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Coordination Chemistry Reviews 237 (2003) 163–181

COORDINATION CHEMISTRY REVIEWS

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Development of the coordination chemistry of vanadium through bis(acetylacetonato)oxovanadium(IV): synthesis, reactivity and structural aspects

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Received 14 June 2002; accepted 11 October 2002

Contents

Abstract

$[VO(acac)_2]$ serves as a good precursor and undergoes ligand exchange reaction where one or both acetylacetonato groups can easily be exchanged with organic ligands having coordinating atoms of different potentialities. Usually oxovanadium(IV) complexes form when $[VO(acac)_2]$ reacts with ligands under anhydrous conditions. Under aerobic conditions most vanadium complexes stabilize in their highest oxidation state (i.e. V). Factors such as nature of ligands, solvents, pH of the reaction and reaction medium etc. have, however, great influence on the stoichiometry and nature of the resulting complexes. The synthesis and structural

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PII: S0010-8545(02)00293-X

characterization of these oxovanadium(V) and dioxovanadium(V) species and their reactivities are considered in this review. Complexes containing phosphorus, and macrocyclic, ligands have also been incorporated. The abstraction of oxygen from $[VO(acac)_2]$ under typical reaction conditions and design of non-oxovanadium complexes have also been demonstrated. Relevant coordination chemistry of oxovanadium(IV) is considered where ever necessary.

Keywords: Application of $[VO(acac)_2]$; Vanadium complexes; Ligand exchange reaction; Coordination chemistry

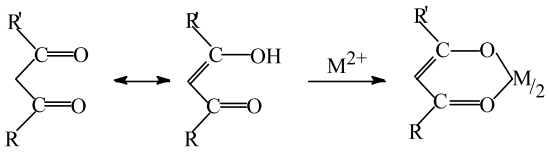
1. Introduction

β-Diketones and related derivatives are considered a class of very important ligands in the growth of coordination chemistry. Their complexes have been thoroughly studied. Due to the presence of two oxygen donor atoms and facile keto–enol tautomerism (**1a** and **1b**, Fig. 1) they easily coordinate with metal ions after deprotonating the enolic hydrogen atom and provide stable metal complexes **2** with six-membered chelate rings.

Water molecules are usually associated with metal β-diketonates when the coordination number of the metal ion is more than four. These water molecules may be exchanged with bases such as ammonia, pyridine, imidazole etc. or other organic ligands to give adducts or may be removed under suitable reaction conditions to give anhydrous metal complexes of interesting structural and chemical properties [1–3].

Due to the weak metal–oxygen bond usually found in metal acetylacetonates, a relatively stronger ligand can replace the acetylacetonato group to give a new type of complex. Replacement of one or both acetylacetonato groups depends upon the ligand to metal acetylacetonates (e.g. $[MO_2(acac)_2]$, M = Mo, W, U) ratio taken, number of donating groups present in the ligand and electronic as well as steric properties of the ligand replacing acetylacetonato group. In this way metal acetylacetonates can act as starting materials to design various types of complexes with varying structural and chemical properties [4].

Vanadium is a trace but essential element with relevant biological properties and has acquired special status among the biometals. Its presence in higher animals and some organisms has been well established. In biomolecules usually oxygen (oxide, hydroxide, water, alcoholate, phenolate, carboxylate, hydroxamate and catecholate), nitrogen (amide and amine) and sulfur (sulfide and thiolate) are present as coordinating atoms. Vanadium interacts with these atoms and forms both anionic and cationic complexes. Vanadium(IV and V) ions experience extensive redox chemistry under physiological (pH 3–7) conditions [5–7]. In aerobic conditions, vanadium(V) is the preferred oxidation state while in intra- as well as extracellular medium both oxidation states exist in equilibrium [8]. Two classes of vanadium containing enzymes have so for been found in nature: vanadate-dependent haloperoxidases and vanadium nitrogenase. Structural and/or functional models for these enzymes have also stimulated the coordination chemistry of vanadium [9–13] and as discussed extensively in this issue of *Coord. Chem. Rev*. A review article by Butler et al. on the catalytic aspects of these complexes further reflects interests on the synthetic vanadium complexes and their possible applications [14].



1(a) (keto form) **1(b)** (enol form) **2** (metal complex)

R = R' = alkyl or aryl group

Fig. 1. Keto (**1a**), enol (**1b**) forms of β-diketone and its metal complex **2**.

Bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$ was first prepared by Rowe and Jones in 1957 [15] and later by Bhattacharjee in 1992 [16]. However, its application to prepare other vanadium complexes began only in the mid 1990s. $[VO(acac)_2]$ serves as a good precursor and undergoes ligand exchange reactions where one or both acetylacetonato groups can easily be exchanged with organic ligands having coordinating atoms of different potentialities. Oxovanadium(IV) complexes usually form if anhydrous condition is maintained. However, under aerobic conditions its reaction with organic ligands may also be manipulated to stabilize vanadium(V) complexes. Vanadium(IV) complexes obtained by this process, usually, contain only one oxygen and stabilize as $[VO]^{2+}$, while the oxidized complexes are associated with one or two oxygen atoms and stabilize with $[VO]^{3+}$, $[VO_2]^{+}$ or $[V_2O_3]^{4+}$ cores. Depending upon the reaction conditions and ligands used, the vanadium(V) complexes may adopt one of the above cores and within the core even they may have different structures. Other precursors such as the vanadate ion are only suitable for water-soluble ligands and thus prevents its use in non-aqueous solvents while $VOSO_4$ can be used in aqueous as well as non-aqueous medium [17–21]. $VO(OEt)_3$–$VO(O^iPr)_3$ requires their in situ generation and use under anhydrous condition in absolute alcohol [22–25].

Recently we have directed our investigations into the coordination chemistry of vanadium in its highest oxidation state. The application of the most suitable starting precursor, $[VO(acac)_2]$ in the development of such coordination chemistry has encouraged us to consider this topic for review. The review mainly deals with the chemistry of oxo-, dioxo-, oxoperoxo- and non oxo-vanadium(V) developed through $[VO(acac)_2]$ along with their reactivity and solution as well as solid state studies. Some interesting vanadium(III and IV) complexes have also been included wherever necessary. Dash has reviewed only the coordination chemistry of vanadium with imidazole or its derivatives and with some multidentate ligands where the synthesis of complexes and their characterization by EPR, NMR spectroscopic and electrochemical techniques were described [26].

The biochemical aspects of these complexes have not been included here as they are presented in other Chapters of this special Volume, and, in addition, several groups have recently reviewed these aspects [9–13,27–29]. Reviews on insulin mimetic properties [5,30,31], metabolism and detoxification under physiological conditions [32,33] and the stability and speciation in biofluids [34] have also been appeared. Works on biological significance of vanadium have also been documented in several books [6,7,10,35–37].

2. Complexes with bidentate ligands

2.1. Complexes with OO/ON donor ligands

Monomeric oxovanadium(IV) complexes of the type $[VOL_2]$ are generally formed when monobasic bidentate ligands (LH) react with $[VO(acac)_2]$ in dry solvents. For example 2-(2′-hydroxyphenyl)benzoxazole (LH) leads to the formation of $[VOL_2]$ [38]. With the sodium salt of 3,5-di-*tert*-butylcatechol (Na_2dtbc) it gave $Na_2[VO(dtbc)_2]$ [39]. Reaction between a methanolic solution of $[VO(acac)_2]$ with H_2dtbc in excess Et_3N gave $(Et_3NH)_2[VO(dtbc)_2]\cdot 2MeOH$ [40]. $[VO(acac)_2]$ also interacts with the sodium salt of saccharides (H_3sacch) viz. D-glucose, D-fructose, D-mannose, D-galactose and D-maltose in methanol to give water soluble oxovanadium(IV) complexes of the type $[VO(sacch)_2]^{2-}$ [41]. Even 2-(salicylideneamine)-1-hydroxyethane (H_2sal-EA), a dibasic tridentate ligand, produced complex $[VO(Hsal\text{-}EA)_2]$ (**3**) (Fig. 2) when the reaction was carried out in 1:2 ($[VO(acac)_2]$ to ligand) molar ratio [42]. The alcoholic group remains free while phenolic oxygen and azomethine nitrogen coordinate to the vanadium.

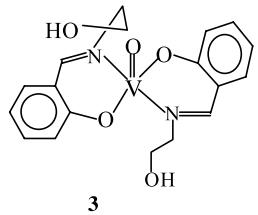


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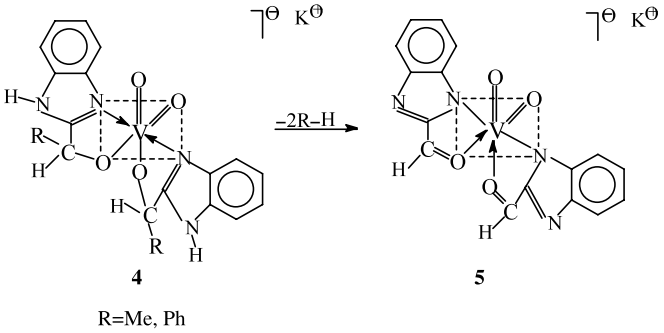
Fig. 2. Structure of $[VO(Hsal\text{-}EA)_2]$.



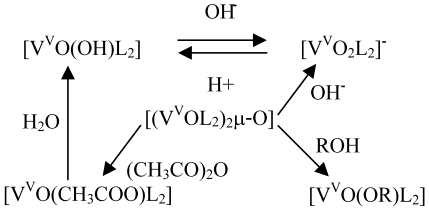
R=Me, Ph

Scheme 1.

Similarly 2(α-hydroxyalkyl/aryl) benzimidazole (LH) gives $[VOL_2]$, which slowly oxidizes to a dioxovanadium(V) species on exposure to air in the presence of KOH. Addition of KOH accelerates the rate of oxidation and stabilizes the dioxovanadium(V) complexes as $K[VO_2L_2]\cdot 2H_2O$ (**4**) [43]. The oxygen of the lattice water is hydrogen bonded with the N–H protons. The dehydrated form, $K[VO_2L_2]$ loses ethyl/phenyl group on heating the complexes as shown by Scheme 1. The loss of the methyl or phenyl group is accompanied by the abstraction of hydrogen from the N–H group of benzimidazole moiety, which ultimately causes several electronic rearrangements to give **5**.

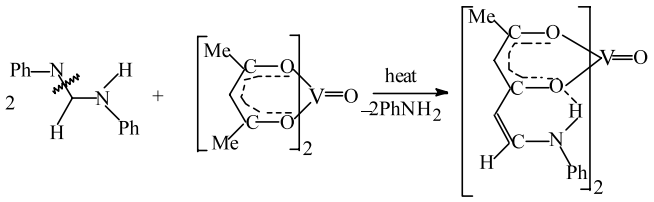
Under aerobic condition $[VO(acac)_2]$ reacts with 8-hydroxyquinoline (LH) in acetone to yield the μ-oxo complex $[(VOL_2)_2\mu\text{-}O]$ [44]. Starting from $[(VOL_2)_2\mu\text{-}O]$ a whole range of complexes have been prepared as summarized in Scheme 2.

The formation of new β-diketonates along with aniline has been reported by the reaction of *N*,*N*′-diphenylformamidine (Hdphf) with $[VO(acac)_2]$ at 150 °C. The substitution of two hydrogen atoms on a coordinated acetylacetonate by new group occurs through the cleavage of C–N bond of the Hdphf as shown in Scheme 3 [45].



LH = 8-hydroxyquinoline

Scheme 2.



Scheme 3.

Reaction of $[Et_4N][HF_2]$ with $[VO(acac)_2]$ in MeCN under nitrogen led to the elimination of one acetylacetonate group and the formation of $[Et_4N][(acac)VOF_2]$ as shown by Eq. (1).

$$[VO(acac)_2] + [Et_4N][HF_2] \xrightarrow[-Hacac]{MeCN} [Et_4N][(acac)VOF_2] \quad (1)$$

$[Et_4N][(acac)VOF_2]$ exhibits an ^{19}F-NMR signal at −124.6 ppm. The geometry around vanadium is best described as trigonal-bipyramidal where one F atom and oxygen of the acetylacetonate are axially bound [46].

