

Chapter 1

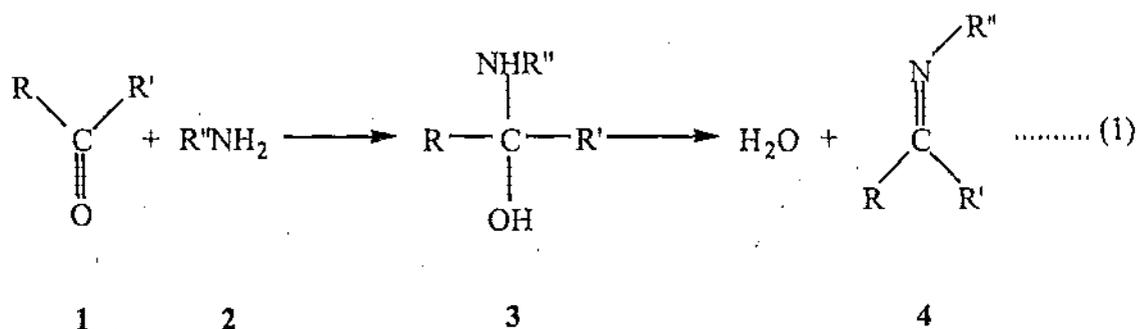
Chapter 1

1. Introduction

Schiff bases still occupy an important position as ligands in metal coordination chemistry even after almost a century since their discovery. Due to the ease of their preparation, diverse properties, medicinal, biochemical and industrial applications, the keen interest in the study of these compounds arose.

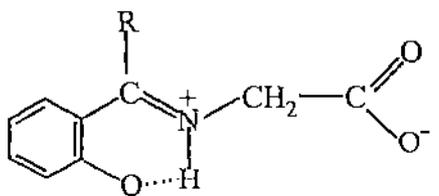
This section describes the silent ground state properties of Schiff bases in general and with amino acids in particular from the point of view of their coordination chemistry rather than its organic chemistry.

The condensation of primary amines with aldehydes and ketone gives products known as imines which contain a C=N double bond. These compounds rapidly decomposes or polymerize unless there is at least an aryl group bonded to the nitrogen or to the carbon atom. The latter imines are called Schiff bases, since their synthesis was first reported by Schiff [1]. The most common method of obtaining a Schiff base **4** is straightforward, as indicated in the condensation reaction (1) between **1** and **2** with the formation of an intermediate hemiaminal **3**.



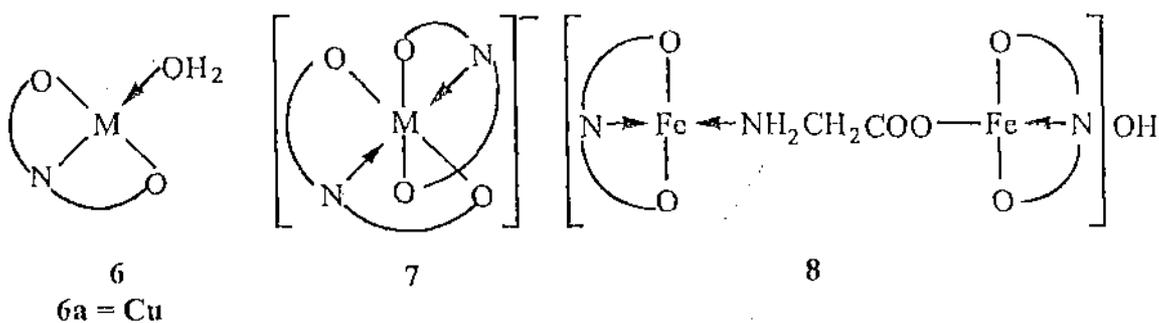
Other methods of synthesis are widely reviewed by Dayagi and Degani [2]. However, it is observed that very few Schiff bases commonly used as ligands have been prepared and characterized in the uncomplexed state, since the corresponding metal complexes have been directly obtained by other procedures.

At this point, we have confined our discussion limited only to the Schiff bases which are derived from aldehydes and ketones with amino acids since they form the subject matter of the thesis. These Schiff bases **5** have been shown to act as tridentate ligand (NO₂ donor sets) through the imine nitrogen, the phenolic oxygen and one of the carboxylate oxygen atoms. However, a relatively small number of free ligands have been

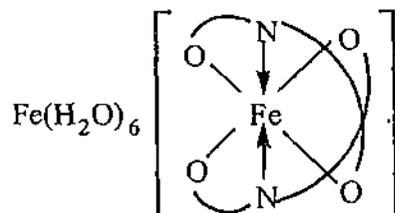


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structurally characterized. It must be recalled that oxygen donor atoms of ligands may often act as a bridge between two metal centres, giving polynuclear or polymeric complexes. The metal complexes of such Schiff bases have been investigated in great detail owing to their apparent usefulness as models for the more complicated metal-pyridoxal-amino acid systems, which are the intermediates in biologically important transamination reactions [3,4]. Salicylaldehyde and amino acid (AA) form Schiff bases which produce complexes with a range of transition metal ions e.g. M(II) (Sal:AA) nH₂O, (**6**) (M(II)=Cu, Co or Ni) and M(I)[M(III)(Sal:AA)₂], (**7**) (M(I)=Na or K; M(III)=Co, Fe or Rh [5-10].

