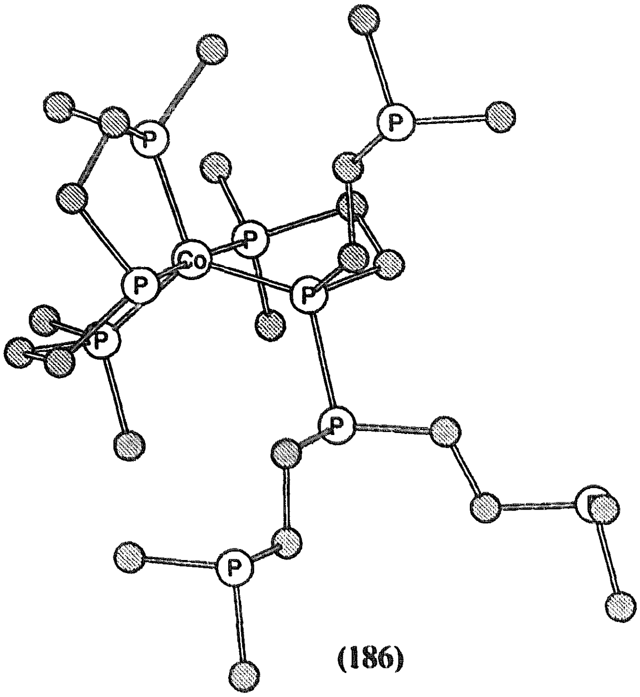
## 5. Cobalt(I) complexes

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 $^{31}P$-{$^1H$} NMR spectroscopy, and the geometry around the Co was similar to that of the first complex.

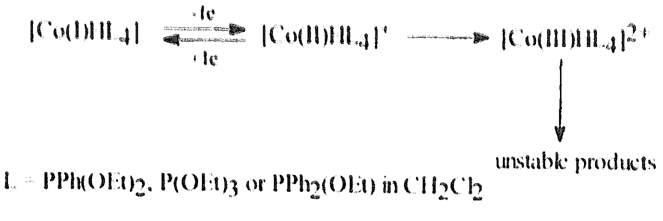


**(185)**



**(186)**

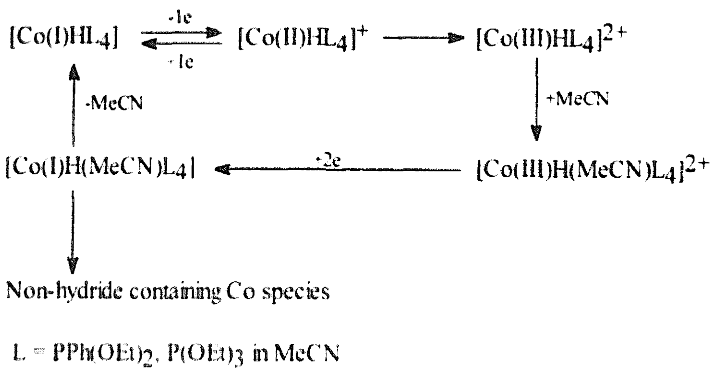
The mechanisms of the oxidation of a range of Co(I) hydride complexes of the form [$CoHL_4$], in which L = $P(OEt)_3$, $PPh(OEt)_2$ or $PPh_2(OEt)$ have been studied using electrochemical methods in $CH_2Cl_2$ and MeCN [327]. There were significant differences in the redox behaviour in the two solvents. 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**).



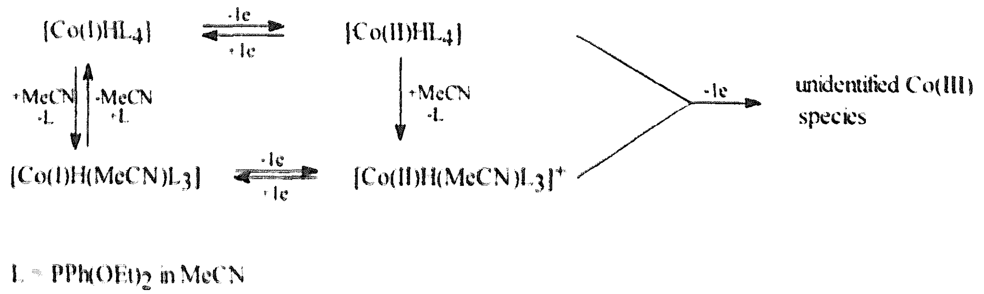
**(187)**

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 [CoLCl]Cl, where L = dibenzo[C,K][1,6,9,14]tetraone [329]. The question of the nature of the bonding of the hydrogen in the complex [$(PP3)Co(H_2)]^+$, where

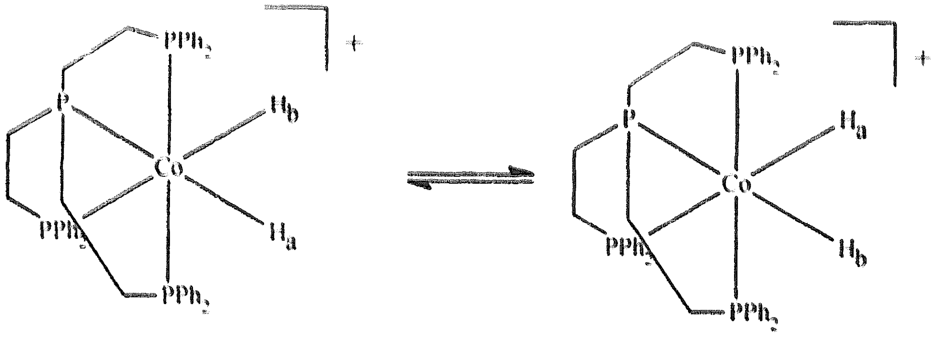


**(188)**



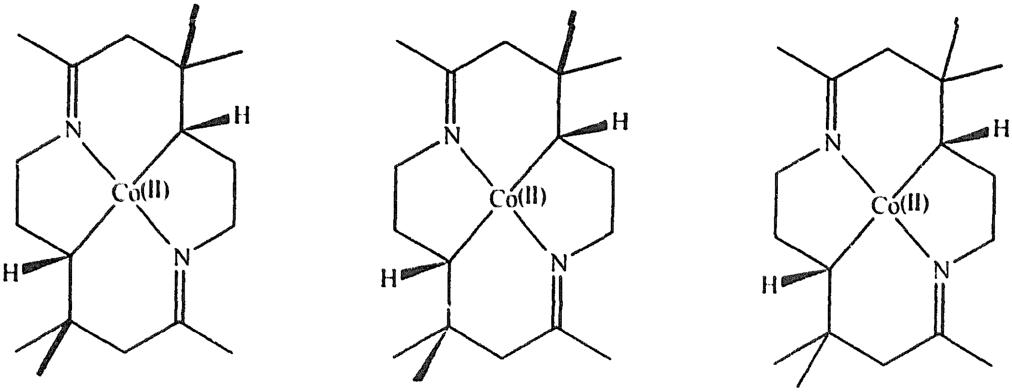
**(189)**

PP3 = $P(CH_2CH_2PPh_2)_3$, has been revisited [330]. It is concluded from $^1H$ and $^1H\{^{31}P\}$ 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 [CoL] prepared from *N-rac*-Co(II)$L^{2+}$ show clear changes arising from H/D exchange involving N–H, giving a rate constant of $5 \times 10^{-4}$ $s^{-1}$ 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.