2.2. Complexes with OS/SS donor ligands

The reaction between $[VO(acac)_2]$ and the sodium salt of 2-mercaptophenol (H_2mp) in the presence of Ph_4PCl gave $Na(Ph_4P)[VO(mp)_2]$. The coordination geometry around the vanadium is square pyramidal [47]. Similarly the sodium salt of ethane-1,2-dithiol (Na_2edt) in the presence of PPh_4Br or Me_4NCl in ethanol generated deep green solutions from which oxovanadium(IV) complexes $(Ph_4P)Na[VO(edt)_2]$ or $(Me_4N)Na[VO(edt)_2]$, respectively, were isolated [48]. $[Na_4(acac)_2][VO(pdt)_2]$ (pdt^{2-} = propane-1,3-dithiolate) was similarly obtained but without using PPh_4Br or Me_4NCl. The reaction between Na_2pdt and $VOSO_4$ in the presence of Me_4NCl, however, gave $(Me_4N)Na[VO(pdt)_2]$ [49]. The analogous complex $[VS(edt)_2]^{2-}$ with the V=S group can also be prepared with $(Me_3Si)_2S$. The vanadium in $[VO(edt)_2]^{2-}$ (**6** of Fig. 3) is in a square pyramidal geometry with the oxo group at the apex (V–O = 1.625(2) Å) and four sulfur atoms in the base. $[VS(edt)_2]^{2-}$ is isostructural with $[VO(edt)_2]^{2-}$ except for the presence of the apical sulfur (V–S = 2.087(1) Å).

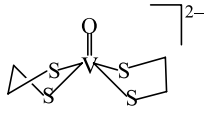


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Fig. 3. Oxovanadium(IV) complex with SS donor ligand.

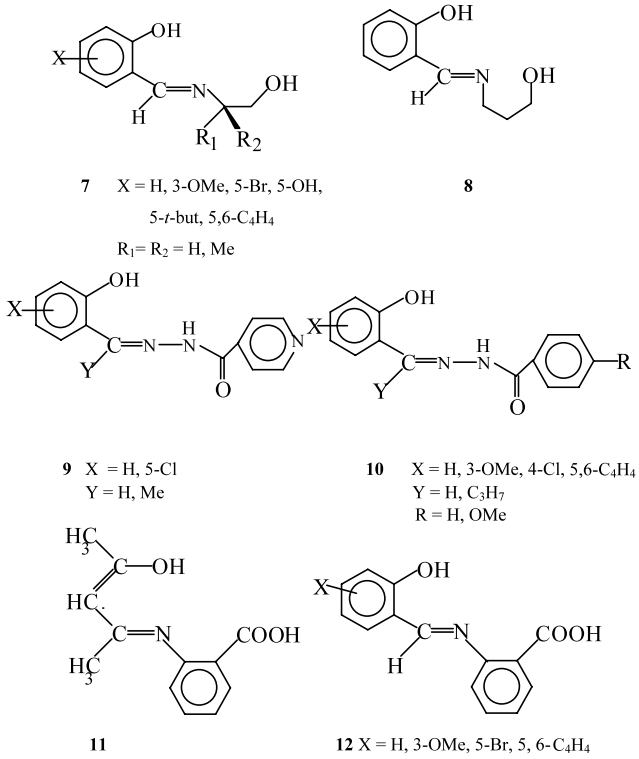
3. Complexes with tridentate ligands

3.1. Complexes with ONO donor ligands

3.1.1. $[VO_2L]^-$, $[VO(OR)L]$, $[VO(OR)(ROH)L]$ and $[(VOL)_2O]$ type complexes

Oxovanadium(IV) complexes are formed with dibasic tridentate ligands such as **7**–**12** of Fig. 4 under anaerobic conditions. They are generally stabilized through dimerization where two [VOL] units are bridged through one of the oxygen atom of each ligand [42,50,51]. An alkoxo bridged structure in complex $[VO(sal\text{-}EA)]_2$ has been confirmed by X-ray single crystal study [42].

On exposure to air, in solvents, most oxovanadium(IV) complexes oxidize to μ-oxovanadium(V), $[(V^{V}OL)_2\mu\text{-}O]$ species [42,51]. However, oxidation of $[VO(acac\text{-}aa)]_2$ ($H_2acac\text{-}aa$ = **11**) in pyridine led to the formation of decavanadate with the pyridinium counter ion, $(PyH)_6[V_{10}O_{28}] \cdot 2H_2O$[50]. Complexes $[(V^{V}OL)_2\mu\text{-}O]$ (LH_2 = **7** with X = H, 5,6-C_4H_4; $R_1 = R_2$ = H and **10** with X = H, 5-OMe; Y = H; R = H, OMe) also seemed to be the oxidation products of oxovanadium(IV) dimers formed in situ as the reaction was carried out in an inert atmosphere and then exposed to air [52–54]. Sometimes when performing reactions in acetonitrile complexes having the $[(VO)_2\mu\text{-}O]^{4+}$ core are formed directly. Fig. 5 presents some complexes having such a core. As shown in structures **13** and **14** alkoxo oxygen



7 X = H, 3-OMe, 5-Br, 5-OH, 5-*t*-but, 5,6-C_4H_4; R_1 = R_2 = H, Me

8

9 X = H, 5-Cl; Y = H, Me

10 X = H, 3-OMe, 4-Cl, 5,6-C_4H_4; Y = H, C_3H_7; R = H, OMe

11

12 X = H, 3-OMe, 5-Br, 5, 6-C_4H_4

Fig. 4. Examples of ONO donor ligands.

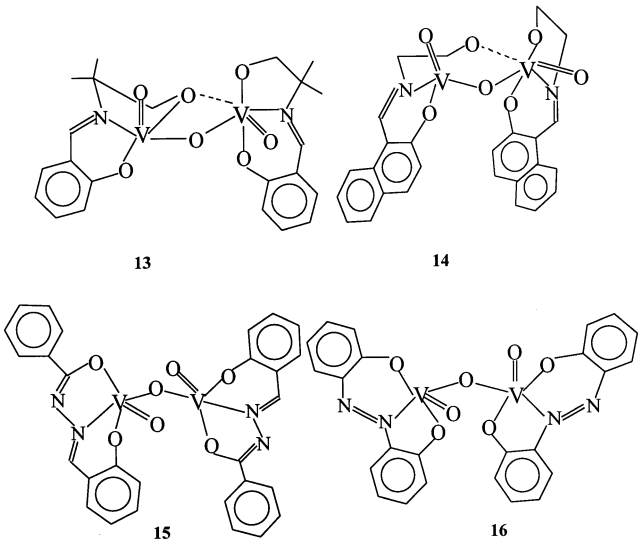
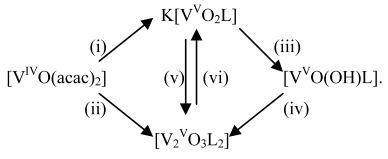


Fig. 5. Structures of $[(V^{V}OL)_2\mu\text{-}O]$ type complexes: **13** [42], **14** [52], **15** [54] and **16** [55].

also interact, though weakly, with other vanadium atoms (e.g. bond length of O···V is 2.404(4) Å in **13** and 2.459 Å in **14**). This is probably due to the presence of a flexible backbone to which the alkoxo oxygen is attached.

In the presence of a suitable base, the formation of $[(V^{V}OL)_2\mu\text{-}O]$ can be prevented and reaction can be tuned towards the formation of $[V^{V}O_2L]^-$ [53,55]. For example, isolated complex $[(V^{V}OL)_2\mu\text{-}O]$ (**16**) prepared from 2,2′-dihydroxyazobenzene (LH_2) can be converted into $K[V^{V}O_2L]$ [55] by the addition of methanolic KOH solution. Dilute HCl converts $[V^{V}O_2L]^-$ back to $[(V^{V}OL)_2\mu\text{-}O]$. Scheme 4 represents the reaction pathway.

Similarly, $[\{VO(X\text{-sal-inh})\}_2\mu\text{-}O]$ (H_2X-sal-inh = **9**; X = H, 5-Cl; Y = H) can also be converted into $K[VO_2(X\text{-sal-inh})]\cdot H_2O$, on treatment with KOH [51]. Recrystallization of $K[VO_2(Cl\text{-sal-inh})]\cdot H_2O$ from methanol slowly yielded [VO(OMe)(MeOH)(Cl-sal-inh)] (**17**) (Fig. 6), whose structure has been confirmed by X-ray study. Reaction in the backward direction is also feasible. For example [VO(OMe)(MeOH)(sal-phala)] (H_2sal-phala = Schiff base derived from salicylaldehyde and L-phenylalanine) can be converted into $[\{VO(sal\text{-}phala)\}_2\mu\text{-}O]$ by stirring a CH_2Cl_2 solution in



Scheme 4. Reaction of 2,2′-dihydroxyazobenzene (LH_2) with [VO(acac)$_2$] under different reaction conditions: (i) 1 mol LH_2 and 2 mol KOH in MeOH (ii) 1 mol LH_2 in MeOH (iii) HCl gas in MeCN (iv) CH_2Cl_2 at room temperature in air (v) 1 mol of HCl or $HClO_4$ in H_2O (vi) 2 mol KOH in MeOH [55].

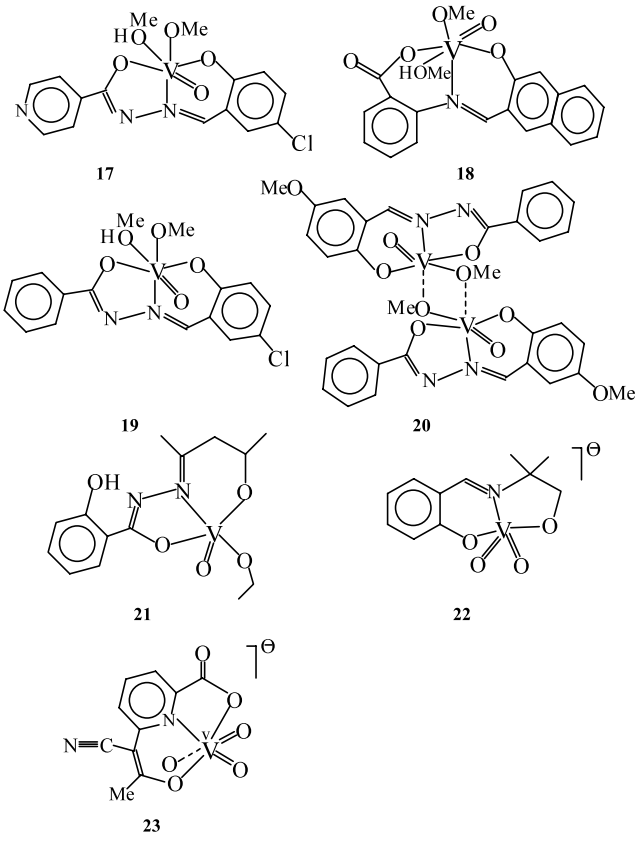


Fig. 6. Oxoalkoxo and dioxo complexes: **17** [51], **18** [50], **19** [58], **20** [58], **21** [60], **22** [61], **23** [62].