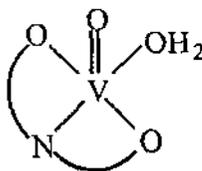


The structure of **6a** has been proved by X-ray crystallography [11] and several such Cu(II) complexes have been prepared involving various amino acids [12]. The structure of **8** is re-investigated by Bowden *et al.* [13] and the new structure **9** has been suggested on the basis of IR, electronic and Mössbauer results.



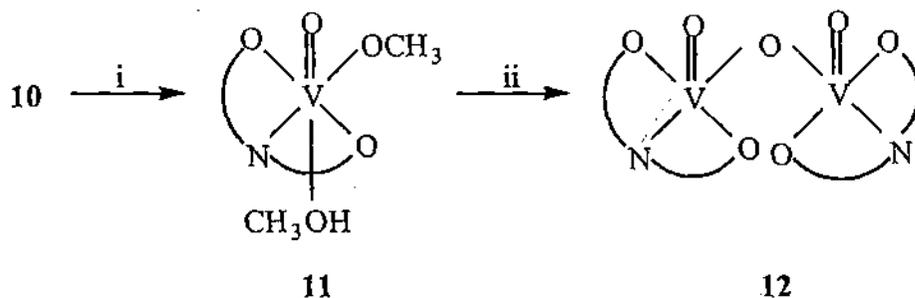
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Theriot *et al.*[14] have reported the preparations and properties of some oxovanadium complexes of composition VO(Sal:AA) (H₂O) **10**. X-ray diffraction study of the *l*-alanine derivative confirmed that the compounds have a square pyramidal geometry with an aqua ligand at the basal site [15]. The coordinated aqua ligand prevents dimerization of the compounds.



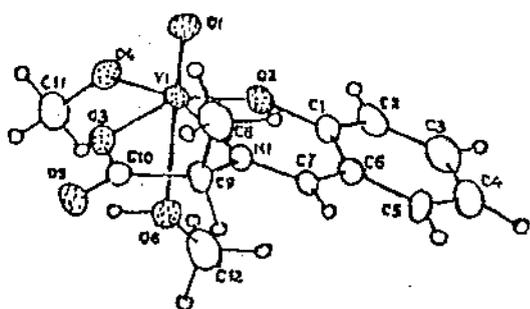
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10 was re-investigated by Gillard and co-workers [16] as a few experiments have lead different conclusions as regards to the oxidation state of the metal. They obtained brown complexes **11** from methanol solutions of the bluish grey complexes **10**. **11** was assigned as monomeric oxovanadium(V) species, the oxidising agent being suggested to be atmospheric oxygen.

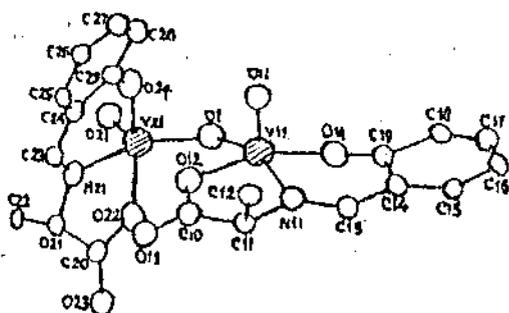


i: CH₃OH; ii: Wet-CH₂Cl₂

The assignments of **11** and **12** were confirmed [17] by the X-ray structures determination on $[V(V)O(Sal:l-Ala)(OCH_3)(CH_3OH)]$ (as **11a**) and $\{V(V)O(Sal:l-Ala)\}_2 \cdot 2CH_2Cl_2$ (as **12a**). In **11**, the tridentate ligand (Sal:l-Ala) and a methoxide ion occupy the basal positions, and form distorted octahedral geometry around the Vanadium(V) ion together with one methanol molecule and the oxide ion of oxovanadium(V). The tetranuclear complex **12** consists of two μ -oxo dinuclear vanadium(V) complexes, and each vanadium(V) ion has a distorted octahedral coordination. The Schiff base coordinates equatorially to each vanadium(V) ion, of which one axial site is occupied by O^{2-} and the other is weakly linked to the carboxylate oxygen atom of a nearby Schiff base. Octahedral coordination on each vanadium(V) is achieved by sharing an equatorial O^{2-} ligand.



