

## Synthesis and Characterization of Oxovanadium (IV) Complexes and Metal (II) Schiff Base Complexes

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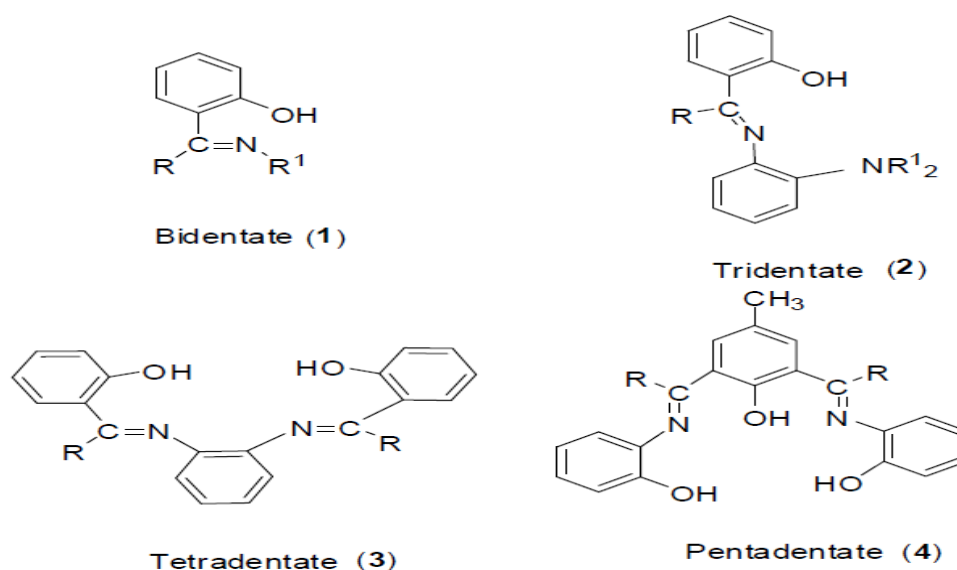
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**Abstract:** Sixteen symmetrical and four unsymmetrical tetradentate Schiff bases with the N2O2 chromophore were isolated in pure form and fully characterized by elemental analyses, melting point, IR. The appearance of two different peaks for each of the azomethine protons and phenolic protons confirm the asymmetry nature of the unsymmetrical Schiff bases. All the Schiff bases were successfully coordinated to oxovanadium (IV) ion to form the corresponding complexes. The unsymmetrical Schiff bases were also successfully coordinated to cobalt (II), nickel (II) and copper (II) ions to form their corresponding complexes. In all thirty-two metal (II) Schiff bases complexes were isolated. These complexes were characterized by elemental analyses, melting point, IR, EPR, cyclic voltammetry, magnetic susceptibility measurements, differential scanning calorimetry and electronic spectra.

**Keywords:** Schiff Bases complexes, Vanadium(IV), Oxovanadium(IV).

### 1. INTRODUCTION

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde/ketone. The resultant compound,  $R_1R_2C=NR_3$ , is called a Schiff base (named after Hugo Schiff), where  $R_1$  is an aryl group,  $R_2$  is a hydrogen atom and  $R_3$  is either an alkyl or aryl group. Schiff bases are generally bidentate (1), tridentate (2), tetradentate (3) or polydentate (4) ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion (Fig. 1.).



**Figure 1.** Some classes of Schiff base ligands

Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [1, 2]. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds. Complexes of Ni(II), Co(II) and Cu(II) with Schiff base ligands derived from

$\beta$ -diketones and *p*-anisidine have been reported [3]. Spectral and magnetic studies on these complexes indicate that they are four coordinate, with square-planar geometry. It has been found that all the complexes are antimicrobially active and show higher activity than the free ligands. Recently, there has been increasing interest in the synthesis and characterization of unsymmetrical Schiff base ligands and their metal complexes. This is due partly to the belief that the systematic investigation of these complexes may shed light on the nature of complexes of biological interest [4]. Unsymmetrical tetradentate Schiff base complexes are required to model the irregular binding of peptides because trace metals have been found to occur in metalloenzymes bound to a macrocycle such as the heme ring, or to donor atoms of peptide chains usually in a distorted environment [5, 6]. Unsymmetrical ligands can clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of metal ion binding sites in metalloproteins and in the development leading to the duplication of enzymatic efficiency and selectivity of natural systems with synthetic materials. A large percentage of enzymes have a metal atom at the active site. These metalloenzymes facilitate a variety of reactions, which include redox reaction (carried out by the oxidases and oxygenases), acid-catalysed hydrolysis (hydrolases) and rearrangement of carbon-carbon bonds (synthases and isomerases) [7, 8].