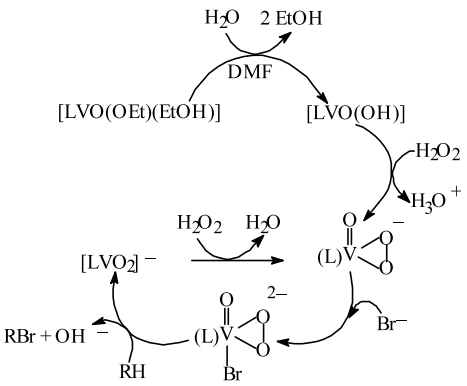
air [56]. Although, $K[VO_2(sal\text{-}bhz)]$ has been prepared from KVO_3, a range of complexes similar to those of $K[VO_2(sal\text{-}inh)]$ are formed. In addition, $K[VO_2(sal\text{-}bhz)]$ can also be converted to the corresponding neutral complex $[VO_2(Hsal\text{-}bhz)]$ by protonation with $HClO_4$ in aqueous solution [57]. Rao et al. reported the formation of [VO(OMe)(MeOH)(hydrox-aa)] (**18**) (where H_2hydrox-aa = **12**, X = 5,6-C_4H_4) by slow oxidation of $[VO(hydrox\text{-}aa)]_2$ in methanol [50]. The ligand H_2Cl-sal-bhz derived from 5-chlorosalicylaldehyde and benzoylhydrazide, also gives a similar type of complex, **19**. However, a dinuclear species $[VO(OMe\text{-}sal\text{-}bhz)(OMe)]_2$ (**20**) was isolated with the Schiff base derived from 5-methoxysalicylaldehyde and benzoylhydrazide where the bridging methoxo oxygen is coordinated at the *trans* position with respect to the oxo group [58]. Similar bridging dinuclear as well as mononuclear complexes of the type [VO(OR)L] (where OR = OMe, OEt, $OCHMe_2$; LH_2 = Schiff bases derived from acetylacetone, benzoylacetone, trifluorobenzoylacetone, trifluorothenoylacetone and *o*-nitrobenzoylhydrazide, *p*-nitrobenzoylhydrazide or *m*-methoxybenzoylhydrazide) have been obtained by the reaction of the appropriate hydrazide and [VO(β-diketonate)$_2$]. The electron attracting substituents favor a monomeric square pyramidal complex while electron donating groups favor the formation of

an alkoxo-bridged dimeric complex [59]. The mononuclear complex [VO(OEt)(acac-shz)] (**21**) can also be prepared by the reaction between [V(acac)$_3$] and salicylhydrazide in ethanol [60].

Complex [VO(OEt)(EtOH)(sal-oap)] (where H_2sal-oap = Schiff base derived from salicylaldehyde and *o*-aminophenol), has not been prepared from [VO(acac)$_2$], though it is similar to oxovanadium(V) complexes **17**, **18** and **19**. This complex catalyzes the oxidation of bromide by H_2O_2 in aqueous DMF solution (Scheme 5). On the basis of ^{51}V-NMR studies, [VO(OEt)(EtOH)(sal-oap)] yields [VO(OH)(sal-oap)] on dissolution in aqueous DMF, which co-ordinates with one equivalent of H_2O_2 forming the monoperoxo, $[VO(O_2)(sal\text{-}oap)]^-$ species and releasing one equivalent of H_3O^+. This peroxo complex then oxidizes bromide along with the formation of dioxo complex [VO$_2$(sal-oap)]. The dioxo species can further coordinate with another equivalent of H_2O_2 and continue the cycle again. A mild acidic condition is essential for performing the catalytic bromination with this catalyst. In the absence of added acid only one turn over was obtained [24].

Acidification of [{VO(sal-inh)}$_2$μ-O] with HCl saturated in methanol led to the formation of [VO(OH)(sal-inh) · H_2O]. This is corroborated by an up field shift of the ^{51}V-NMR resonance from $\delta(^{51}V) = -533$ to $\delta = -544$ for the species formed on acidification. One of the doubly bonded oxo groups of K[VO$_2$(sal-inh) · H_2O] can also be replaced by peroxide to form the unstable oxoperoxovanadium(V) complex. Thus, oxohydroxo and peroxo species, observed as intermediates in haloperoxidases during their catalytic cycles, can also be generated with these complexes. Reaction of [{VO(sal-amp)}$_2$μ-O] (H_2sal-amp = **7**, X = H; $R_1 = R_2$ = Me) with $NaBH_4$ in methanol reduces the azomethine group of one of the Schiff base unit followed by breaking of the dimer to give $[VO_2(sal\text{-}amp)]^-$ (**22**) having the reduced Schiff base as counter cation [61].

Reaction of [VO(acac)$_2$] with monosodium salt of 6-(1-cyano-2-hydroxyprop-1-enyl)pyridine-2-carboxylic acid (NaLH) in absolute methanol is very interesting as, in spite of the inert atmosphere, the reaction gives the dioxovanadium(V) complex, [Na(MeOH)$_2$][VO$_2$L] [62]. A most probable source for oxidation seems to be residual oxygen, though, authors claim it to be disproportionation of the reactants as the reaction was carried out under nitrogen and in absolute oxygen free solvents. The crystal structure analysis of the complex shows an octahedral environment for both the vanadium and sodium ions (structure **23** of Fig. 6). The enolate oxygen, pyridinic nitrogen and carboxylate oxygen atoms are simultaneously coordinated to vanadium, the two doubly bonded oxo groups being *cis* to one another. One of the oxo atoms is weakly associated (bond length 2.214(2) Å) with an adjacent molecule and thus there is a V=O···V interaction leading to the formation of linear polymeric chain. Some of these structures are collected in Fig. 6.

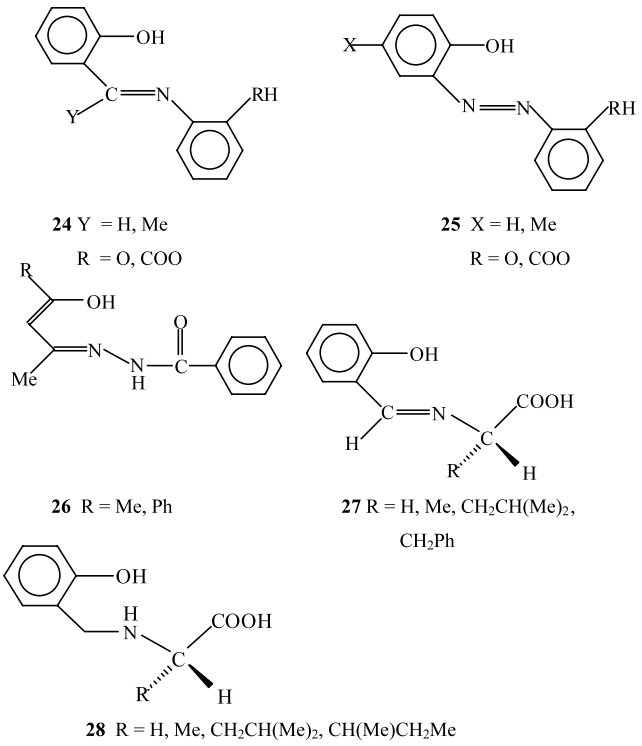


Scheme 5.

3.1.2. *[VOL(ON)] and [VOL(OO)] type complexes*

The oxovanadium(V) complexes of the type [VOL(*ON*)] (where LH_2 = **7** (X = H, $R_1 = R_2 = CH_3$) and **10** of Fig. 4, and **24**–**28** of Fig. 7; *ON*H = monobasic bidentate benzohydroxamic acid or 8-hydroxyquinoline) were prepared under aerobic conditions by the reaction of [VO(acac)$_2$] with a mixture of LH_2 and bidentate ligand [61,63–67].

The isolated complexes are usually dark in appearance and exhibit an intense but relatively broad band at ~500 nm due to ligand-to-metal charge transfer (LMCT) from the filled p_π orbital on the phenolato



24 Y = H, Me; R = O, COO

25 X = H, Me; R = O, COO

26 R = Me, Ph

27 R = H, Me, $CH_2CH(Me)_2$, CH_2Ph

28 R = H, Me, $CH_2CH(Me)_2$, CH(Me)CH_2Me

Fig. 7. Ligands used to prepare [VOL(*ON*/*OO*)] type complexes.

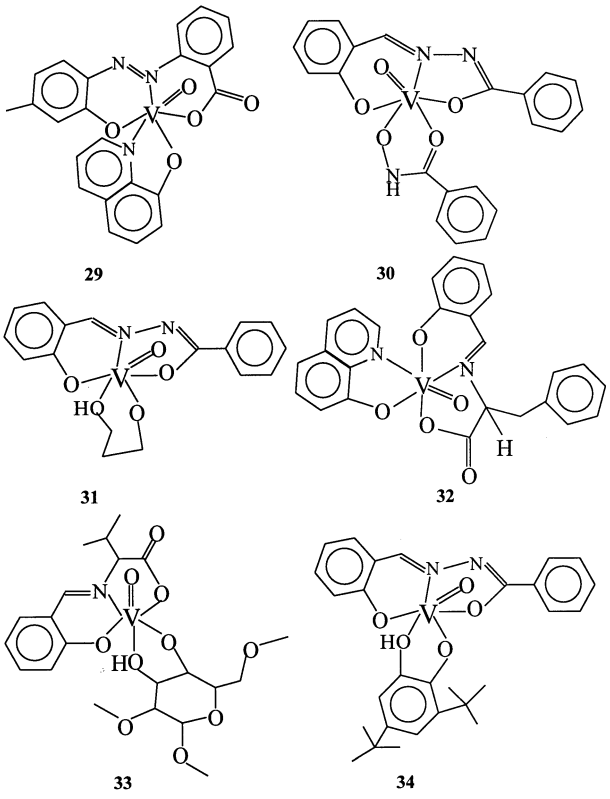


Fig. 8. [VOL(*ON*)/[VOL(*OO*)] type complexes, **29** [63], **30** [65], **31** [67], **32** [73], **33** [74] and **34** [75].

oxygen to the empty 3d orbital of the vanadium. However, in oxovanadium(V) complexes of **28** (i.e. the reduced Schiff base of **27**), this band is resolved into two appearing at ca. 400 and 500 nm. As the co-ligand (i.e. hq^-) in the complexes of **27** and **28** is same, the former band belongs to the ligand **28** while the latter is due to 8-hydroxyquinoline [68].

These complexes uniformly exhibit quasi-reversible cyclic voltammetric behavior (Eq. (2)). The species $[V^{IV}OL(ON)]^-$ can be quantitatively generated in solution via coulometry of $[V^{V}OL(ON)]$ and vice-versa.

$$[V^{V}OL(ON)] + \rightleftharpoons [V^{IV}OL(ON)]^- \quad (2)$$

The direct reaction of $[VO(acac)_2]$ with benzoylhydrazide followed by 8-hydroxyquinoline (Hhq) leads to

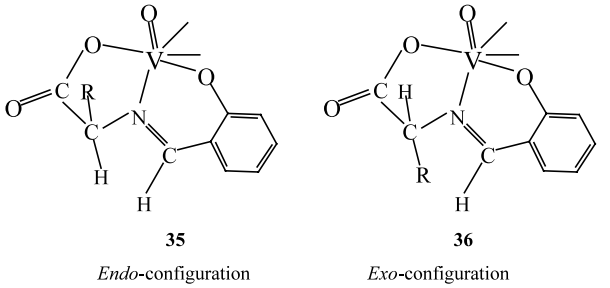


Fig. 9. *Endo* and *exo*-configurations in [VOL(*ON*)] type complexes due to disposition of the V=O and C–R of amino acid group.

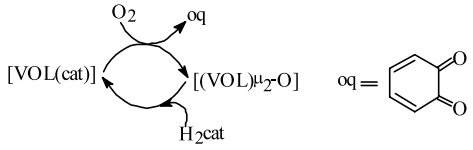
the condensation of benzoylhydrazide with one of the acetylacetonato groups and formation of [VOL(hq)] (where LH_2 = Schiff base derived from acetylacetone and benzoylhydrazide) [69]. Ethane-1,2-diol, propane-1,2-diol, glycerol and methyl-4,6-dimethoxy-α-D-mannopyranoside or related glucosides have been incorporated successfully in place of 8-hydroxyquinoline [70–73]. The geometry around the vanadium is a distorted [VO(*ONO*)(*ON*)]/[VO(*ONO*)(*OO*)] octahedron. Fig. 8 represents some selected complexes (**29**–**34**) of this type.