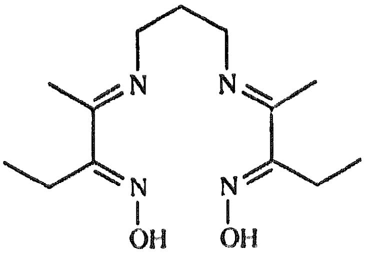


N-*rac*-Co(II)$L^{2+}$ N-*meso*-Co(II)$L^{2+}$ Co(II)$L^{2+}$

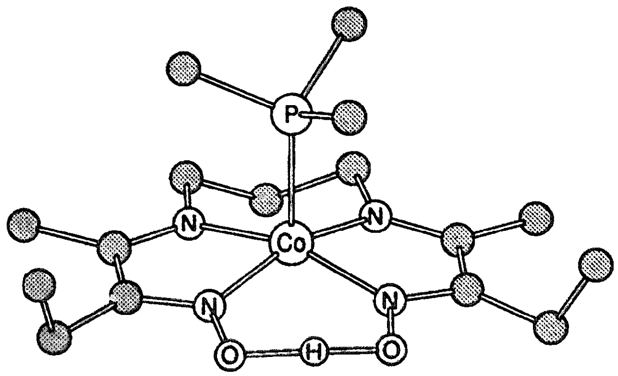
**(191)**

An insoluble tetrapyridinoporphyrazinocobalt(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)**



**(193)**

## 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 $[Co(S_2C_2R_2)_2L]$ ($R=CN$, $L=Et_3$; $R=CF_3$ or Ph, $L=PPh_3$ or $P(OPh)_3$; $R=C_6H_4Me$, $L=PPh_3$ or $PEt_3$; $R=C_6H_4OMe$, $L=PPh_3$) has been studied using isotropic and frozen solution ESR spectra in solution in $CH_2Cl_2$–$ClCH_2CH_2Cl$. The spectra confirm that the Co is low spin $d^5$ and formally Co(IV). The crystal structures of $[Co(S_2C_2(CF_3)_2)_2(P(OPh)_3]$ and $[Co(S_2C_2(CF_3)_2)_2(PPh)_3]$ were also determined. The geometry around the Co was found to be approximately square pyramidal.

## 7. Reactions involving vitamin $B_{12}$ and model compounds

Many of the reactions of vitamin $B_{12}$ 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 $B_{12}$ 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 $\alpha$ 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 $a = 15.335$, $b = 21.974$, $c = 25.501$ Å and $V = 8705$ Å$^3$. 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-of reactions for a series of alkyl cobalaminins, 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 ($I^-$, $S_2O_3^{2-}$, $NO_2^-$, $SCN^-$, $N_3^-$) 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 cm$^3$ 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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## References

[1] M.B. Davies, Coord. Chem. Rev. 152 (1996) 1.
[2] M.B. Davies, Coord. Chem. Rev. 195 (1994) 305.
[3] T. Ohno, K. Nozaki, A. Yoshimura, N. Ikeda, T. Iguro, Research in Chem. Intermediates 20 (1994) 807.
[4] J.M. Christensen, O.M. Poulsen, Sci Total Envir. 150 (1994) 95.
[5] R. Lauwerys, D. Lison, Sci. Total Envir. 150 (1994) 1.
[6] Z.D. Zivkovic, J. Thermal Anal. 41 (1994) 99.
[7] C.G. Baumann, V.A. Bloomfield, Biophys. J. 66 (1994) A157.
[8] J. Wenner, V.A. Bloomfield, Biophys. J. 66 (1994) A157.
[9] C.B. Black, J.A. Cowan, J. Am. Chem. Soc. 116 (1994) 1174.
[10] Y.Y. Chen, J. Hyldtoft, C.J.H. Jacobsen, D.H. Christensen, O.F. Nielsen, Spectrochim. Acta A 50 (1994) 1879.
[11] D.B. Hamilton, J.E. House, Transition Metal Chem. 19 (1994) 527.
[12] M. Kimura, I. Miyamoto, Bull. Chem. Soc. Jpn. 67 (1994) 2136.
[13] G. Calvaruso, F.P. Cavasino, C. Sbirziolo, M.L.T. Liveri, J. Chem. Soc., Faraday Trans. 90 (1994) 2505.
[14] Y.H. Chen, U. Nickel, M. Spiro, J. Chem. Soc. Faraday. Trans. 90 (1994) 617.
[15] J.S. Jaworski, Z. Kebede, J. Electroanal. Chem. 370 (1994) 259.
[16] D.A. Buckingham, Coord. Chem. Rev. 135 (1994) 587.
[17] P.M. Angus, W.G. Jackson, Inorg. Chem. 33 (1994) 477.
[18] W.G. Jackson, S. Cortez, Inorg. Chem. 33 (1994) 1921.
[19] N. Masciocchi, A. Kolyshev, V. Dulepov, E. Boldyreva, A. Sironi, Inorg. Chem. 33 (1994) 2579.
[20] P.M. Angus, W.G. Jackson, Inorg. Chem. 33 (1994) 1569.
[21] K.H. Halawani, C.F. Wells, Transition Metal Chem. 19 (1994) 364.
[22] C.S. Alexander, R.J. Balahara, Inorg. Chem. 1399 (1994) 33.
[23] R.J. Balahara, M.D. Johnson, Inorg. Chim. Acta 225 (1994) 245.
[24] M. Martinez, M-A. Pitarque, R. van Eldik, J. Chem. Soc., Dalton Trans., (1994) 3159.
[25] H. Kunkely, V. Pawlowski, A. Vogler, Inorg. Chim. Acta 225 (1994) 327.
[26] L.A.A. de Oliveira, L.D. Ciana, A. Haim, Inorg. Chim. Acta 225 (1994) 129.
[27] I. Bernal, J. Cetrullo, J. Myrczek, J. Coord. Chem. 30 (1993) 367.
[28] T. Konno, H. Umehara, K. Okanoto, J. Hidaka, Bull. Chem. Soc. Jpn. 67 (1994) 416.
[29] H. Sekizaki, C. Chinan, E. Toyoto, Y. Yamamoto, Bull. Chem. Soc., Jpn. 67 (1994) 1189.
[30] J.E. House, R.W. Eveland, Transition Metal Chem. 19 (1994) 191.
[31] K. Abdurrashid, T.P. Dasgupta, J. Burgess, J. Chem. Soc., Dalton Trans., (1994) 2327.
[32] T.A. Watt, J.G. Collins, A.P. Arnold, Inorg. Chem. 33 (1994) 609.
[33] M.C. Morón, F. Palacio, J. Pons, J. Casabó, X. Solans, K.E. Merabet, D. Huang, X. Shi, B.K. Teo, R.J. Carlin, Inorg. Chem. 33 (1994) 746.
[34] J.M. Arsuaga, J. Nunez, J. Chem. Engineering Data 39 (1994) 324.
[35] O. Grancicová, M. Lezovic, Transition Metal Chem. 19 (1994) 465.
[36] K.K.W. Ho, W.Y. Choy, C. Yuxin, S.C.F. Auyeung, J. Mag. Res., Series A 108 (1994) 196.
[37] S. Ohba, K. Rasmussen, Acta Chem. Scand. 48 (1994) 189.
[38] S.S. Massoud, R.B. Jordan, Inorg. Chim. Acta 221 (1994) 9.
[39] G. González, B. Moullet, M. Martinez, A.E. Merbach, Inorg. Chem. 33 (1994) 2330.
[40] R.C.Y. Bruggemann, U. Thewalt, Z. Naturforsch.. Teil B 49 (1994) 1531.
[41] I. Bernal, J. Cetrullo, W.G. Jackson, J. Coord. Chem. 28 (1993) 89.
[42] P. Mohanty, N. Das, J.K. Dei, J. Indian Chem. Soc. 71 (1994) 143.
[43] K. Yoshitani, Y. Kitamura, A. Shibata, Polyhedron 13 (1994) 2843.
[44] H. Masuda, C. Masuda, K. Jitsukawa, H. Einaga, Bull. Chem. Soc. Jpn. 67 (1994) 67.
[45] I. Bernal, J. Centrullo, J. Cai, Transition Metal Chem. 19 (1994) 221.
[46] D.A. Buckingham, L.R. Clark, Inorg. Chem. 33 (1994) 6171.
[47] K. Yamanari, M. Mori, S. Dogi, A. Fuyuhiro, Inorg. Chem. 33 (1994) 4807.