## 2. EXPERIMENTAL

### 2.1. Materials

All reagents and chemicals purchased from Aldrich-Sigma were of analytical/spectroscopic grade and used without further purification. Chemicals and solvents used for the preparation of Schiff base ligands and metal complexes are: salicylaldehyde, 5-chlorosalicylaldehyde, 5-nitrosalicylaldehyde, 3-ethoxysalicylaldehyde, 5-methoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde, ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 2-hydroxybenzophenone, 1,2-phenylenediamine, oxovanadium (IV) sulphate hydrate, tetrabutylammonium perchlorate, cobalt (II) acetate, nickel (II) acetate, copper (II) acetate, ethanol, methanol, triethylamine, chloroform, dimethylsulphoxide, toluene, and dichloromethane.

### 2.2. Synthesis

#### 2.1.1. Preparation of Unsymmetrical Schiff Bases

Ethanol solutions of 2-hydroxy-1-naphthaldehyde (3.444 g, 20 mmol), 1,2-phenylenediamine (2.163 g, 20 mmol) and salicylaldehyde or substituted salicylaldehyde (20 mmol) in absolute ethanol (75 mL each) were prepared and chilled in the refrigerator at 4°C for 15 min. To a stirred solution of the cold 2-hydroxy-1-naphthaldehyde, cold solution of 1, 2-phenylenediamine was added dropwise followed by the addition of cold solution of salicylaldehyde (or substituted salicylaldehyde) over a period of 2 min. The mixture was kept stirred at room temperature for 4 days, after which the mixture was warmed to, and kept at, 70°C for 20 min with stirring to dissolve any unreacted reactants and to complete the reaction. The product was filtered hot and washed twice with ice cold ethanol. The orange product obtained was purified by digesting in hot ethanol, filtered hot, and dried in a desiccator over silica gel.

#### 2.1.2. Preparation of Symmetrical Schiff Bases

The ligands were prepared according to established procedures [9]. A typical procedure for the synthesis of the symmetrical Schiff base is as follows: To a stirred solution of 0.08 mole of the appropriate 2-hydroxycarbonyl compound (aldehyde and ketone) in 60 mL absolute ethanol was added, drop wise, 0.04 mol of an ethanolic solution of aliphatic or aromatic diamines. This mixture was then stirred for 2 h at 50°C. Afterwards the mixture was cooled to room temperature, or in ice, and the products formed were collected by filtration. The crystals were washed with cold absolute ethanol and re-crystallized from ethanol-chloroform (1:3 v/v) mixture. The yellow crystals were dried in a desiccator over silica gel.

#### 2.1.3. Preparation of Oxovanadium(IV) Complexes

The following general procedure was used in the synthesis of all the oxovanadium(IV) complexes [10]. Oxovanadium(IV) sulphate (6 mmol, 0.978 g) was dissolved in hot absolute methanol (300 mL) and a mixture of triethylamine (12 mmol, 1.214 g) and the corresponding Schiff bases (6 mmol), dissolved in methanol (20 mL), was added with stirring, which resulted in an instant colour change to green/orange. The mixture was stirred for 3 h at 50°C and then concentrated to half of its volume

using a rotary evaporator. The product was filtered and washed twice with cold absolute ethanol and allowed to dry in a desiccator over silica gel.

#### 2.1.4. Preparation of the Cobalt(II), Nickel(II) and Copper(II) Complexes

The various complexes were prepared by addition of 3 mmol of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.53 g),  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.75 g) or  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.60 g) dissolved in hot absolute methanol (60 mL) to a stirring 3 mmol of the respective unsymmetrical Schiff bases in methanol (40 mL). The colour of the mixture changed instantly. The mixture was refluxed for 3 h and the precipitated solids were filtered, washed with cold methanol and allowed to dry in a desiccator over silica gel.

### 2.3. Characterization of the Ligands and Complexes

The ligands were characterized by elemental analysis, infrared and  $^1\text{H}$  NMR while the metal complexes were characterized by elemental analyses, infrared, and electronic spectral, cyclic voltammetry, electron paramagnetic resonance, and room temperature magnetic susceptibility measurements, and differential scanning calorimetry.

#### 2.3.1. Microanalysis

Carbon, hydrogen and nitrogen analysis was done on a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer.