The tridentate ligand spans meridionally and the axial position *trans* to the oxo group is occupied by one of the atoms of the *ON*/*OO* ligand. This axial position is N in case of hq, carbonyl O in hydroxamate and protonated O in case of diols or sugars. Chakravorty et al. have mentioned the possibility of *exo*/*endo* (**35** and **36** of Fig. 9) due to the relative position of the V=O and C–R group (R = various substituents on the α-C of the amino acid) in complexes with **27** and other co-ligands [74]. However, in most cases only the *endo*-configuration has been observed (cf. structure **32** and **33** of Fig. 8).

Oxovanadium(V) complexes of **10** (X = H, 5-Cl; Y = R = H) in the presence of catechol or substituted catechols are very interesting as the catechols are coordinated in their mono ionized form. The structure **34** (Fig. 8) is the first structurally characterized complex in this series [75]. The [VO(sal-bhz)(*cat*)] (H_2sal-bhz = **10**; X = Y = R = H, Hcat = catechol) displays irreversible catechol oxidation in $MeCN–CH_2Cl_2$ with an anodic peak potential of 0.68 versus SCE. It changes color in $MeCN–CH_2Cl_2$ in the presence of O_2. However, the original color is fully restored upon further addition of catechol. The intermediate complex, $[(VOL)_2\mu\text{-}O]$ and *o*-quinone were isolated from the solution. The whole catalytic cycle for the formation of *o*-quinone through $[(VOL)_2\mu\text{-}O]$ is represented in Scheme 6.

3.2. Complexes with ONS donor ligands

Reaction between $[VO(acac)_2]$ and *S*-methyl-3-({2-hydroxyphenyl}methyl) dithiocarbazate (H_2sal-smdt) in the presence of imidazole/benzimidazole results in the formation of oxovanadium(IV) complexes [VO(sal-smdt)(im)] or [VO(sal-smdt)(bzim)]. In the absence of added imidazole the reaction mixture is oxidized by air in alcohol to give the corresponding oxovanadium(V) complexes [VO(OR)(sal-smdt)] (OR = OMe, OEt,



Scheme 6. Formation of *o*-quinone (oq) during the catalytic cycle between [VO(Hcat)(X-sal-bhz)] and $[\{VO(X\text{-sal-bhz})\}_2\mu\text{-}O]$ [75].

O^{i}Pr). The geometry of [VO(OMe)(sal-smdt)] is best described as a distorted square pyramidal in which the basal plane is defined by O, N, and S atoms of ligand and the O atom of methoxide; the apical position is occupied by the oxo group [76]. Reaction of the similar ligand H_2X-sal-sbdt (H_2X-sal-sbdt = Schiff base derived from salicylaldehyde and *S*-benzyldithiocarbazate, X = H, 5-Cl, 5-Br) with [VO(acac)$_2$] in the presence of KOH directly gives dioxovanadium(V) complexes of the type K[VO_2(X-sal-sbdt)] · H_2O. The presence of the *cis*-VO_2 group has been confirmed in these complexes by single crystal X-ray study (see **37** of Fig. 10) [77]. Water is weakly coordinated with potassium (K–O = 2.675 Å) which in turn is weakly coordinated with the phenolic oxygen and dioxo oxygen atoms (bond lengths 2.809 and 2.770 Å, respectively).

3.3. Complexes with ONN/NNN donor ligands

3.3.1. [VOL(OO)] type complexes

Only one molecule of acetylacetone of [VO(acac)$_2$] undergoes a ligand exchange reaction and the other remains intact with vanadium when monobasic tridentate ligands react with [VO(acac)$_2$] under anhydrous condition. Thus, hydrido tris(3,5-diisopropyl-1-pyrazolyl)borate (LH) and other related ligands react with [VO(acac)$_2$] to give [VO(acac)L] (LH = ligand) [78–80]. Similarly ligands such as Hsal-im, Hacpy-bhz and Hacpy-inh also form complexes of the type [V^{IV}O(acac)L] (LH = ligand) where one acetylacetonato group remains coordinated and Schiff bases behave as a monobasic *ONN* tridentate ligand [81,82]. Even, *N*-salicylidene-*N*′-(2-hydroxyethyl)ethylenediamine (H_2shed) and *N*-(benzimidazole-2-yl-methyl)iminodiethanol (H_2bmide) form [V^{IV}O(acac)(Hshed)] [83] and [V^{IV}O(acac)(Hbmide)] [84], respectively, but the hydroxyl group remains free as confirmed by X-ray single crystal study.

The three-pulse Electron Spin-Echo Envelop Modulation (ESEEM) spectrum of [VO(acac)(sal-im)], recorded at $m_I(^{51}V) = -7/2$, displays two pairs of double-quantum (DQ) lines. The first pair of peaks at 5.0 and 8.1 MHz, are ascribed to the coordination of azomethine nitrogen while other pairs at 5.7 and 8.7 MHz are assigned to the coordination of imidazole nitrogen. Addition of one equivalent of acid to this causes the disappearance of the first set of DQ lines, indicating the breaking of V–N (azomethine) bond [85]. Some structurally characterized complexes (**38**–**41**) of this kind are grouped together in Fig. 11.

Oxovanadium(V) complexes associated with one molecule of acetylacetone have also been isolated with ligand, PhN(CH_2CH_2OH)$_2$. The complex [VO(acac){PhN(CH_2CH_2O)$_2$}] has a tetragonal pyramidal structure, **42** (Fig. 12) with the plane defined by acetylacetone and the two alkoxides, the oxo oxygen being at apex. Vanadium deviates from the plane by 0.331 Å possibly due to a long distance bonding (2.559 Å) interaction of vanadium with the amine nitrogen. This complex has been proposed as the active intermediate in peroxide oxidation of thioether to sulfoxide [52].

Dianionic coordination of catechol, substituted catechols, pyrogallol and even benzohyrdoxamic acids has been reported when monobasic tridentate ligands react with [VO(acac)$_2$] in the presence of these molecules [75,86]. [VO(sal-im)(cat)] can also be prepared from [VO(acac)(sal-im)] (Hsal-im = 4-[2-(salicylideneamino)ethyl]imidazole) [87]. These non-innocent ligands induce strong charge transfer to the metal center. The complex **43** (Fig. 13) containing benzohydroxamic acid exhibits a ^{51}V-NMR signal at 180 ppm relative to $VOCl_3$. [9]. This is somewhat downfield from the normal range of ^{51}V chemical shifts for vanadium complexes containing ON ligand sets. Simple catechol containing complexes [VO(sal-amq)(cat)] (Hsal-amq = Schiff base derived from salicylaldehyde, substituted salicylalde-

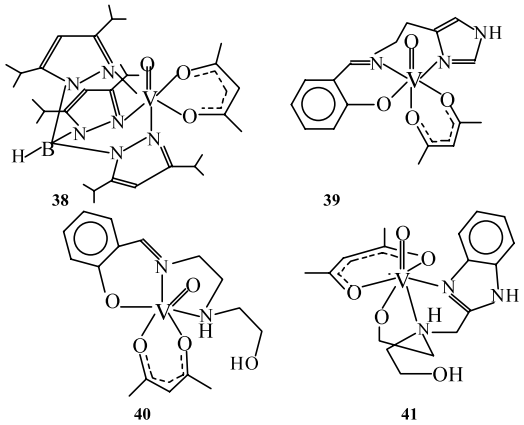


Fig. 11. Structurally characterized [V^{IV}O(acac)L] type complexes: **38** [78], **39** [81], **40** [83], **41** [84].

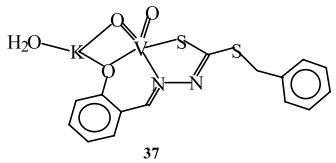


Fig. 10. Dioxovanadium(V) complex, K[VO_2(sal-sbdt)] · H_2O with the *ONS* donor ligand.

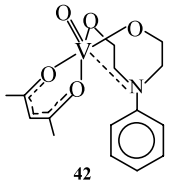


Fig. 12. Example of an oxovanadium(V) complex having one acetylacetonato group coordinated to vanadium.

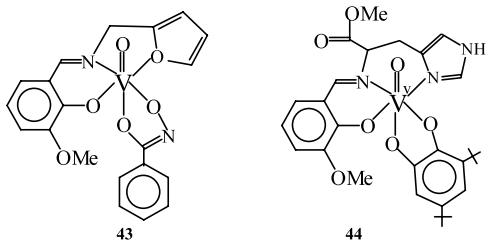


Fig. 13. [VOL(*OO*)] type complexes with monobasic tridentate ligands.

hydes and 8-aminoquinoline) also display only one signal but further downfield of 309–374 ppm while *tert*-butyl catechol and pyrogallol containing complexes display two such signals (in 70:30 ratio) in the 366–487 ppm region. These are possibly due to two orientations of these ligands [86]. Rehder has explained the appearance of such a strong deshielded signal in **44** (Fig. 13) at 591 ppm due to the participation of a semiquinone form in the resonance hybrid which finally leads to vanadium(IV) catechol complex [9]. Addition of water to [VO(sal-amq)(*cat*)] causes decomposition of these complexes to the corresponding dioxovanadium(V) species with the appearance of an additional signal at −535 ppm [86].

3.3.2. $[VO_2L]$, $[VO_2L]_2$ and $[VO(O_2)L]$ type complexes

Aerial oxidation of methanolic solution of $[V^{IV}O$(acac)(Hshed)] yields dimeric dioxovanadium(V) species, $[VO_2$(Hshed)$]_2$ [83]. An X-ray study of $[VO_2$(Hshed)$]_2$ (H_2shed = *N*-salicylidene-*N*′-(2-hydroxyethyl)ethylenediamine), **45** (Fig. 14) shows that one of the dioxo oxygen of each vanadium group weakly interacts with other vanadium where each metal center acquires pseudo-octahedral structure. The complex $[VO_2$(Hshed)$]_2$ can be converted into non-isolable $[VO(OH)(Hshed)]^-$ by the addition of one equivalent of acid per vanadium(V). Excess acid gives $[VO(Hshed)]^{2-}$ as a deep blue non-isolable complex. The reaction of $[VO(acac)_2]$ with *N*-anisoyl-*N*′-(picolinylidene)hydrazine (Hpic-anh) directly produces the dimeric dioxovanadium(V) complex, $[VO_2$(pic-anh)$]_2$ (**46** of Fig. 14) in acetonitrile under aerobic conditions [88] while very similar ligands, *N*-(4-X-benzoyl)-*N*′-(picolinylidene)hydrazine (Hpic-4-X-bhz; X = H, 4-Cl, 4-Me, 4-NMe_2) produce only the monomeric distorted trigonal bipyramidal complexes $[VO_2$(pic-4-X-bhz)](see **47** in Fig. 14) [89,90]. Intermolecular azomethine–H···O (when X = H or 4-Me) or methyl–H···O (when X = NMe_2) interactions, however, result into a two-dimensional network for these complexes.

Aerial oxidation of [VO(acac(acpy-inh)] and [VO(acac)(acpy-bhz)] in methanol yields only mononuclear dioxo complexes $[VO_2$(acpy-inh)] and $[VO_2$(acpy-bhz)] (**48** and **49** of Fig. 14), respectively. Acidification of these complexes affords oxohydroxo complexes. Treatment of [VO(acac)(acpy-bhz)] or [VO(acac)(acpy-inh)] (in methanol) or their dioxovanadium(V) complexes (in DMF) with excess of 30% H_2O_2 give the corresponding oxoperoxo complexes [82]. The coordination geometry around vanadium in these dioxo complexes can best be described as distorted square pyramidal with one of the doubly bonded oxo groups, the enolate oxygen and two nitrogen atoms forming the tetragonal plane. There is substantial distortion towards a trigonal bipyramid, quantified by a τ parameter of 0.37 ($\tau = 0$ for an ideal tetragonal pyramid, $\tau = 1$ for an ideal trigonal bipyramid). In $[VO_2L]$ type complexes there is a distinct tendency towards dimerization to $[VO(\mu\text{-}O)L]_2$ with an octahedral arrangement as has been observed in **45** and **46**.