[48] M. Kojima, Y. Shimizu, K. Nakajima, Y. Yoshikawa, Bull. Chem. Soc. Jpn. 67 (1994) 869.
[49] J.A. Connolly, M. Banaszczyk, R.C. Hynes, J. Chin, Inorg. Chem. 33 (1994) 665.
[50] S.S. Massoud, J. Inorg. Biochem. 55 (1994) 183.
[51] F.M. Akhter, M. Kojima, T. Yoshii, S. Kashino, Y. Yoshikawa, Chem. Lett., (1994) 171.
[52] T. Arcos, B. de Castro, M.J. Ferreira, M. Rangel, J.B. Raynor, J. Chem. Soc., Dalton Trans., (1994) 369.
[53] M. Kumar, E. Natarajan, P. Neta, J. Phys. Chem. 98 (1994) 8024.
[54] B.L. De, S.K. Bhar, J. Indian Chem. Soc. 71 (1994) 245.
[55] K.C. Dash, J. Indian Chem. Soc. 71 (1994) 227.
[56] A. Sekine, H. Tatsuki, Y. Ohashi, Molecular Crystals and Liquid Crystals 242 (1994) 1058.
[57] Y.A. Simonov, O.A. Bologa, A.A. Dvorkin, A.P. Gulya, D.I. Gredinaru, N.V. Gerbelcu, T.I. ÊMalinovskii, Koord. Khim. 20 (1994) 106.
[58] S. Németh, L.I. Simándi, Inorg. Chem. 33 (1994) 5964.
[59] U. Belluco, L. Cattalini, F. Basolo, R. Pearson, A. Turco, J. Amer. Chem. Soc. 87 (1965) 241.
[60] Y.Z. Voloshin, V.V. Trachevskii, J. Coord. Chem. 31 (1994) 147.
[61] M. Megnamisibelombe, I. Jokwi, E. Ngameni, R. Roux, B. Nuber, Z. Naturforsch., Teil B 48 (1993) 1719.
[62] K.M. Davies, A. Hussam, B.R. Rector, Jr., I.M. Owen, P. King, Inorg. Chem. 33 (1994) 1741.
[63] P.W. Dimmock, D.M. Saysell, A.G. Sykes, Inorg. Chim. Acta 225 (1994) 157.
[64] M. Nasreldin, Y.J. Li, F.E. Mabbs, A.G. Sykes, Inorg. Chem. 33 (1994) 4283.
[65] M. Nasreldin, C.A. Routledge, A.G. Sykes, J Chem. Soc., Dalton Trans., (1994) 2809.
[66] K. Harada, K. Komiya, Y. Miyake, S. Harada, H. Saitoh, M. Umehara, Nippon Kayaku Kaishi, (1994) 39.
[67] C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani, A.F. Williams, J. Am. Chem. Soc. 114 (1992) 7440.
[68] C. Piguet, G. Bernadinelli, B. Bocquet, O. Schaad, A.F. Williams, Inorg. Chem. 33 (1994) 4112.
[69] L.J. Charbonniere, B. Bernardinelli, C. Piguet, A.M. Sargeson, A.F. Wiiliams, J. Chem. Soc., Chem. Commun., (1994) 1419.
[70] K. Bernauer, E. Fuchs, D. Hugi-Cleary, Inorg. Chim. Acta 218 (1994) 73.
[71] B.H. Ye, X.M. Chen, T.X. Zeng, L.N. Ji, Polyhedron 13 (1994) 2185.
[72] L.G. Marzilli, New J. Chem. 14 (1990) 409.
[73] M. Lin, L.G. Marzilli, Inorg. Chem. 33 (1994) 5309.
[74] W.D. McGuinn, L. Baxter, L. Pei, I. Petrikovics, E.P. Cannon, J.L. Way, Fundamental Appl. Toxicology 23 (1994) 76.
[75] M. Yuasa, Y. Shiba, I. Sekine, Denki Kagaku 62 (1994) 360.
[76] A.L. Balch, M. Mazzanti, M.M. Olmstead, J. Chem. Soc., Dalton Trans., (1994) 269.
[77] J.S. Summers, J.L. Petersen, A.M. Stolzenberg, J. Am. Chem. Soc. 116 (1994) 7189.
[78] M. Endregard, D.G. Nicolson, R.J. Abraham, I. Marsden, B. Beagley, Acta. Chem. Scand. 48 (1994) 640.
[79] M. Endregard, D.G. Nicholson, R.J. Abraham, B. Beagley, J. Chem. Soc., Dalton Trans., (1994) 90.
[80] R. Paolesse, S. Liccoccia, G. Bandoli, A. Dolmella, T. Boschi, Inorg. Chem. 33 (1994) 1171.
[81] M.A. Cox, P.D. Newman, F.S. Stephens, R.S. Vagg, P.A. Williams, Inorg. Chim. Acta 221 (1994) 191.
[82] S.P. Sovilj, G. Vuckovic, K. Babic, N. Matsumoto, M. Avramovivic, V.M. Jovanovic, J. Coord. Chem. 31 (1994) 167.
[83] V. Goby, R. Ramaraj, J. Chem. Soc., Dalton Trans., (1994) 2445.
[84] L. Ma, B.Y. Zhang, H.L. Li, J.Q. Chambers, J. Electroanalyt. Chem. 362 (1993) 201.
[85] M. Yashiro, S. Miura, T. Matsuyama, S. Yoshikawa, M. Komiyama, S. Yano, Inorg. Chem. 33 (1994) 1003.
[86] S.S. Massoud, Polyhedron 13 (1994) 1647.
[87] T.H. Lu, C.Y. Lai, C.S. Chung, Acta Cryst. C 50 (1994) 202.
[88] M. Yamaguchi, M. Saburi, S. Yoshikawa, T. Yamagishi, Bull. Chem. Soc. Jpn. 67 (1994) 1341.
[89] A.N. Acharya, A.C. Dash, J. Chem. Soc., Faraday Trans. 90 (1994) 3293.