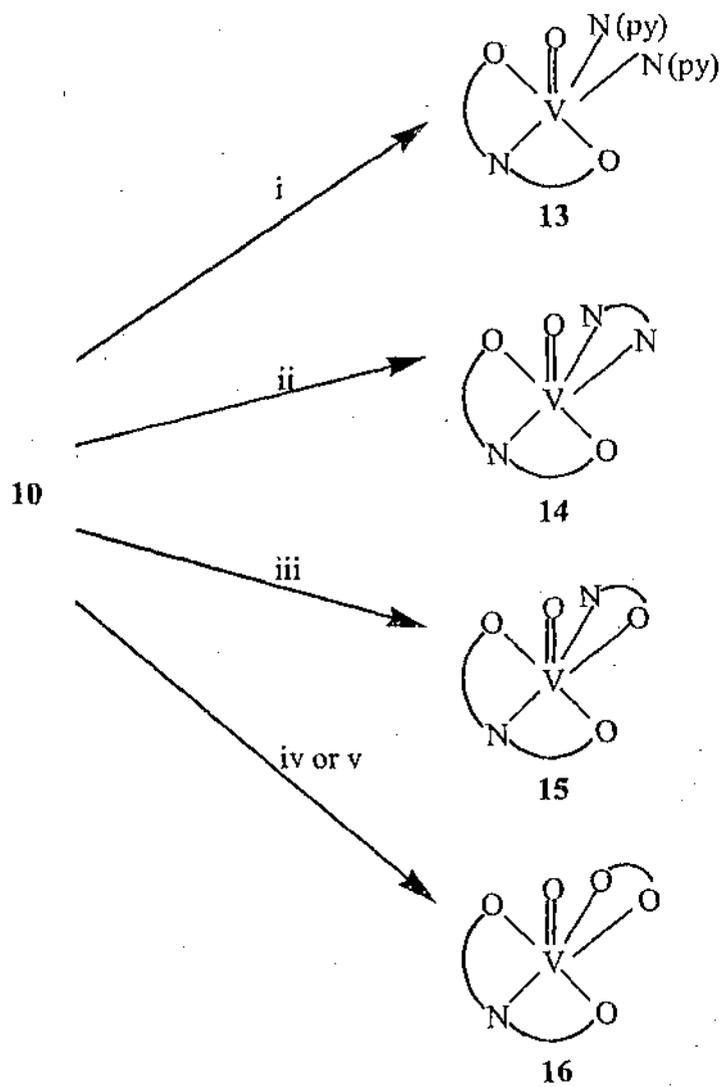
11a



12a

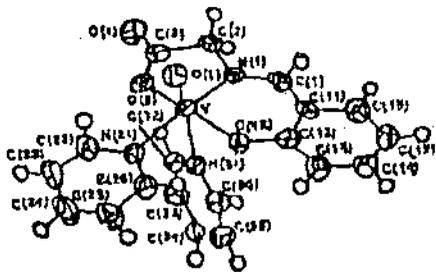
Shortly after the discovery of complexes **11** and **12**, a mixed-valence complex of vanadium-(IV) and -(V), $Na[V_2O_3(Sal:d,l-Ser)_2] \cdot 5H_2O$ has been isolated and characterized by X-ray diffraction [18].

The reactivity of $[V(IV)O(Sal:AA)(H_2O)]$ **10** has been shown towards various mono- and bidentate chelating agents which offer interesting metal complexes of the types **13-16** [19-21]. The X-ray structures of the complexes with specific compositions are also shown for ready reference.

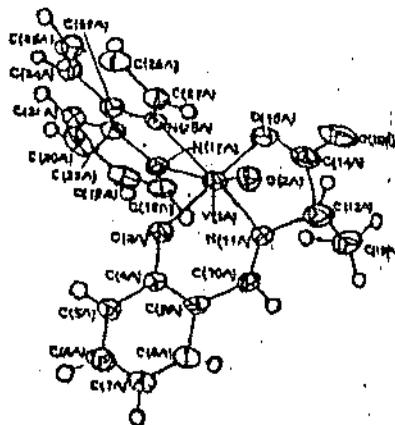


i: pyridine (py); ii: 2,2'-bipyridine (bipy); iii: quinoline-8-ol (Hhquin);

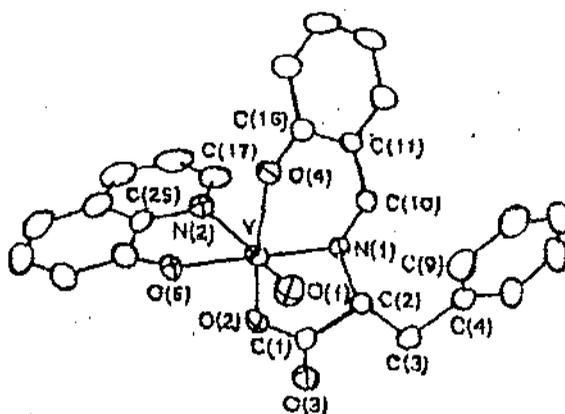
iv: propane-1,3-diol (H₂pd); v: glycerol (H₂pt)