#### 2.3.2. Melting/Decomposition Points

The melting/decomposition points were determined by placing a finely powdered sample in a glass capillary and heating by using Barnstead/electrothermal digital melting point apparatus and are uncorrected.

#### 2.3.3. Infrared Spectroscopy

Infrared spectra were recorded on a spectrophotometer directly on small samples of the compounds in the range  $200\text{--}4000\text{ cm}^{-1}$ .

#### 2.3.4. Electronic Absorption Spectra

Electronic absorption spectra in the UV-Visible region were recorded on a Cary Model 50 spectrophotometer between  $200\text{--}1100\text{ nm}$  in both chloroform and DMSO as solvents.

#### 2.3.5. Electron Paramagnetic Resonance (EPR)

EPR spectra were measured using a EMX Micro Premium X Spectrometer at X-band (9.4 GHz) on the powder and on the fluid and frozen solutions in toluene/dichloromethane (90/10 v/v).

#### 2.3.6. Magnetic Moments

Magnetic susceptibility measurements done in house were made on powdered samples using a Sherwood Scientific magnetic susceptibility balance.  $\text{Hg}[\text{Co}(\text{SCN})_4]$  was used as the calibrant and corrections for diamagnetism were estimated from Pascal's constants.

#### 2.3.7. Cyclic Voltammetry

The cyclic voltammetry on electrochemical detector. Glassy carbon electrode, platinum wire and  $\text{Ag}/\text{Ag}^+$  were used as working, supporting and reference electrodes respectively. Sample solutions were  $10^{-3}\text{ M}$  of each complex in spectroscopic grade DMSO containing  $0.1\text{ M}$  tetrabutylammonium perchlorate as the supporting electrolyte. Each solution was degassed with ultra pure  $\text{N}_2$  gas for 5 min before each measurement was made.

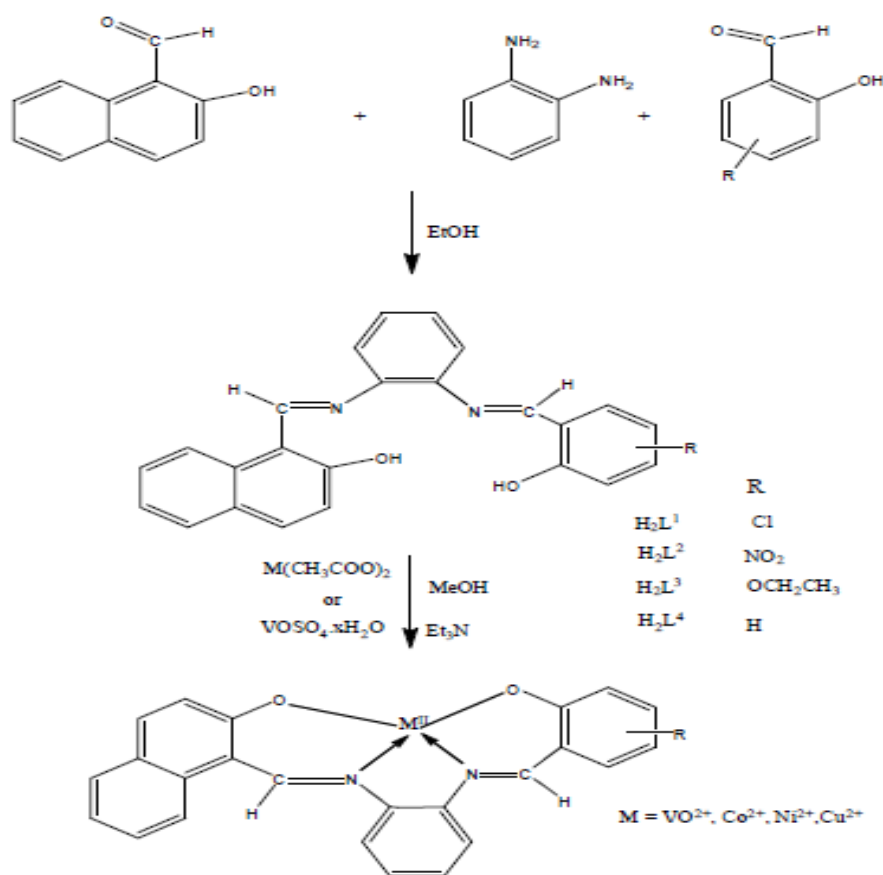
#### 2.3.8. Differential Scanning Calorimetry (DSC)