[90] A.N. Acharya, A.C. Dash, Int. J. Chem. Kinetics 26 (1994) 681.

[91] R.J. Geue, A. Höhn, S.F. Ralph, A.M. Sargeson, A.C. Willis, J. Chem. Soc., Chem. Commun., (1994) 1513.

[92] R.J. Geue, M.B. McDonnell, A.W.H. Mall, A.M. Sargeson, A.C.Willis, J. Chem. Soc., Chem Commun., (1994) 667.

[93] R.J. Geue, P. Osvath, A.M. Sargeson, K.R. Acharya, S.B. Noor, T.N.G. Row, K. Venkatesan, Aust. J. Chem. 47 (1994) 511.

[94] G.A. Bottomley, I.J. Clark, I.I. Creaser, L.M. Engelhardt, R.J. Gene, K.S. Hagen, J.M. Harrowfield, G.A. Lawrance, P.A. Lay, A.M. Sargeson, A.J. See, B.W. Skelton, A.N. White, F. R Wilner, Inorg. Chem. 45 (1994) 143.

[95] I.I. Creaser, T. Komorita, A.M. Sargeson, A.C. Willis, K. Amanari, Aust. J. Chem. 47 (1994) 529.

[96] P.V. Bernhardt, A.M.T. Bygott, R.J. Gene, A.J. Hendry, B.R. Korybut-Daszkiewicz, P.A. Lay, J.R. Pladziewicz, A.M. Sargeson, A.C. Willis, Inorg. Chem. 33 (1994) 4553.

[97] K. Mochizuki, S. Higashiya, M. Uyama, T. Kimura, J. Chem. Soc., Chem. Commun., (1994) 2673.

[98] T.H. Tahirov, T.H. Lu, B.H. Chen, T.Y. Chi, C.S. Chung, Acta Crystallogr., Sect. C 50 (1994) 1686.

[99] B.H. Chen, C.Y. Lai, Y. Yuan, C.S. Chung, J. Chem. Soc., Dalton Trans. (1994) 2959.

[100] P.W. Crawford, F.A. Schultz, Inorg. Chem. 33 (1994) 4345.

[101] E. Cole, R.C.B. Copley, J.A.K. Howard, D. Parker, G. Ferguson, J.F. Gallagher, B. Kaitner, A. Harrison, L. Royle, J. Chem. Soc., Dalton Trans., (1994) 1619.

[102] L. Hauscherr-Primo, K. Hegetschweiler, H. Rüegger, L. Odier, R.D. Hancock, H.W. Schmalle, V. Gramlich, J. Chem. Soc., Dalton Trans., (1994) 1689.

[103] J.D. Tan, E.T. Farinas, S.S. David, P.K. Mascharak, Inorg. Chem. 33 (1994) 4295.

[104] J.L. Tueting, K.L. Spence, M. Zimmer, J. Chem. Soc., Dalton Trans., (1994) 551.

[105] T.Takita, Y. Muraoka, T. Nakatini, A. Fuji, Y. Iitaka, H. Umezawa J. Antibiot., 31 (1978) 1073; M.A.J. Akkerman, E.W.J.F. Neijman, S.S. Wijmenga, C.W. Hilbers, W. Bermel, J. Am. Chem. Soc., 112 (1990) 7462.

[106] K.P. Nightingale, K.R. Fox, European J. Biochem. 220 (1994) 173.

[107] R.X. Xu, D. Nettesheim, J.D. Otvos, D.H. Petering, Biochem. 33 (1994) 907.

[108] M. Kato, T. Sasagawa, Y. Ishihara, S. Yamada, S. Funitani, M. Kimura, J. Chem. Soc., Dalton Trans., (1994) 583.

[109] H. Sukane, I. Watanake, Y. Yokoyama, S. Ikeda, T. Taura, Polyhedron 13 (1994) 1625.

[110] R.M.L. Warren, A. Tatehata, A.G. Lappin, J. Chem. Soc., Dalton Trans., (1994) 1655.

[111] V.A. Reutov, E.V. Gukhman, Zh. Obs. Khim. 64 (1994) 889.

[112] O.L. Shcheka, T.B. Emelina, V.D. Yumatov, J. Electron Spectrosc. Related Phenomena 70 (1994) 83.

[113] L. Plaggenborg, W.D. Buchannon, B.W. Wenclawiak, J.B. Westmore, Fresenius J. Analyt. Chem. 348 (1994) 639.

[114] T.T. Dang, S.F. Pederson, J.A. Leary, J. Amer. Soc. Mass Sepctrometry 5 (1994) 1044.

[115] P. Comba, H. Jakob, B. Nuber, B.K. Keppler, Inorg. Chem. 33 (1994) 3400.

[116] F. Mizukami, H. Izutsu, T. Osaka, Advanced Materials 6 (1994) 854.

[117] K. Ohkubo, T. Hamada, H. Iskida, M. Fukushima, M. Watanabe, H. Kobayashi, J. Chem. Soc., Dalton Trans., (1994) 239.

[118] B. Kiatner, E. Mestovic, Z Kristallogr. 209 (1994) 818.

[119] O. Oyetunji, J.F. Ojo, O. Olubuyide, Abstr. Papers Amer. Chem. Soc. 208 (1994) 512.

[120] U. Bossek, G. Haselhorst, S. Ross, K. Wieghardt, B. Nuber, J. Chem. Soc., Dalton Trans., (1994) 2041.

[121] C.W. Lange, B.J. Conklin, C.G. Pierpoint, Inorg. Chem. 33 (1994) 1276.

[122] O.S. Jung, C.G. Pierpont, J. Amer. Chem. Soc. 116 (1994) 1127.

[123] O.S. Jung, C.G. Pierpont, Inorg. Chem. 33 (1994) 2227.

[124] O.S. Jung, C.G. Pierpont, J. Am. Chem. Soc. 116 (1994) 2229.

[125] M.A. Olatunji, G.A. Ayoko, F.O. Ohiani, Transition Metal Chem. 19 (1994) 253.

[126] G.A. Ayoko, J.F. Iyun, S. Mamman, Transition Metal Chem. 19 (1994) 151.

[127] T. Mizuta, A. Uchiyama, K. Ueda, K. Miyoshi, H. Yoneda, Chem. Letters, (1994) 101.