IR spectroscopic data are also very helpful to identify the presence of V=O, VO_2, $[(VO)_2\mu\text{-}O]$ and $[VO(O_2)]$ groups in vanadium complexes [51,82]. For example, oxovanadium(IV) or oxovanadium(V) complexes having a V=O group exhibit only one sharp band at ca. 950 cm^{-1} due to the ν(V=O) stretch. Two such bands in the 900–970 cm^{-1} region, due to ν_{sym}(O=V=O) and ν_{asym}(O=V=O) stretches, are observed in the dioxovanadium(V) complexes. Complexes with the $[(VO)_2\mu\text{-}O]$ grouping display one sharp band at ca. 950 cm^{-1} due to ν(O=V=O) stretch and a strong but broad band at ca. 750 cm^{-1} due to weakened ν(V=O) stretch as a result of (V···O→V) interaction. The spectra of the peroxo complexes exhibit three IR active vibrational modes, at ca. 550, 700 and 900 cm^{-1} due the symmetric $V(O_2)$ stretch (ν_2), the antisymmetric $V(O_2)$ stretch (ν_3) and the O–O intra-stretching (ν_1) mode, respectively. In addi-

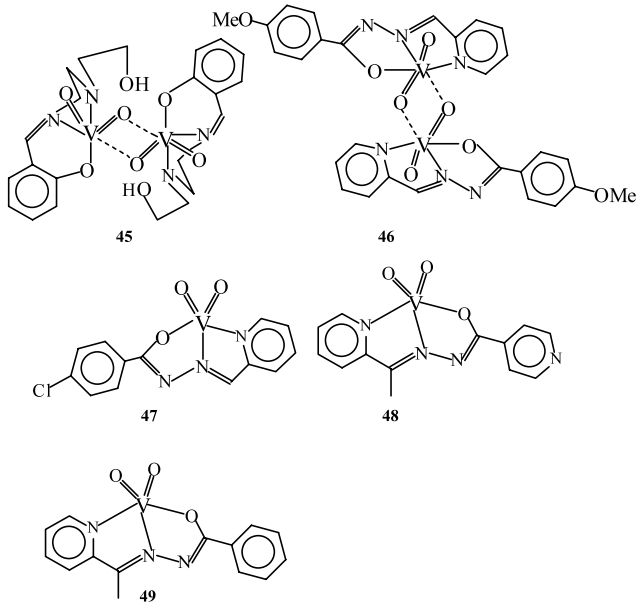
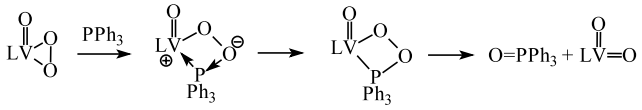


Fig. 14. Examples of dimeric (**45** [83] and **46** [88]) and monomeric (**47** [89], **48** and **49** [82]) complexes having monobasic tridentate ligands.



Scheme 7. Reaction mechanism showing the transfer of oxygen from the peroxo group to PPh_3.

tion, they display the diagnostic ν(V=O) band at ca. 950 cm^{-1}.

The peroxo complexes $[VO(O_2)(acpy\text{-}inh)]$ and $[VO(O_2)(acpy\text{-}bhz)]$ undergo an oxygen transfer reaction with PPh_3 in DMF to give the corresponding dioxovanadium(V) complexes, $[VO_2L]$ (LH = Hacpy-inh or Hacpy-bhz). During the reaction PPh_3 inserts directly into one of the metal–peroxo bonds and then oxygen is transferred from the peroxo group to PPh_3 probably through a reaction mechanism as shown in Scheme 7.

3.4. Complexes with NNS donor ligands

The dioxovanadium(V) complexes $[VO_2L]$ (where LH = monobasic tridentate *NNS* donor Schiff bases derived from acetylpyridine (acpy) and *S*-methyldithiocarbazate (smdt) or *S*-benzyldithiocarbazate (sbdt)) were isolated by reacting ligands with $[VO(acac)_2]$ in the presence of air and KOH in dry methanol. The reaction of Hacpy-smdt with aerated $[VO(acac)_2]$ in wet (few drops of water) methanol yielded the malonate complex [VO(malonate)(acpy-smdt)] (**50** of Fig. 15) [91]. The formation of malonate from acetylacetonate is apparently due to the oxidative removal of methyl groups from acetylacetone activated by coordination, and catalyzed by OH^-, as depicted in Scheme 8.

The geometry of $[VO_2(acpy\text{-}sbdt)$ can be described in terms of a trigonal bipyramid, distorted towards a tetragonal pyramid or in terms of a tetragonal pyramid, distorted towards a trigonal bipyramid ($\tau = 0.47$; str. **51** of Fig. 15). The two alternative views are depicted in Scheme 9. In both views, the distortion comes about by the steric requirements resulting from the small bite angles of the bicyclic structure constituted by the two five-membered chelate rings.

In dry methanol, $[VO(acac)_2]$ reacts with these ligands to give oxovanadium(IV) complexes [VO(acac)L], aerial oxidation of which also give their corresponding dioxovanadium(V) complexes. In the presence of catechol

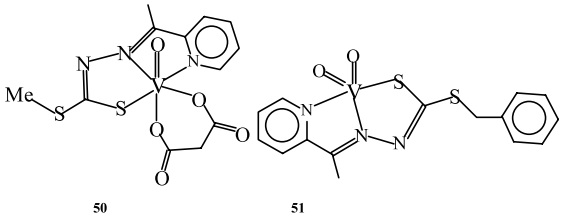
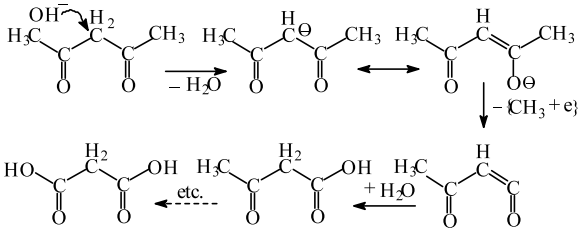
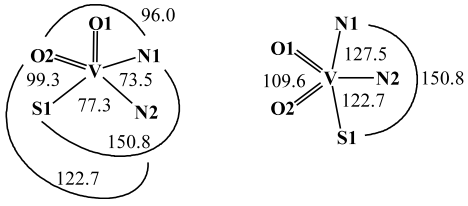


Fig. 15. Structure of [VO(malonate)(acpy-smdt)] (**50**) and $[VO_2(sal\text{-}sbdt)]$ (**51**).



Scheme 8.



Scheme 9.

(H$_2$cat) or benzohydroxamic acid (H$_2$bha) they provide mixed chelate complexes of the type [VOL(cat)] or [VOL(bha)], respectively. Further, [VO(acac)L] or $[VO_2L]$ can be oxidized in the presence of the strong oxidant H_2O_2 to give the corresponding oxoperoxovanadium(V) complexes as shown by Eqs. (3) and (4).

$$2[VO(acac)L] + 3H_2O_2 \rightarrow 2[VO(O_2)L] + 2Hacac + 2H_2O \quad (3)$$

$$[VO_2L] + H_2O \rightarrow [VO(O_2)L] + H_2O \quad (4)$$

Interestingly, acidification of dioxo complexes with HCl dissolved in methanol also afforded oxohydroxo complexes similar to those reported for other dioxo complexes with *ONO* or *ONN* donor ligands.

3.5. Mixed valence complexes

A novel mixed-valence (μ-oxo)divanadium(IV,V) complex, (bzimH)[{VO(sal-smdt)}$_2$μ-O] was reported by Dutta et al. [76]. It was prepared by the reaction between $[V^{V}O(OMe)(sal\text{-}smdt)]$ and $[V^{IV}O(sal\text{-}smdt)(bzim)]$ in acetonitrile. The anionic unit is stabilized by a protonated benzimidazole counter ion as confirmed by X-ray study. Oxygen, nitrogen and sulfur atoms of the ligand, a terminal oxo group and bridging oxygen atom coordinate the vanadium center of each molecule leading to the five-coordination geometry. Chakravorty et al. isolated the tetraethyl ammonium salt of [{VO(sal-L-ala)}$_2$μ-O]$^-$ by reducing [{VO(sal-L-ala)}$_2$μ-O] coulometrically at a constant potential of 0.2 V versus SCE in the presence of salt under an N_2 atmosphere [56]. In the binuclear anion both the vanadium atoms have a distorted square pyramidal geometry of coordination type VO_4N. Similar reduction of [(VOL)$_2$μ-O] (LH_2 = 2,2′-dihydroxyazobenzene) at 0.0 V also leads to the quantitative generation of the one electron reduced complex [(VOL)$_2$μ-O]$^-$ in solution

(Eq. (5)) [55]. Reoxidation at 0.6 V regenerates the original complex.

$$[LOV^{V}\text{–}O\text{–}V^{V}OL] \underset{+c}{\rightleftharpoons} [LOV^{IV}\text{–}O\text{–}V^{V}OL]^{-} \quad (5)$$

4. Complexes with tetradentate ligands

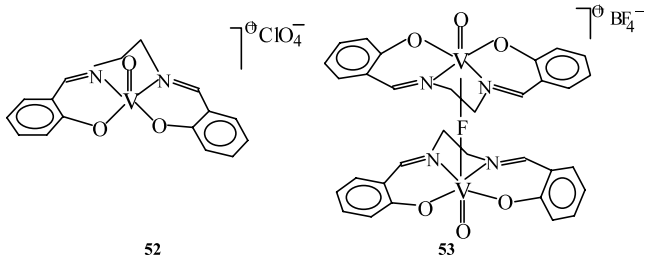
4.1. Complexes with ONNO/OOON/ONNN donor ligands

$[VO(pmida)H_2O]$ was probably the first compound prepared by the reaction of $[VO(acac)_2]$ and a tetradentate ligand, *N*-(2-pyridylmethyl)iminodiacetic acid (H_2pmida) in acetonitrile [92]. This process is applicable to a whole range of tetradentate ligands with slight variations thereof. [VO(salen)] (H_2salen = *N*,*N*′-ethylenebis(salicylideneamine)) and other related complexes have been isolated by this method under anaerobic conditions [93–95]. $[V(acac)_3]$ even reacts with H_2salen in aerobic conditions to give [VO(salen)] [96]. [VO(salen)] and related complexes display a rich coordination chemistry in acidic solution and variety of complexes can be isolated depending on the choice of solvent, the proton source, and the presence or absence of oxygen. For example, controlled addition of $HBF_4 \cdot Et_2O$ to [VO(salen)] in MeCN under N_2 produces oxovanadium(IV) complexes of various nuclearity [97,98] while in air it gives oxovanadium(V) complexes [99] as shown in Scheme 10.

Such complexes with other counter anions have also been reported. Exposing the reaction of $HBF_4 \cdot Et_2O$ with [VO(salen)] (1:1) or other related complexes to air causes the oxidation and formation of fluoro-bridged oxovanadium(V) complexes (e.g. $[\{VO(salen)\}_2\mu\text{-}F](BF_4)$) [99] except [VO(salnptn)] (where H_2salnptn = *N*,*N*′-2,2-dimethyltrimethylenebis(salicylideneimine)) which is reported to give a polymeric solid having a $\cdots V{=}O \rightarrow V{=}O \rightarrow V{=}O \cdots$ chain [100]. An acetonitrile solution of [VO(salen)], in the presence of gaseous HI, gives $[\{V(salen)\}_2\mu\text{-}O]_2[I_3]$ [95]. Perchloric acid, however, oxidizes [VO(salen)] to oxovanadium(V) complex, $[VO(salen)]ClO_4$ [101]. $[VO(salen)]ClO_4$ or $[\{VO(salen)\}_2\mu\text{-}F](BF_4)$ reacts very easily with LiOMe and produces [VO(OMe)(salen)] [100]. The complex [VO(acacen)] (H_2acacen = Schiff base derived from acetylacetone and ethylenediamine) has also been isolated by the reaction of $[VO(acac)_2]$ and the ligand in tetraline [102]. Representative structures of mononuclear oxovanadium(V) and dinuclear oxovanadium(V) complexes are presented in Fig. 16.