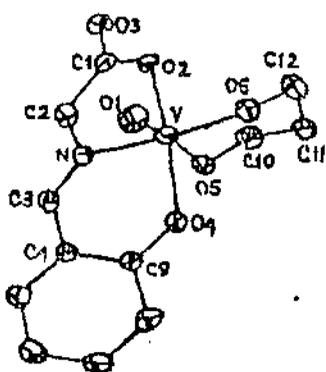
[VO(Sal:Gly)(py)₂] 13



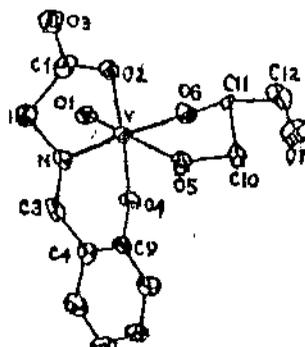
[VO(Sal:-Ala)(bipy)] 14



[VO(Sal:-Phenala)(Hquin)] 15



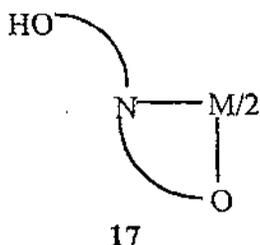
[VO(Sal:Gly)(Hpd)]



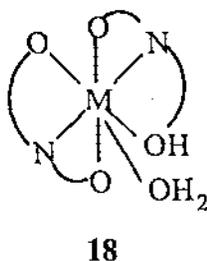
[VO(Sal:Gly)(H₂pt)]

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Recently, Pd(II) and Pt(II) complexes of composition $[Pd(Hap:Gly)_2]$ (Hap=substituted o-hydroxyacetophenone) have been synthesized [22]. The spectroscopic data indicated that the ligands are monobasic bidentate, coordinating through imino nitrogen and the carboxylate group as shown in 17.



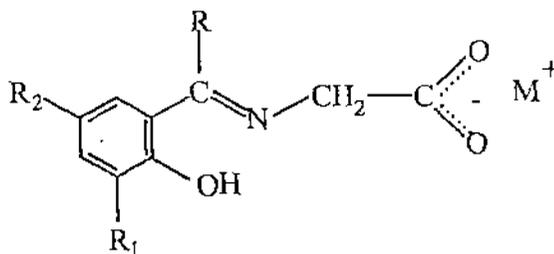
In contrast to the extensive work on transition metals, the investigations on lanthanide elements involving such Schiff base systems are somewhat restricted. Recently, some new complexes of the light lanthanide elements, viz., M=La, Ce, Pr, Nd, Sm and Eu have been reported [23]. The possible structure 18 (in the case of M=Ce, aqua co-ordination is absent) is suggested on the basis of spectroscopic, magnetic moments and thermogravimetric results, however, complete structural information from X-ray crystallography is still awaited.



More recently, two Zn(II) complexes of composition $[Zn(Sal:Ala)(H_2O)]$ and $[Zn(Sal:Val)(H_2O)]$ have been characterized by single crystal X-ray [24] and their structures are found to be analogous to 6.

From foregoing discussion, it is clear that the Schiff bases derived from amino acids offer a variety of interesting possibilities of coordination with metal ions. Compared with the rich transition metal chemistry of such ligands, the chemistry of organotin remain almost unexplored. This has prompted us to initiate a systematic research in this area as a part of our program on organotin(IV) chemistry.

The alkali metal salts of schiff base **19** were chosen as ligand precursors to introduce different ligand skeletons to organotin(IV).



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$R=H, CH_3$; $M=Na$ or K ; R_1 and R_2 = various substituents (refer to Chapter 2.1)

The major purpose of the work is of many fold:

- (i) The first focus aims at comparing systematically the structure of these compounds in the solid state, as assessed by X-ray diffraction, and in the solution state, as assessed by solution ^{119}Sn NMR data. In particular, it is analyzed to which extent varying the organic substituents on the tin atom modulates the solid-state geometry of the organotin carboxylate around the tin atom.
- (ii) The second focus, given that X-ray diffraction structures are available, is to investigate to what extent solid-state ^{119}Sn Mössbauer spectroscopy may serve as reliable indicators of the solid-state structure, whenever X-ray data unavailable.
- (iii) The third focus is to develop dendritic complexes which is of current interest owing to the possibility of obtaining compounds whose structure result in modified and new chemical properties since such complexes have applications as homogeneous catalysts and new materials science.
- (iv) The fourth focus is to investigate the structural consequences of organotin(IV) complexes in relation to their antitumour property.