[128] K. Jitsukawa, K. Iwai, H. Masuda, H. Ogoslin, Chem. Letters (1994) 303.
[129] N. Juranic, S. Macura, Inorg. Chim. Acta 217 (1994) 213.
[130] R.K. Ray, G.B. Kauffman, Polyhedron 13 (1994) 2591.
[131] K. Jitsukawa, T. Hata, T. Yamamoto, K. Kano, H. Masuda, H. Einaga, Chem. Lett., (1994) 1169.
[132] K. Jitsukawa, T. Morioka, H. Masuda, H. Ogoshi, H. Einaga, Inorg. Chim. Acta 216 (1994) 249.
[133] E. Danilizuk, B. Sikorska, Polish J. Chem. 68 (1994) 2617.
[134] T. Ama, T. Yonemura, H. Kawaguchi, T. Yasui, Bull. Chem. Soc. Jpn. 67 (1994) 410.
[135] R.M.L. Warren, K.J. Haller, A. Tatchata, A.G. Lappin, Inorg. Chem. 33 (1994) 227.
[136] T. Yasui, T. Ama, H. Kawaguchi, Polyhedron 13 (1994) 1963.
[137] S. Chakrabarti, P.C. Mandal, S.N. Bhattacharyya, Int. J. Chem. Kinetics 26 (1994) 693.
[138] L.M. Shkolnikova, A.L. Poznyak, V.S. Fundamenskii, Koord. Khim. 20 (1994) 511.
[139] M. Yashiro, T. Moata, M. Sato, M. Kosuka, K. Kobayashi, T. Sakurai, S. Yoshikawa, M. Koniyama, S. Yano, J. Chem. Soc., Dalton Trans., (1994) 1511.
[140] M. Yashiro, T. Murata, S. Yoshikawa, S. Yano, J. Chem. Soc., Dalton Trans., (1994) 1073.
[141] S. Yano, M. Kato, K. Tsukahara, M. Sato, T. Shibahara, K. Lee, Y. Sugihara, M. Iida, K. Goto, S. Aoki, Y. Shibahara, H. Nakahara, S. Yanagisawa, H. Myagawa, Inorg. Chem. 33 (1994) 5030.
[142] D.J. Radanovic, S.R. Trifunovic, C. Maricondi, B.E. Douglas, Inorg. Chim. Acta 219 (1994) 147.
[143] M.J. Jun, J.W. Cheon, Polyhedron 13 (1994) 63.
[144] S.A. Samath, K. Jeyasubramanian, S. Thambidurai, S. Kamardeen, S.K. Ramalingam, Transition Metal Chem. 19 (1994) 157.
[145] N. Sakagami, T. Yasui, H. Kawaguchi, T. Ama, S. Kaizaki, Bull. Chem. Soc. Jpn. 67 (1994) 680.
[146] J. Sima, Polish J. Chem. 68 (1994) 1689.
[147] E. Eichhorn, B. Speiser, Electroanalytical Chem. 365 (1994) 207.
[148] R.P. Sharma, V. Gupta, K.K. Bhasin, E.R. T Tiekink, J. Coord. Chem. 33 (1994) 117.
[149] K. Jitsukawa, T. Yamamoto, T. Atsumi, H. Masuda, H. Einaga, J. Chem. Soc., Chem. Commun., (1994) 2335.
[150] H.M. Haendler, Acta Crystallogr., Sect. C 50 (1994) 1419.
[151] Y. Elerman, K. Kobak, I. Svokoda, M. Giselle, Acta Crystallogr., Sect. C 50 (1994) 1694.
[152] P.V. Bernhardt, T.W. Hambley, G.A. Lawrance, K.J. Molloy, Aust.. J. Chem. 47 (1994) 817.
[153] T.W. Hambley, G.A. Lawrance, M. Malder, G. Wei, J. Chem. Soc., Dalton Trans., (1994) 355.
[154] P.A. Angus, B.T. Golding, S.S. Jurisson, A.M. Sargeson, A.C. Willis, Aust. J. Chem. 47 (1994) 501.
[155] C. Fraser, B. Bosnich, Inorg. Chem. 33 (1994) 338.
[156] M.J. Grannas, B.F. Hoskins, R. Robson, Inorg. Chem. 33 (1994) 1071.
[157] D. Heineke, S.J. Franklin, K.N. Raymond, Inorg. Chem. 33 (1994) 2413.
[158] J.V. Rodrigues, I.C. Santos, V. Gama, R.T. Henriques, J.C. Waerenborgh, M.T. Duarte, M. Almeida, J. Chem. Soc., Dalton Trans., (1994) 2655.
[159] W. Bensch, M. Schuster, Z. Anorg. Allg. Chem. 620 (1994) 1479.
[160] K. Okamoto, K. Arashi, J. Hidaka, T. Konno, Bull. Chem. Soc. Jpn. 67 (1994) 2736.
[161] P. Kofod, E. Larsen, J. Springborg, S. Larsen, T.A. Larsen, R.J. Geue, G.H. Searle, Aust. J. Chem. 47 (1994) 111.
[162] P. Kofod, E. Larsen, J. Springborg, Acta Chem. Scand. 48 (1994) 611.
[163] E. Larsen, S. Larsen, G.B. Paulsen, J. Springborg, D.N. Wang, Acta Chem. Scand. 48 (1994) 107.
[164] P. Kofod, E. Larsen, S. Larsen, D.N. Wang, J. Springborg, G.B. Paulsen, Acta Chem. Scand. 8 (1994) 283.
[165] A. Castineiras, D.X. West, H. Gebremedhin, T.J. Romack, Inorg. Chim. Acta 216 (1994) 229.
[166] M. Ul-Haque, M.S. Hussain, Transition Metal Chem. 19 (1994) 95.
[167] P. Sonawane, R. Chikate, A. Kumbhar, S. Padhye, R.J. Doedens, Polyhedron 13 (1994) 395.
[168] S. Seth, Acta Crystallogr., Sect. C 50 (1994) 1196.
[169] K. Yamanari, S. Dogi, K. Okusako, T. Fujihara, A. Fuyuhiro, S. Kaizaki, Bull. Chem. Soc. Jpn. 67 (1994) 3004.
[170] T. Kajiwara, T. Ito, J. Chem. Soc., Chem. Commun., (1994) 1773.
[171] I. Bernal, J. Cetrullo, J.H. Worrell, T. Li, Polyhedron 13 (1994) 463.
[172] A.J. Blake, G. Reid, M. Schröder, J. Chem. Soc., Dalton Trans., (1994) 291.