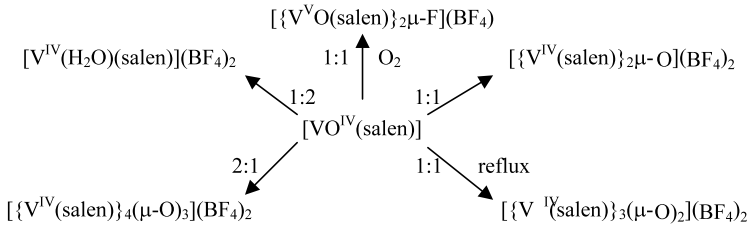
Ligands such as (*S*)-*N*-[1-(2-pyridyl)ethyl]iminodiacetic acid (*S*-H_2peida), *N*-(2-hydroxyethyl)iminodiacetic acid (H_3hida) and *N*-(benzimidazole-2-ylmethyl)iminodiacetic acid (H_2bmida) in methanol–water or only water generate oxovanadium(IV) complexes, [VO(*S*-peida)(H_2O)] [103], [VO(Hhida)] [104] and [VO(bmida)(H_2O)] [84], respectively. H_3hida, though a tribasic ligand, gives only an oxovanadium(IV) complex where the alkoxo oxygen is coordinated in its protonated form. In the presence of excess $LiNO_2$, [VO(*S*-peida)(H_2O)] oxidizes directly to the dioxovanadium(V) complex, Li[VO_2(*S*-peida)] [103]. Similarly [VO(pmida)(H_2O)] (H_2pmida = *N*-(2-pyridylmethyl)iminodiacetic acid) and [VO(ada)(H_2O)] (H_2ada = *N*-(2-amidomethyl)iminodiacetic acid) can be oxidized by KNO_2 in H_2O–MeOH to the corresponding dioxo complexes [105]. [VO(*S*-peida)(H_2O)] can also be converted into oxoperoxo complex Na[$VO(O_2)$(*S*-peida)] on treating it with excess of 30% H_2O_2 followed by adjusting pH to 6 with aqueous NaOH [103]. The structures of [VO(*S*-peida)(H_2O)] and [VO_2(*S*-peida)]$^-$ are very similar except oxygen of water in the former is replaced by oxo group in the latter [106]. Fig. 17 presents structures of some of these complexes confirmed by X-ray crystallography.

The first oxovanadium(IV) complex containing a vanadium–amide bond, reported by Kabanos et al.



52 53

Fig. 16. Mononuclear oxovanadium(V) (**52** [101]) and dinuclear oxovanadium(V) (**53** [99]) complexes of tetradentate ligands.



Scheme 10. Reaction of [VO(salen)] with $HBF_4 \cdot Et_2O$ in various ratios (complex: acid) in MeCN. All reactions are at room temperature under a dry N_2 atmosphere unless mentioned.

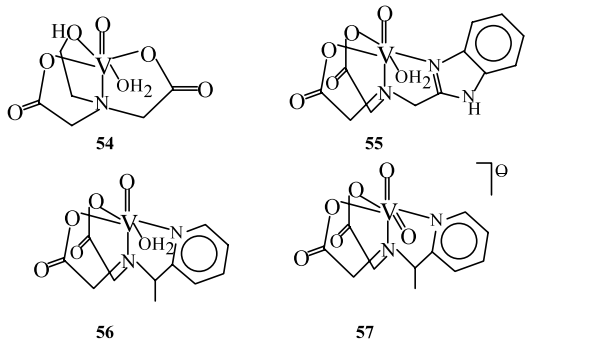


Fig. 17. Structurally characterized oxovanadium(IV) and dioxovanadium(V) complexes with tetradentate ligands: **54** [104], **55** [84], **56** and **57** [106].

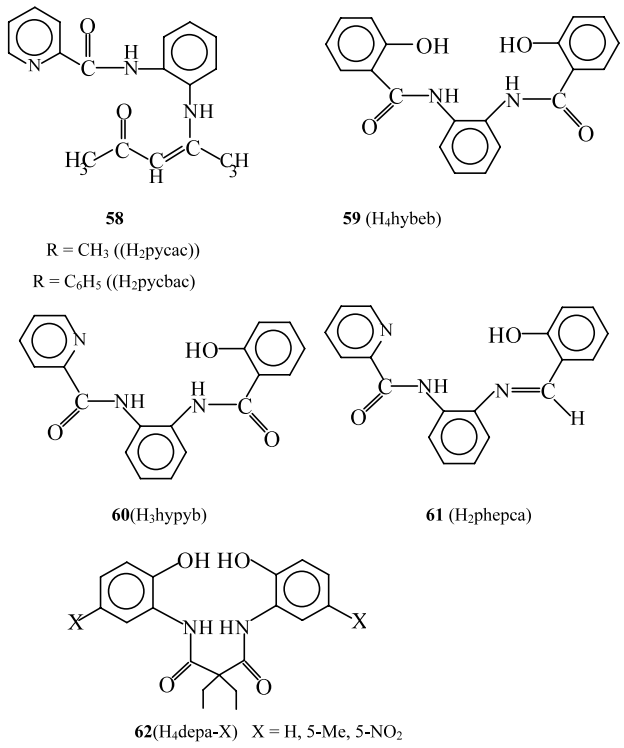


Fig. 18. Amide containing tetradentate ligands.

[107,108], was isolated by reacting **58** (Fig. 18) with $[VO(acac)_2]$. The complex is stable towards aerial oxidation in the solid state but decomposes slowly in solution. The presence of a base, in the reaction of $[VO(acac)_2]$ with ligands **59** (H_4hybeb), **60** (H_3hypyb), **61** (H_2phepca) [109–111] and **62** (H_4depa–X; X = H, 5-Me, 5-NO_2) [112] (Fig. 18), facilitate the deprotonation of the amide nitrogen followed by coordination to vanadium.

Thus, complexes $[VO(hybeb)]^{2-}$, $[VO(hypyb)]^{-}$, [VO(phepca)] [109–111] and $[VO(depa\text{-}X)]^{2-}$ [112] have been isolated where the amide group(s) are deprotonated. A representative reaction can be shown by Eq. (6). $Na_2[VO(hybeb)]$ can be oxidized with silver nitrate to give its vanadium(V) analogue, Na[VO(hybeb)] (Eq. (7)), which can also be isolated as its corresponding tetraethyl ammonium salt by reacting it with Et_4NCl (Eq. (8)). 1,4-Bis(2,3-dihydroxybenzamido)benzene (H_4bhbb) containing catechol moieties behaves similarly and gives $K_2[VO(bhbb)]$ when the reaction was carried out in the presence of four equivalents of KOH [113]. Two other hydroxyl rich ligands 3,5-bis[2-(2,3-dihydroxybenzamido)ethyl]phenol (H_4phencam) 1,3-bis[2-(2,3-dihydroxybenzamido)ethyl]-benzene (H_4bencam) designed by Dewey et al. also gives similar type of complexes $K_2[VO(phencam)]$ and $K_2[VO(bencam)]$, respectively [114]. The structures of these complexes have been confirmed by single crystal X-ray study.

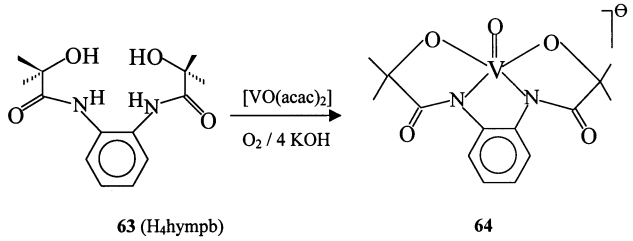
$$[VO(acac)_2] + H_4hybeb + 2NaOH \xrightarrow{MeOH} Na_2[V^{IV}O(hybeb)] + 2Hacac + 2H_2O \quad (6)$$

$$Na_2[V^{IV}O(hybeb)] + AgNO_3 \xrightarrow{MeCN} Na[V^{V}O(hybeb)] + NaNO_3 + Ag \quad (7)$$

$$Na[V^{V}O(hybeb)] + Et_4NCl \xrightarrow{MeCN} Et_4N[V^{V}O(hybeb)] + NaCl \quad (8)$$

A novel oxovanadium(V) complex, **64** of 1,2-bis(2-hydroxy-2-methylpropanamido) benzene (LH_4, **63**) was prepared by the reaction of $[VO(acac)_2]$ and ligand in acetonitrile–methanol in the presence of air and four equivalent of KOH as shown by Scheme 11 [115]. Its $(C_4H_9)_4N^+$ salt was similarly prepared using $(C_4H_9)_4NOH$ in place of KOH [111]. Base again plays an important role in the deprotonation of the amide group in $K[V^{V}OL]$.

The ligand **65** (LH_4) (Fig. 19) readily produces dinuclear oxovanadium(V) complexes of the type $[VOL]_2$ by performing the reaction in air [61,116,117]. Though, one of the CH_2OH groups remains uncoordinated in these complexes, the single crystal X-ray study confirmed a marked structural difference in the dinuclear complexes **66** (where LH_4 = **65** with X = 3-OMe) and **67** (where LH_4 is the reduced form of **65** with X = H) (Fig. 19). In **66**, one of the alkoxo groups of the first ligand is bridged between two vanadium atoms and the other alkoxo group is coordinated to other vanadium and vice versa. In **67** one of the alkoxo groups of the first ligand is bridged similarly as that of **66** but the other group is coordinated to the same vanadium atom. Some of these complexes show reversible redox behavior in the presence of L-ascorbic acid or L-cysteine



Scheme 11.

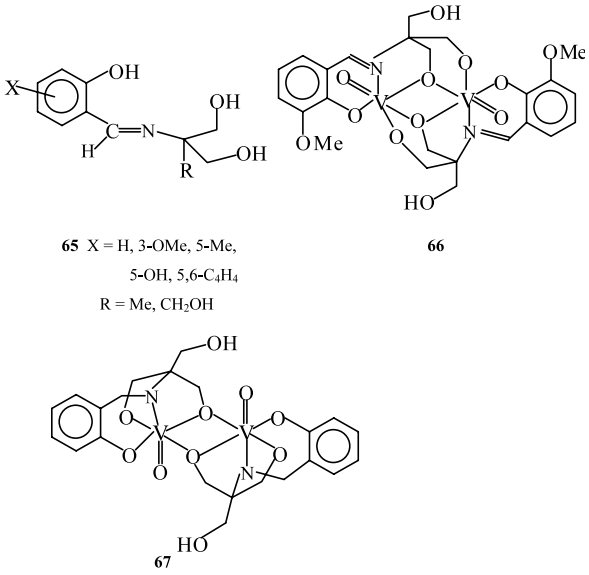


Fig. 19. Tribasic tetradentate ligand (**65**), its oxovanadium(V) complex (**66**) and the oxovanadium(V) complex of the reduced form of **65** (**67**) with no substituent at the salicylaldehyde moiety [61].

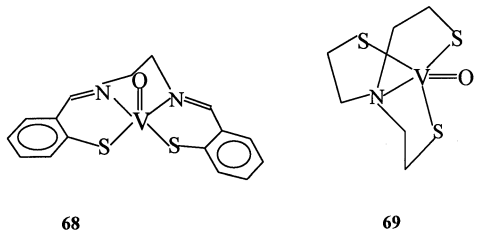


Fig. 20. Structure of [VO(tsalen)], **68** [120] and [VO{N(CH$_2$CH$_2$S)$_3$}], **69** [121].

ethyl ester in air, monitored by electronic and EPR spectroscopy. In the presence of KOH, these ligands provide complexes of the type K[VO$_2$L] which slowly change back to [VOL] in DMF and DMSO. The rate of conversion becomes faster with the addition of HCl solution. Some of these complexes brominate dyes xylene cyanole and phenol red in the presence of $HClO_4$, H_2O_2 and KBr [118] but the rate of bromination varies from complex to complex. The ligands **65** (X = H, Br; R = CH_2OH) and their reduced analogues show an excellent capability in the quantitative separation of the corresponding oxovanadium(V) species in the presence of other metal ions such as MoO_2^{2+}, UO_2^{2+}, Fe(III) and Mn(III) or their mixtures. All these are good for the selective extraction of $[VO]^{3+}$ from a mixture of [VO(acac)$_2$] and [MoO$_2$(acac)$_2$] or [VO(acac)$_2$] and [UO$_2$(acac)$_2$] or even mixture of all these [117,119].