Thermal analysis was carried on sample and reference pan are in separate furnaces heated by separate heaters. Both the sample and reference are maintained at the same temperature and the difference in thermal power required to maintain them at the same temperature is measured and plotted as a function of temperature or time. The differential heat flow is therefore only due to the heat capacity associated with heating the sample. Small samples ( $5\text{--}10\text{ mg}$ ) were weighed in an aluminium pan and the mass noted. The pan was then covered with its cover, usually slightly smaller. The pans are then crimped close using TA's Blue DSC sample press. The enclosed sample was placed in the furnace

side by side with the crimped closedempty aluminium pan as reference. The instrument is purged with ultra pure  $N_2$  gas at regulated pressure between 100 and 140 kPa gauge (15 and 20 psig). The gasflow rate was set at 50 mL per min. Experiments were run from room temperature to  $500^\circ C$  at scan rates of  $10^\circ C/min$ .

### 3. RESULTS AND DISCUSSION

A series of new structurally novel unsymmetrical Schiff base ligands were prepared by the condensation reaction in a 1:1:1 molar ratio of 2-hydroxy-1-naphthaldehyde, *o*-phenylenediamine, and substituted salicylaldehyde or salicylaldehyde and kept stirring at room temperature for four days. All ligands formed were orange-yellow and melted at  $134-195^\circ C$ . They were also obtained in high yield and in high purity. The procedure for the preparation of the unsymmetrical Schiff bases was developed in laboratory. The sequence of reaction is shown as part of the Scheme presented in Figure 2. The following factors were found to affect the course of the synthesis: (i) the sequence of addition of the reagents, (ii) temperature of the solution of the starting reagents (solution chilled to about  $4^\circ C$ ), (iii) the nature of the diamine (aliphatic or aromatic) used and (iv) the reaction time. A change of amine from *o*-phenylenediamine to 1, 3-diaminopropane led to the formation of symmetrical Schiff base, *N,N'*-bis(2-hydroxy-1-naphthalidene)-1, 3-diaminopropane, following the same procedure. From the above observation, it may be concluded that the resonance stabilization energy, arising from extended conjugation, reinforces the formation of the *o*-phen-bridged Schiff base as against the symmetrical Schiff base formed with the aliphatic diamine. A change in reaction time from four days to just three hours or the use of warm solutions of the starting reagents produced mixed products. From the above observations, it seems that the condensation reactions occurred stepwise.



**Figure 2.** Preparation of the unsymmetrical Schiff bases and their metal (II) complexes.

### 4. CONCLUSIONS

The involvement of azomethine *N* and phenolic *O* of the tertadentate Schiff bases to the metal ions was confirmed by comparing the IR data of the ligands with those of the metal(II) complexes. Further conclusive evidence of the coordination of these Schiff-bases with the metal ions was shown by the appearance of new bands due to  $\nu(M-N)$  and  $\nu(M-O)$  in the metal complexes. The unsymmetrical nature of the unsymmetrical Schiff bases and their metal(II) complexes was confirmed by their IR

spectra where two bands were observed for each of  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{C}-\text{O})$ ,  $\nu(\text{V}-\text{N})$  and  $\nu(\text{V}=\text{O})$ , taking their origin from the different aldehydes contained in each ligand.

Most of the oxovanadium(IV) complexes exhibit a strong band in the range 959–989  $\text{cm}^{-1}$ , which have been assigned to  $\nu(\text{V}=\text{O})$  in a monomeric squarepyramidal environment. The oxovanadium(IV) complexes with trimethylene bridge, in which the  $\nu(\text{V}=\text{O})$  appeared at 848–860  $\text{cm}^{-1}$ , have been assigned polymeric structure with  $\cdots\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots$  interactions, which afforded distorted octahedral coordination geometry. The electronic spectral and magnetic susceptibility measurements were used for assigning the stereochemistry of each metal(II) complexes. For four-coordinate metal(II) complexes, either a square planar or a tetrahedral configuration is possible. On the basis of electronic spectra, together with the magnetic moments, it was possible for us to assign the preferred configuration for the metal(II) complexes reported herein. The electronic spectra indicate a low spin square-planar geometry for all the cobalt(II) complexes. This was also corroborated by the effective magnetic moment of the complexes, which lie in the range of 2.23–2.61 B.M., corresponding to one unpaired electron for low spin square-planar cobalt(II) complexes. The appearance of a single  $d-d$  transition in DMSO is attributed to solvent effect, indicating the possibility of formation of five- or six-coordinate species.

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