[173] P. Osvath, A.M. Sargeson, Aust. J. Chem. 47 (1994) 807.
[174] T.M. Donlevy, L.R. Gahan, T.W. Hambley, Inorg. Chem. 33 (1994) 2668.
[175] M. Kojima, I. Sugimoto, Y. Shimizu, Y. Yoshikawa, Proc. Jpn. Acad Series B 70 (1994) 101.
[176] N. Ehlers, D. Funkemeier, R. Mattes, Z. Anorg. Allg. Chem. 620 (1994) 796.
[177] P. Chakraborty, S. Karmakar, S. Chandra, A. Chakravorty, Inorg. Chem. 33 (1994) 816.
[178] P. Chakraborty, S.K. Chandra, A. Chakravorty, Inorg. Chem. 53 (1994) 4959.
[179] P. Sonawane, A. Kumbhar, S. Padhye, R.J. Butcher, Transition Metal Chem. 19 (1994) 277.
[180] K. Kashiwabara, M. Kita, J. Fujita, S. Kurachi, S. Ohba, Bull. Chem. Soc. Jpn. 67 (1994) 2145.
[181] V. Korner, A. Asam, G. Huttner, L. Zsolnai, M. Buchner, Z Naturforsch., Teil B 49 (1994) 1183.
[182] N.E. Kob, J.E. House, Transition Metal Chem. 19 (1994) 31.
[183] S. Peschel, D. Babel, Z. Naturforsch., Teil B 49 (1994) 1373.
[184] S.S. Massoud, Polyhedron 13 (1994) 3127.
[185] S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc., Chem. Commun., (1994) 45.
[186] T.E. Elgren, L.-J. Ming, L. Que, Inorg. Chem. 33 (1994) 8917.
[187] C. Strong, S.L. Harrison, W. Zeger, Inorg. Chem. 33 (1994) 606.
[188] H. Chakraborty, M.L. Rahman, Transition Metal Chem. 19 (1994) 481.
[189] R.M.Z. Kocker, G. Frenzen, B. Neumuller, E. Dehnicke, J. Magull, Z. Anorg. Allg. Chem. 620 (1994) 431.
[190] I.A. Salem, J. Molec. Catalysis 87 (1994) 25.
[191] M.S. Hussain, G.D. Khattak, J. Magnetism Magnetic Mater. 134 (1994) 137.
[192] Sevindir, R. Mirzaoglu, E. Ozcan, S. Ertul, E. Guler, Synth. React. Inorg. Metal-Org. Chem. 24 (1994) 613.
[193] A.N. Acharya, Indian J. Chem., Sect. A 33 (1994) 668.
[194] P. Tsiveriotis, G. Varvounis, C. Papadimitriou, N. Hadjiliadis, Transition Metal Chem. 19 (1994) 335.
[195] G. Kenessey, K. Lashgari, G. Machula, G. Liptay, Acta Chem. Scand. 48 (1994) 705.
[196] S. Wang, S. yu, Q. Luo, Q. Wang, J. Shi, Q. Wu, Transition Metal Chem. 19 (1994) 205.
[197] L. Hiltunen, L. Niinisto, G. Kenessey, G.M. Keseru, G. Liptay, Acta Chem. Scand. 48 (1994) 456.
[198] F.R. Keene, E.R. T Tiekink, Z. Kristallogr. 209 (1994) 548.
[199] D.E. Fenton, R.W. Matthews, M. McPartlin, B.P. Murphy, I.J. Scowen, P.A. Tasker, J. Chem. Soc., Chem. Commun., (1994) 1391.
[200] E.C. Constable, R.Martinez-Manez, A.M.W.C. Thompson, J.V. Walker, J. Chem. Soc, Chem. Commun., (1994) 1585.
[201] V. Shlover, I.L. Eremenko, H. Berke, R. Nesper, S.M. Zakeeruddin, M.K. Nazeeruddin, M. GrŠtzel, Inorg. Chim. Acta 219 (1994) 11.
[202] G.M. Keseru, Z. Hajnal, G. Kenessey, G. Liptay, Theochem-J. Molec. Struct. 112 (1994) 289.
[203] G. Kenessey, L. Parkanyi, P.E. Werner, G.M. Keseru, T. Wadsten, G. Liptay, Struct. Chem. 5 (1994) 123.
[204] G. De Munno, M. Julve, F. Lloret, J. Faus, A. Caneschi, J. Chem. Soc., Dalton Trans., (1994) 1175.
[205] B. Viossat, N.H. Dung, J. Lehuede, J.M. Vierfond, Acta Crystallogr., Sect. C 50 (1994) 211.
[206] S.L. Ma, D.Z. Liao, Z.H. Jiang, S.P. Yan, F.C. Xue, G.L. Wang, Synth. React. Inorg. Metal-Org. Chem. 24 (1994) 137.
[207] N. Kobayashi, H. Lam, W.A. Nevin, P. Janda, C.C. Leznoff, T. Koyama, A. Monden, H. Shirai, J. Am. Chem. Soc. 116 (1994) 879.
[208] A. Rosa, E.J. Baerends, Inorg. Chem. 33 (1994) 584.
[209] T. Watanabe, R.D. Archer, J. Molec. Catal. 93 (1994) 253.
[210] H. Shirai, Nippon Kagaku Kaishi, (1994) 1.
[211] M. Kimura, T. Dakeno, E. Adachi, T. Koyama, K. Hanabusa, H. Shirai, Macro Molecular Chem. Phys. 195 (1994) 2423.
[212] E.T.W.M. Schipper, J.P.A. Heuts, P. Piet, T.P.M. Beelen, A.L. German, J. Molec. Catalysis 87 (1994) 161.
[213] BalkusK.J., Jr., A.G. Gabrielov, S.L. Bell, F. Bedioui, L. Roue, J. Devynck, Inorg. Chem. 33 (1994) 67.

[214] N. Kobayashi, T. Osa, H. Konami, Inorg. Chem. 33 (1994) 1735.

[215] C. Bernard, J.P. Gisselbrecht, M. Gross, E. Vogel, M. Lausmann, Inorg. Chem. 33 (1994) 2393.

[216] L.D. Sparks, K.K. Anderson, C.J. Medforth, K.M. Smith, J.A. Shelnutt, Inorg. Chem. 33 (1994) 2297.

[217] H. Imai, A. Sunohara, S. Nakagawa, H. Munakata, Y. Uemori, E. Kyuno, Thermochim. Acta 240 (1994) 109.

[218] W.R. Scheidt, I. Turowska-Tyrk, Inorg. Chem. 33 (1994) 1314.

[219] D.J. Liu, X.Q. Lin, Acta Chim. Sinica 52 (1994) 23.

[220] L. Ukrainczyk, M. Chibwe, T.J. Pinnavaia, S.A. Bond, J. Phys. Chem. 98 (1994) 2668.

[221] D.W. Pang, B.H. Deng, Z.L. Wang, Electrochimica Acta 39 (1994) 847.

[222] G.J. Vanberkel, K.G. Asasno, S.A. McCluckey, J. Am. Soc. Mass Spectrometry 5 (1994) 689.

[223] A L. Balch, M. Mazzanti, B.C. Noll, M.M. Olmstead, J. Am. Chem. Soc. 116 (1994) 9114.

[224] R.W. Saalfrank, O. Struck, K. Peters, H.G. von Schnering, Z. Naturforsch., Teil B 49 (1994) 1415.

[225] W.K. Chang, G.H. Lee, Y. Wang, T.I. Ho, Y.O. Su, Y.C. Lin, Inorg. Chim. Acta 223 (1994) 139.

[226] J.A. Aguilar, A. Bianchi, E. Garcia-Espania, S.V. Luis, J.M. Llinares, J.A. Ramirez, C. Soriano, J. Chem. Soc., Dalton Trans., (1994) 637.

[227] P.M. van Berkel, W.L. Driessen, R. Hamalainen, J. Reedjik, U. Turpeinen, Inorg. Chem. 33 (1994) 5920.

[228] O.M. Reinaud, A.L. Rheingold, K.H. Theopold, Inorg. Chem. 33 (1994) 2306.

[229] D. Zhang, D.H. Busch, Inorg. Chem. 33 (1994) 5138.

[230] M. Shakir, S.P. Varkey, F. Firdaus, P.S. Hameed, Polyhedron 13 (1994) 2319.

[231] A. Ceulemans, R. Debuyst, F. Dejehet, P. Janssen, L.G. Vanquickenborne, Inorg. Chem. 33 (1994) 3188.

[232] W.L. Driessen, R.A.G. Degraaff, F.J. Parleviet, J. Reedijk, R.M. Devos, Inorg. Chim. Acta 216 (1994) 43.

[233] S.S. Tandon, L.K. Thompson, J.N. Bridson, J.C. Dewan, Inorg. Chem. 33 (1994) 54.

[234] R.J. Balahura, R.A. Kirby, Inorg. Chem. 33 (1994) 1021.

[235] S.T. Lang, L.G. Bachas, Talanta 41 (1994) 963.

[236] K. Rajapandian, J. Thomas, P. Tharmaraj, V. Chandrasekhar, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (1994) 1301.