4.2. Complexes with NSSN and NSSS donor ligands

A series of oxovanadium(IV) complexes of SNNS donor ligands derived from 2-mercaptobenzaldehyde (tsal) and ethylenediamine, 1,3-diaminopropane, *o*-phenylenediamine or 4,5-dimethyl-*o*-phenylenediamine have been isolated by displacement of acetylacetonato groups from [VO(acac)$_2$] in ethanol or 2-methoxyethanol. All the complexes display a ν(V=O) band in their IR spectrum at ca. 970 cm^{-1} except [VO(tsaltn)], in which this band is at 840 cm^{-1}, indicative of weak $\cdots$V=O$\cdots$V=O$\cdots$ interactions in the solid state. The structure of a representative complex [VO(tsalen)] has also been solved (see **68** of Fig. 20) and is similar to that of [VO(salen)] [120].

The first oxovanadium(V) thiolate complex, [VO{N(CH$_2$CH$_2$S)$_3$}] was prepared by Nanda et al. by reacting [VO(acac)$_2$] with the thio ligand [121]. The geometry around the vanadium atom is a slightly distorted trigonal bipyramid (**69** of Fig. 20) in which thiolate sulfur atoms occupy the equatorial position. The vanadium atom deviates from the equatorial plane towards the doubly bonded oxygen atom by 0.277 Å.

4.3. Mixed valence complexes

Mixed valence oxovanadium(IV, V) complexes have also been reported. [VO(salen)]ClO_4 on reaction with an equimolar quantity of [VO(salen)] in acetonitrile gives the dimer [(salen)OV^{V}(μ-O)V^{IV}O(salen)]ClO_4 (**70**) (Fig. 21) whose structure has been solved. The corresponding hexafluorophosphate was made similarly while I_3, I_5, I_7 salts were prepared by reacting [VO(salen)] or related complexes with iodine in various molar ratios [122]. In the presence of half a mole equivalent of $NaNO_2$, [VO(*S*-peida)] $\cdot$ H_2O was partially oxidized to give the mixed valence complex Na[(*S*-peida)OV^{IV}(μ-O)V^{V}O(*S*-peida)] in methanol [103].

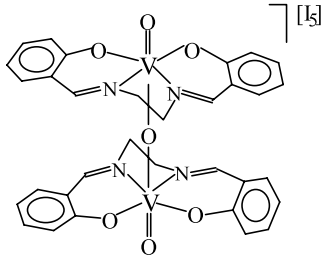
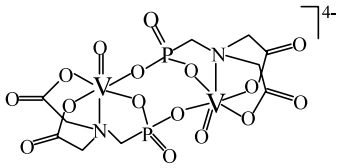


Fig. 21. Example of mixed-valence complex.

5. Complexes with phosphorus containing ligands

N-(2-phosphonomethyl)iminodiacetic acid (H_4pida) is an important precursor of *N*-(2-phosphonomethyl)glycine, an active herbicide, commercially sold as PMG. The vanadium catalyzed oxidation of H_4pida to PMG has been suggested an alternative process over the old one [123]. Oxovanadium(IV) complexes of H_4pida have also been reported. The reaction of



71

Fig. 22. Phosphorus containing complex.

$[VO(acac)_2]$ with H_4pida at pH 5 and saturating the resulting solution with MeOH–EtOH gives blue crystals of the oxovanadium(IV) complex, $Na_2[VO(pida)] \cdot H_2O$ [124]. However, two closely related dinuclear oxovanadium(IV) complexes were isolated in acidic (pH 2 or 4) and slightly basic (pH ~ 8) on keeping the reaction mixture for 24 h at ambient temperature [125]. Although both complexes crystallize out in two different monoclinic systems, they have similar dinuclear frameworks of distorted octahedron where two vanadium centers are linked by two phosphonate groups of two $pida^{4-}$ ligands, bridging through their four oxygen atoms. The structure of one such dinuclear complex, **71**, is presented in Fig. 22. Even when using $NaVO_3$, an oxovanadium(V) starting material, the species isolated is an oxovanadium(IV) complex. However, in aqueous solution, at below pH 2, an oxovanadium(V) complex of 1:1 stoichiometry was characterized by employing multinuclear NMR and visible spectroscopy [126]. It is evident from the studies that the initially formed oxovanadium(V) complex in solution slowly reduces to an oxovanadium(IV) monomer, which on suitably adjusting the pH, crystallized out as dinuclear complex with different hydrates. Spectroscopic studies of the complexes indicate that both complexes again generate an mononuclear oxovanadium(IV) species in solution similar to the one isolated by Saito et al. [124]. It seems that water is simply replaced by another oxygen atom of a coordinated phosphonate group in the dimer.

6. Macrocyclic complexes

A novel macrocyclic ligand, 9,10,21,22-tetrahydroxy - 7,12,19,24 - tetraoxo - 2,3,4,5:8,9,10,11:14,15,16,17: 20,21,22,23-tetrabenzena-1,6,13,18-tetraazacyclotetracosane (LH_4) (**72**) (Fig. 23) containing catachol moieties was designed by Ma et al. to prepare its oxovanadium(IV) complexes [113]. The complex $K_2[VOL]$ was prepared from $[VO(acac)_2]$ in the presence of four equivalent of KOH. One of the K^+ was also substituted by bis(triphenylphosphine)iminium ion (ppn^+). The appearance of ν(V=O) in K(ppn)[VOL] at a relatively low frequency of 949 cm^{-1} was interpreted in terms of a weakened ν(V=O) band due to strong σ and π electron donation of catechol moieties to the antibonding orbital of the ν(V=O) group. As expected, the complex exhibits an intense band at 334 nm due to π–π* transition of the aromatic ring and a d–d band at 464 nm in its electronic spectrum. The ESR spectrum in DMF–CH_2Cl_2 (80:20) displays a typical eight-line pattern of the d^1 vanadium(IV) center due to hyperfine splitting by the ^{51}V nucleus ($I = 7/2$). The signals are centered at $g = 1.973$, with an isotopic hyperfine splitting constant of 81×10^{-4} cm^{-1}. These complexes show a rhombic distortion in a square pyramidal structure due to the bowl-like organization of the ligand around vanadium.

The dinucleating tetraaminodiphenol macrocycle H_2L^1, **73** (Fig. 24) reacts with $[VO(acac)_2]$ to give $[VOL^1] \cdot H_2O$. This complex serves as precursor to design the dinuclear V^{IV}–Ni^{II} complex $[VOL^1Ni(\mu\text{-}SO_4)(H_2O)] \cdot 2H_2O$. The ESR and IR spectra of $[VOL^1] \cdot H_2O$ indicate stacking of the molecules due to $\cdots V{=}O \cdots V{=}O \cdots$ interactions. The sulfate ion in $[VOL^1Ni(\mu\text{-}SO_4)(H_2O)]$ is believed to bridge between V^{IV} and Ni^{II}. The electronic spectrum exhibits bands at 1120, 710, 680, 570, 470 and 350 nm which have been assigned [127,128]. Changing the size of the cavity by an ethylene and propylene bridge between the two sets of amine groups, in the macrocycle H_2L^2, **74** (Fig. 24) caused the formation of a mixture of $[V^{IV}OL^2]$, $[L^2V^{IV}O]$ and $[V^{V}O(OH)L^2]$ (L^2 on right to the V indicates the insertion of V in the cavity having ethylene bridge while L^2 on left to the V indicates the insertion of V in the cavity having propylene bridge). However, these were difficult to separate. This mixture of complexes reacted with $Ni(ClO_4)_2$ giving a wine red solution in methanol from which three compounds of composition $[(V^{IV}O)L^2Ni(H_2O)_2](ClO_4)_2$, $[\{(V^{IV}O)L^2$-

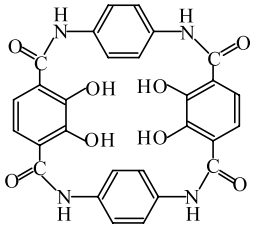


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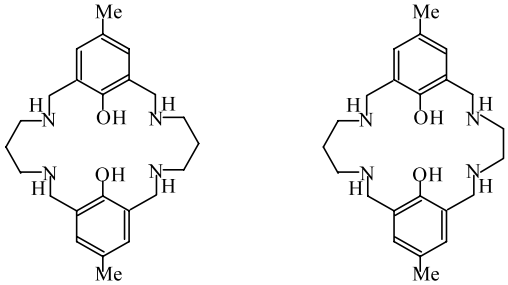
Fig. 23. Catechol containing macrocycle.



73 74

Fig. 24. Dinucleating macrocyclic ligands.

$Ni(H_2O)\}\{(V^VO_2)HL^2)\}](ClO_4)_2$ and $[NiL^2(V^{I-V}O)](ClO_4)_2$ could be isolated by fractional crystallization. Complex $[(V^{IV}O)L^2Ni(H_2O)_2](ClO_4)_2$ also reacts with pyridine to give $[(V^{IV}O)L^2Ni(py)](ClO_4)_2$. All these complexes have been characterized spectroscopically except $[\{(V^{IV}O)L^2Ni(H_2O)\}\{(V^VO_2)HL^2)\}](ClO_4)_2$, whose structure has been solved. The two metal centers in $\{(V^{IV}O)L^2Ni(H_2O)\}^{2+}$ unit are bridged by the two phenolate oxygen atoms of the ligand and have N_2O_2 equatorial planes. While both the metal ions acquire distorted octahedral geometry the vanadium occupies the larger ligand compartment. In the mononuclear $\{(V^VO_2)HL^2)\}$ unit the vanadium atom occupies the smaller ligand compartment, while the empty ligand compartment adopts a folded configuration with one of its amine nitrogen protonated. The coordination environment around vanadium in this unit is octahedral with the vanadium displaced by 0.18 Å towards one of the *cis* oxo-groups from its basal plane N_2O_2 [129].

7. Non-oxo vanadium complexes

7.1. Complexes with OO/ON/NN/ONO/ONNO donor ligands

There are only a few reports dealing with non-oxo (so called 'bare') vanadium complexes prepared from $[VO(acac)_2]$. Displacement of vanadyl oxygen has been demonstrated during the syntheses of tris(catecholate)vanadium(IV) complexes. Addition of mild base (Et_3N) facilitates such a reaction [40]. A mild base Et_3N stabilizes the isolated species as $(Et_3NH)_2[V(cat)_3]$. Strong σ and π donor atoms also facilitate stabilization of such species. $Na_2[VO(dtbc)_2]$ has also been deoxygenated easily with $SOCl_2$ to give $Na_2[VCl_2(dtbc)_2]$ as shown by Eq. (9) [39].

$$Na_2[VO(dtbc)_2 + SOCl_2 \rightarrow Na_2[VCl_2(dtbc)_2] + SO_2 \quad (9)$$

In methanol $Na_2[VCl_2(dtbc)_2]$ slowly oxidizes according to Eq. (10).

$$Na_2[V^{IV}Cl_2(dtbc)_2] + MeOH \rightarrow [V^V(OMe)(dtbc)_2] + 0.5H_2 + 2NaCl \quad (10)$$

A sequential addition of 1,10-phenanthroline (phen) or 2,2′-dipyridine (dipy) to $[VO(acac)_2]$ in CH_2Cl_2 followed by 3,5-di-*tert*-butylcatechol(H_2dtbc) leads to the deoxygenation of $[VO(acac)_2]$ and formation of non-oxo vanadium(IV) complexes as shown by Eq. (11) [130].

$$[V^{IV}O(acac)_2] + L + 2H_2dtbc \rightarrow [V^{IV}(dtbc)_2L] + H_2O + 2Hacac \quad (11)$$

(L = dipy or phen).