[237] S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Am. Chem. Soc. 116 (1994) 5702.

[238] C. Janiak, J. Chem. Soc., Chem. Commun., (1994) 545.

[239] J. Podlaha, J. Podlahova, P. Stepnicka, M. Rieder, Polyhedron 13 (1994) 2847.

[240] R.N. Pandey, M.G. Bapat, Bull. Chem. Soc. Jpn. 67 (1994) 1792.

[241] R.A. Wajszczuk, W.A. Charewicz, Hydrometallurgy 35 (1994) 99.

[242] R.A. Wajszczuk, W.A. Charewicz, Hydrometallurgy 35 (1994) 91.

[243] A.A. Elasmy, E.M. Saad, M.S. Shahawi, Transition Metal Chem. 19 (1994) 406.

[244] Y. Inada, K.-i. Sugimoto, K. Ozutsumi, S. Funahashi, Inorg. Chem. 33 (1994) 1875.

[245] M. Koskenlinna, J. Kansikas, T. Leskela, Acta Chem. Scand. 48 (1994) 783.

[246] Z. Micka, I. Nemec, P. Vojtisek, J. Ondracek, J. Holsa, J. Solid State Chem. 112 (1994) 237.

[247] Th. Fetzer, R. Jooss, A. Lentz, T. Debaerdemaeker, Z. Anorg. Allg. Chem. 620 (1994) 1750.

[248] M. Saladini, Acta Crystallogr., Sect C 50 (1994) 1561.

[249] A.I. Ibrahim, Transition Metal Chem. 19 (1994) 561.

[250] A.I. Ibrahim, M. Elbehairy, A.A. Taha, S.L. Stefan, Synth. React. Inorg. Metal-Org. Chem. 24 (1994) 291.

[251] A.J. Blake, R.O. Gould, C.M. Grant, P.E.Y. Milne, Winpenney, Polyhedron 13 (1994) 187.

[252] M.G. Marei, M. El-Ghanam, A.M. El-Korily, A. El-Dissouky, Transition Metal Chem. 19 (1994) 70.

[253] J.S. Chen, R.H. Jones, S. Natarajan, M.B. Hursthouse, J.M. Thomas, Angew. Chem. Int. Eng. Ed. 33 (1994) 639.

[254] P. Caro, J. Derouet, M.S. Belkhiria, M. Dabbabi, G. Leflem, J. Chim. Phys. Phys.-Chim. Biol. 91 (1994) 293.

[255] G.A. Ayoko, J. Arabel, Transition Metal Chem. 19 (1994) 212.

[256] D.M.L. Goodgame, S.P.W. Hill, A.M. Smith, D.J. Williams, J. Chem. Soc., Dalton Trans., (1994) 859.

[257] J.-F. Gadais, M.A. Khan, G.M. Bouet, A.D. Thanh, Transition Metal Chem. 19 (1994) 651.

[258] S.-L. Ma, Z.-H. Jiang, D.-Z. Liao, S.-P. Yan, G.-L. Wang, Transition Metal Chem. 19 (1994) 531.

[259] R. Kaplonek, U. Baumeister, H. Hartung, Z. Anorg. Allg. Chem. 620 (1994) 574.

[260] G.M. Escandar, L.F. Sala, M.G. Sierra, Polyhedron 13 (1994) 143.

[261] H.A. Azab, A.M. Elnady, A. Hassan, R.S.A. Azkal, Monats. Chem. 125 (1994) 1059.

[262] M. Kimura, I. Miyamoto, Bull. Chem. Soc. Jpn. 67 (1994) 2357.

[263] S.P. Chattopadhyay, D. Banerjea, Polyhedron 13 (1994) 1981.

[264] P.C. Kang, G.R. Eaton, S.S. Eaton, Inorg. Chem. 33 (1994) 3660.

[265] M.A. Cobb, D.N. Hague, A.R. White, J. Chem. Soc., Dalton Trans., (1994) 51.

[266] D.N. Hague, A.R. White, J. Chem. Soc., Dalton Trans., (1994) 3645.

[267] D.M. Palade, I.D. Ozherelev, I.V. Belyaeva, Koord. Khim. 20 (1994) 462.

[268] C.V.R. Reddy, M.G.R. Reddy, A.J. Shivar, Indian J. Chem., Sect. A 33 (1994) 792.

[269] W. Zhong, W. Zishen, Y. Zhenhuan, H. Qinghua, Transition Metal Chem. 19 (1994) 235.

[270] J. Faus, M. Julve, F. Lloret, J.A. Real, J. Sletten, Inorg. Chem. 33 (1994) 5535.

[271] D.S. Rani, P.V.A. Lakshmi, V. Jayatyagaraju, Transition Metal Chem. 19 (1994) 75.

[272] A.A. Razik and A.K.A. Hadi; V.H. Arali, V.K. Revankar, V.B. Mahale and P.J. Kulkarni, Transition Metal Chem., 19 (1994) 57; 19 (1994) 84.

[273] V.H. Arali, V.K. Revankar, V.B. Mahale, P.J. Kulkarni, Transition Metal Chem. 19 (1994) 57.

[274] J. Castro, J. Romero, J.A. Garciavazquez, A. Souza, A. Castineiras, J. Chem. Crystallogr. 24 (1994) 469.

[275] O. Costisor, W. Linert, S. Deutsch, C. Stanescu, J. Coord. Chem. 33 (1994) 229.

[276] K.R. Adam, L.F. Lindoy, B.W. Skelton, S.V. Smith, A.H. White, J. Chem. Soc., Dalton Trans., (1994) 3361.

[277] J.D.G. McCollum, C. Fraser, R. Ostrander, A.L. Rheingold, B. Bosnich, Inorg. Chem. 33 (1994) 2383.

[278] C. Amari, C. Pelizzi, G. Pelizzi, G. Predieri, G. Sartori, Inorg. Chim. Acta 223 (1994) 97.

[279] T. Tanase, M. Nakagoshi, A. Teratani, M. Kato, Y. Yamamoto, S. Yano, Inorg. Chem. 33 (1994) 5.

[280] M. Hirotsu, M. Kojima, K. Nakajima, S. Kashino, Y. Yoshikawa, Chem. Letters, (1994) 2183.

[281] Y. Ohashi, M. Nakagoshi, Bull. Chem. Soc. Jpn. 67 (1994) 2921.

[282] I.J. Sallomi, A.J. Shaheen, Transition Metal Chem. 19 (1994) 275.

[283] L.F. Veiros, M.J. Calhorda, E. Canadell, Inorg. Chem. 33 (1994) 4290.

[284] M.R. Grace, H. Takagi, T.W. Swaddle, Inorg. Chem. 33 (1994) 1915.

[285] Z. Atherton, D.M.L. Goodgame, D.A. Katahira, S. Menzer, D.J. Williams, J. Chem. Soc., Dalton Trans., (1994) 1423.

[286] J. Sanmartin, M.R. Bernrmejo, J.A. Gracia-Vázquez, J. Romero, A. Sousa, Transition Metal Chem. 19 (1994) 209.

[287] Siddiq, F. Arjmand, S. Tabassum, S.A.A. Zaidi, Transition Metal Chem. 19 (1994) 399.

[288] A.L. Nivorozhkin, H. Toftlund, M. Nielsen, J. Chem. Soc., Dalton Trans., (1994) 361.

[289] M.S. Masoud, O.H.A. Elhamid, Z.M. Zaki, Transition Metal Chem. 19 (1994) 21.

[290] P. Tseriotis, G. Varvounis, C. Papadimitriou, N. Hadjiliadis, Transition Metal Chem. 19 (1994) 335.

[291] G. Sanchez, M.D. Santana, M.J. Vidal, G. Garcia, G. Lopez, E. Perez, Transition Metal Chem. 19 (1994) 230.

[292] M. Rahman, M.A. Mridha, M.A. Ali, Transition Metal Chem. 19 (1994) 237.

[293] E. Bouwman, J. Reedijk, Inorg. Chim. Acta 215 (1994) 151.

[294] P. Braunstein, D.G. Kelly, Y. Dusausoy, D. Bayeul, M. Lanfranchi, A. Tiripicchio, Inorg. Chem. 33 (1994) 233.

[295] B.C. Janssen, A. Asam, G. Huttner, V. Sernau, L. Zsolnai, Chem. Ber. 127 (1994) 501.

[296] M. Pilarczik, W. Grzybkowski, L. Klinsporn, Polish J. Chem. 68 (1994) 591.

[297] M. Pilarczik, L. Klinsporn, Polish J. Chem. 68 (1994) 577.

[298] M.B. Rozenkevitch, Y.A. Sakharovski, D.C. Luehrs, J. Photochem. Photobiol. Section A 79 (1994) 33.

[299] C.A.L. Becker, J. Coord Chem. 31 (1994) 337.

[300] C.A.L. Becker, Synth. React. Inorg. Metal-Org. Chem. 24 (1994) 855.

[301] M. Momenteau, C.A. Reed, Chem. Rev. 94 (1994) 659.

[302] M. Hoshino, K. Yamamoto, J.P. Lillis, T. Chijimatsu, J. Uzawa, Coord. Chem. Rev. 132 (1994) 235.

[303] G.Q. Li, R. Govind, Industrial Engineering Chem. Research 33 (1994) 755.

[304] R. Antiochia, S. Canepari, V. Carunchio, Transition Metal Chem. 19 (1994) 359.

[305] J.D. Wang, E. Collange, D.J. Aymes, M.R. Paris, R. Fournaise, Bull. Soc. Chim. Fr. 131 (1994) 131.

[306] A. Vogt, A. Kuffelnicki, B. Lesniewska, Polyhedron 13 (1994) 1027.

[307] O.M. Reinaud, K.H. Theopold, J. Am. Chem. Soc. 116 (1994) 6979.

[308] D. Ramprasad, A.G. Gilicinski, T.J. Markley, G.D. Pez, Inorg. Chem. 33 (1994) 2841.

[309] H. Bahron, L.F. Larkworthy, A. Marecaux, D.C. Povey, G.W. Smith, J. Chem. Crystallogr. 24 (1994) 145.

[310] D.E. Moore, G.C. Lisensky, A.B. Ellis, J. Am. Chem. Soc. 116 (1994) 9487.

[311] A. Bottcher, H. Elias, B. Eisenmann, E. Hilms, A. Huber, R. Kniep, C. Rohr, M. Zehnder, M. Neuberger, J. Springborg, Z. Naturforsch., Teil A 49 (1994) 1089.

[312] A. Nishinaga, T. Kuwashige, T. Tsutsui, T. Mashino, K. Maruyama, J. Chem. Soc., Dalton Trans., (1994) 805.

[313] D.E. De Vos, E.J.P. Feijen, R.A. Schoonheydt, P.A. Jacobs, J. Am. Chem. Soc. 116 (1994) 4746.

[314] G.Q. Li, R. Govind, Inorg. Chim. Acta 217 (1994) 135.

[315] H. Nishide, T. Suzuki, H. Kawakami, E. Tsuchida, J. Phys. Chem. 98 (1994) 5084.

[316] B. Steiger, F. Anson, Inorg. Chem. 33 (1994) 5767.

[317] T. Kayatani, Y. Hayashi, M. Suzuki, A. Uehara, Bull.Chem. Soc. Jpn. 67 (1994) 2980.

[318] M. Maeder, H.R. Mäcke, Inorg. Chem. 33 (1994) 3135.

[319] A.E. Martell, R.J. Motekaitis, D. Rockcliffe, R. Menif, P.M. Ngwenya, Pure Appl. Chem. 66 (1994) 859.

[320] R.J. Motekaitis, A.E. Martell, Inorg. Chem. 33 (1994) 1032.

[321] D.H. Busch, P.J. Jackson, M. Kojima, P. Chmielewski, N. Matsumoto, J.C. Stevens, W. Wu, D. Nosco, N. Herron, N. Ye, P.R. Warburton, M. Masarwa, N.A. Stephenson, G. Christoph, N.W. Alcock, Inorg. Chem. 33 (1994) 910.

[322] E.V. Rybakakimova, D.H. Busch, M. Masarwa, R. Warburton, Abstr. Papers Am. Chem. Soc., 208 (1994) 613-INOR.

[323] M. Zhang, R. van Eldik, J.H. Espenson, A. Bakac, Inorg. Chem. 33 (1994) 130.

[324] C.X. Zhao, J.A. Ma, B.L. Ha, Acta Chim. Sinica 52 (1994) 199.

[324a] E. Farinasl, N. Baidya, P.K. Mascharak, Inorg. Chem. 33 (1994) 5970.

[325] P. Deming, M. Gangoda, M.C. Ghosh, E.S. Gould, Research on Chem. Intermediates 20 (1994) 595.

[326] P.G. Edwards, P.W. Read, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Dalton Trans., (1994) 971.

[327] S. Daniele, G.A. Mazzocchin, P. Ugo, G. Albertin, S. Antniutti, E. Bordignon, J. Chem. Soc., Dalton Trans., (1994) 695.

[328] H.G.M. Edwards, I.R. Lewis, P.H. Turner, Inorg. Chem. Acta 216 (1994) 191.

[329] Z.A. Siddiqi, V.J. Mathew, Polyhedron 13 (1994) 799.

[330] D.M. Heinekey, A. Liegeois, M. van Roon, J. Am. Chem. Soc. 116 (1994) 8388.

[331] E. Fujita, C. Creutz, Inorg. Chem. 33 (1994) 1729.

[332] Y.H. Tse, P. Janda, A.B.P. Lever, Analytical Chem. 66 (1994) 384.

[333] T.J.R. Weakley, J. Marks, F.G. Finke, Acta Crystallogr., Sect. C 50 (1994) 1690.

[334] G.B. Carpenter, G.S. Clark, A.L. Rieger, P.H. Rieger, D.A. Sweigart, J. Chem. Soc., Dalton Trans., (1994) 2903.

[335] E.M. Scheuring, I. Sagi, M.R. Chance, Biochem. 33 (1994) 6310.

[336] M.S.A. Hamza, J.M. Pratt, J. Chem. Soc., Dalton Trans., (1994) 1373.

[337] M.S.A. Hamza, J.M. Pratt, J. Chem. Soc., Dalton Trans., (1994) 1377.

[338] C. Brink-Shoemaker, D.W.J. Cruickshank, D.C. Hodgkin, M.J. Kamper, Proc. Roy. Soc. London 278 (1964) 1.