Based on the formation of $(Et_3NH)_2[VO(dtbc)_2]$, when $[VO(acac)_2]$ reacts with H_2dtbc in 1:3.5 M ratio in the presence of excess NEt_3, the addition of dipy or phen, probably produces a seven-coordinate $[VO(acac)_2(dipy)/(phen)]$ with weakened V=O bond, which breaks up on subsequent addition of H_2dtbc. The non oxo-vanadium(V), an oxidized form of these complexes can also be obtained easily by treating the corresponding vanadium(IV) complexes with $Ag[SbF_6]$ as shown by Eq. (12).

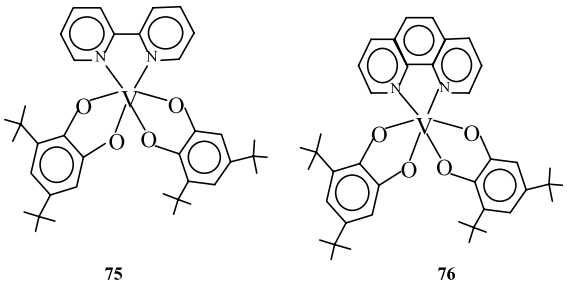
$$[V^{IV}(dtbc)_2L] + Ag[SbF_6] \rightarrow [V^V(dtbc)_2L][SbF_6] + Ag \quad (12)$$

The tetrafluoroborate analogues has been similarly isolated. In the crystal structures of $[V^{IV}(dtbc)_2(dipy)]$ and $[V^V(dtbc)_2(phen)][SbF_6]$, the *tert*-butyl groups of catechol adopt a *syn*-configuration, a sterically demanding isomer, despite their different oxidation states. However, there is a considerable difference in their coordination angles. Because of this, the structure of $[V^{IV}(dtbc)_2(dipy)]$ (**75**) is inclined towards trigonal prismatic geometry while $[V^V(dtbc)_2(phen)][SbF_6]$ (**76**) (Fig. 25) acquires distorted octahedral structure [131].

The reaction of gaseous HCl with [VO(salen)] in a dry solvent yields a dark blue air stable vanadium(IV) complex, $[VCl_2(salen)]$ [101,132]. It is believed to proceed through Eq. (13).

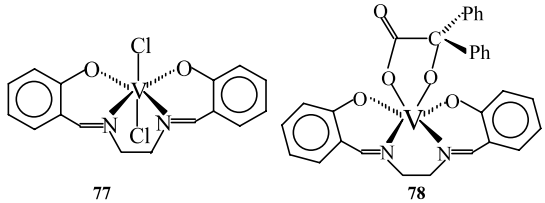
$$[VO(salen)] \xrightarrow{2H^+} [V(OH_2)(salen)]^{2+} \xrightarrow{2Cl^-} [VCl_2(salen)] + H_2O \quad (13)$$

Alternatively $SOCl_2$ or PCl_5 in a suitable solvent can effect the deoxygenation followed by chlorination [52,133]. For example $[VCl_2(salen)]$ (**77** of Fig. 26), $[VCl_2(3\text{-MeOsal-cyclohexen})]$ (cyclohexen = cyclohexane-1,2-diamine) and $[VCl_2(3\text{-MeOsal-}S,S\text{-dpen})]$ (S,S-dpen = (1S,2S)-1,2-diphenyl-1,2-diaminoethane) can be obtained by the reaction of $SOCl_2$ with the respective oxovanadium(IV) complexes [52,134,135]. The dichloro complexes $[VCl_2(salen)]$ and $[VCl_2(3\text{-MeOsal-}S,S\text{-dpen})]$ yield [V(salen)(benzilate)] (**78** of Fig. 26) and [V(3-MeOsal-S,S-dpen)(benzilate)], respec-



75 **76**

Fig. 25. Structure of non-oxovanadium complexes: **75** [130], **76** [131].



77 **78**

Fig. 26. Non-oxovanadium(IV) complexes with tetradentate ligands.

tively, via salt metathesis with lithium benzilate [134,135]. These complexes represent structural models for the homocitrate binding at the vanadium site in vanadium-nitrogenase. Similarly, reaction of [VO(sal-*N*-Bu)$_2$] (Hsal-*N*-Bu = bis[*N*-*n*-butyl(salicylidenimine)], a bidentate ligand) with SO_2Cl_2 provides [VCl_2(sal-*N*-Bu)$_2$]. The $PPh_3 \cdot Br_2$ is also an effective reagent to obtain [VBr_2(salen)] [136]. The chloro, bromo and iodo complexes can also be obtained by the reaction of [VO(salen)] with Me_3SiX (X = Cl, Br, I) in quantitative yield [93].

7.2. Complexes with OS/SS/ONS/NSSN donor ligands

Reaction of [VO(acac)$_2$] with 2-mercaptophenol (H_2mp) in the presence of triethylamine results in the formation of the non-oxovanadium(IV) complex $(Et_3NH)_2[V(mp)_3]$ [47]. The triethylamine facilitates the protonation of oxo-group as shown by Eq. (14).

$$[VO(acac)_2] + 3mpH_2 + Et_3N \rightarrow (Et_3NH)_2[V(mp)_3] + 2acacH + H_2O \quad (14)$$

The analogous reaction with 2-mercapto-4-methylphenol (H_2mmp) in the presence of triethylamine and bis(triphenylphosphine)iminium ion (ppn^+) yields $(Et_3NH)(ppn)[V(mmp)_3]$ (**79** of Fig. 27) which has been structurally characterized. The coordination geometry around the vanadium is between octahedral and trigonal prismatic [47].

Abstraction of oxygen from $(Ph_4P)Na[VO(edt)_2]$ with excess of $(Me_3Si)_2S$ followed by coordination of $[OSiMe_3]^-$ anion in vanadium(IV) complex $(Ph_4P)[V(O\text{-}SiMe_3)(edt)_2]$ (**80** of Fig. 27) has been reported by Money et al. [49] The anion contains a discrete, five-coordinate, approximately square-pyramidal vanadium(IV) center with V–O = 1.7608(27) Å, mean V–S = 2.322 Å and mean O–V–S = 107.39°. This complex can further be converted into $[VS(edt)_2]^{2-}$ by treatment with one equivalent of $NaSSiMe_3$ in MeCN.

A bis(tridentate) non-oxovanadium(IV) complex [V(tsal-oap)$_2$] (H_2tsal-oap = *N*-(2-hydroxyphenyl)thiosalicylideneimine) has been isolated through abstraction of oxygen from [VO(acac)$_2$] in methanol under a nitrogen atmosphere. The two tridentate ligands provide enough electron density to stabilize the non-oxovanadium(IV) species. The steric hindrance and π-bonding effects provided by the two coplanar chelate rings with the ligands also partly aid in stabilizing this species. The absence of ν(V=O) band in the IR spectrum and the presence of a strong charge transfer band at 532 nm in the visible spectrum are characteristic feature of non-oxovanadium(IV) species [120].

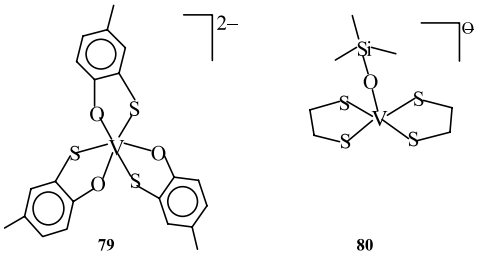


Fig. 27. Non-oxovanadium complexes having OS (**79** [47]) and SS (**80** [49]) donor ligands.

8. Vanadium(III) complexes

Reductive deoxygenation of [VO(acacen)] by $TiCl_3(THF)_3$ afforded the vanadium(III) complex, [V(acacen)Cl(THF)] (Eq. (15)) when reaction was carried out in refluxing THF [102].

$$[VO(acacen)] + TiCl_3(THF)_3 \rightarrow [V(acacen)Cl(THF)] + TiOCl_2 \quad (15)$$

However, carrying out this reaction at very low temperature gave an intermediate complex, [Cl(acacen)V(μ-O)$TiCl_3(THF)_2$] where [V(acacen)Cl] and [$TiCl_3(THF)_2$] units are bridged through oxygen atom. Consistent with the formulation, this is paramagnetic with a magnetic moment of 1.85 B.M. Exchange of labile THF in [V(acacen)Cl(THF)] by pyridine gave [V(acacen)Cl(py)] while substitution of Cl^- by O, N or S donor ligands such as OPh^-, SPh^- and SCN^- leads to the formation of [VO(acacen)(OPh)(THF)], [V(acacen)(SPh)] and [V(acacen)(SCN)(THF)], respectively, as shown by Eqs. (16) and (17).

$$[V(acacen)Cl(THF)] + py \rightarrow [V(acacen)Cl(py)] + THF \quad (16)$$

$$[V(acacen)Cl(THF)] + L^- \rightarrow [V(acacen)Cl(L)] + Cl^- \quad (17)$$

($L^- = OPh^-$, SPh^- and SCN^-).

The structures of all these complexes including [V(acacen)Cl(THF)] and [Cl(acacen)V(μ-O)$TiCl_3$-$(THF)_2$] have been solved, except [VO(acacen)(SPh)] for which a dimeric structure has been suggested. Some structurally characterized vanadium(III) complexes (**81**–**83**) are presented in Fig. 28.

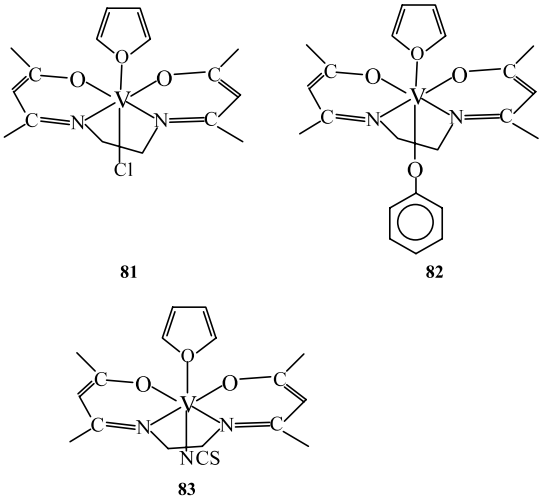


Fig. 28. Structurally characterized vanadium(III) complexes [102].

Organometallic derivatives [R–V(acacen)] (R = Me, Ph, CH_2Ph) have also been prepared according to Eq. (17) (see above) and using Grignard reagents, RMgX. These V–C σ-bond containing complexes have a dimeric structure via the sharing of one of the oxygen atoms of the Schiff base [137].

9. Conclusion

Recent advances in catalytic and medicinal properties of vanadium complexes have stimulated their design and synthesis. The biochemical aspects of vanadium complexes have further promoted the coordination chemistry of vanadium. Several precursors have been tried including $[VO(acac)_2]$ to design these complexes. This review is a comprehensive presentation of the complexes, which were prepared directly or indirectly by the reaction of $[VO(acac)_2]$. Several factors are responsible for the stoichiometry and nature of the resulting complexes. The chemistry reported herein presents a clear picture that this precursor leads to the design of complexes not only of biochemical interest but in all desired areas of vanadium chemistry. Several research groups are involved worldwide in the development of the coordination chemistry of vanadium and their efficacy in various fields. We must wait with eager anticipation for more unexpected discoveries in these fields and see if vanadium chemistry can then compete with other thoroughly studied areas of transition metal chemistry such as copper and manganese.

Acknowledgements

This work was supported by the Council of Scientific and Industrial Research, New Delhi 110 012 (Grant No. 01(1564)/98/EMR-II) and Department of Science and Technology, New Delhi 110 016 (Grant No. SP/S1/F-07/2001). The author is thankful to Professor Dr. Dieter Rehder (Universität Hamburg, Germany) for his keen interest in vanadium chemistry developed in our group. Help received from Shilpa Khurana, in drawing structures of some of the complexes appearing in this review, is gratefully acknowledged.

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