Synthesis, spectral, thermal and biological studies of some unsymmetrical Schiff base metal complexes

G.B. Pethe, A.D. Bansod, J.B. Devhade, A.K. Maldhure and A.S. Aswar*
Department of Chemistry, Sant Gadge Baba Amravati University Amravati-444 602, MS, India
aswaranand@gmail.com

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Abstract

Unsymmetrical tetradentate Schiff base derived from Salicylaldehyde, 2-hydroxy-3-methoxy benzaldehyde and ethylenediamine and its complexes with VO(IV), Cr(III), Mn(III), Fe(III) and UO₂(VI) have been prepared. These complexes have been characterized by elemental analysis, IR and electronic spectra, magnetic moments, XRD and thermal analysis. The complexes are colored and stable in air at room temperature. The thermal behavior of metal complexes shows that the hydrated complexes loses water molecules of hydration in the first step; followed by decomposition of ligand molecule in the subsequent steps leaving behind metal oxide as end product. The IR spectra suggest that ligand behaves as bi-negative tetradentate nature with ONNO donor sequence sites of the azomethine nitrogen and phenolic oxygen towards central metal ion. The solid state electrical conductivity of compounds was measured by two probe method over 313-403 K temperature range. Solid state electrical conductivity studies reflect semiconducting behavior of the compounds in the studied temperature range as their conductivity increases with increase in temperature. The powder XRD analysis of VO(IV) complex suggests the triclinic crystal system. The ligand and its complexes were screened for their biological activity against bacteria E. coli, S. abony, S. aureus and B. subtilis by the agar well diffusion method and most of complexes were found to be moderately active against the organisms.

Keywords: Unsymmetrical Schiff base, complexes, D.C. conductivity, TGA, XRD, Biological activity.

Introduction

Tetradentate Schiff bases are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their novel structural features, interesting spectral and magnetic properties, thermal stabilities, biological and industrial importance. Schiff bases provide potential sites for bio-chemically active compounds. Metal complexes make the compounds effective as a stereospecific catalyst towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry. Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carriers. Oxo-vanadium (V) complexes was applied for oxidation of alkenes, aryl alcohols, alcohols and sulfides.

An unsymmetrical complexes are useful in biological process systems as well as in industrial catalysis and it is interesting also from theoretical point of view. Many unsymmetrical tetradeentate bis-Schiff bases of 1,2-diamines with different aldehyde/ketones have been prepared and studied extensively. However much less attention has been focused on unsymmetrical tetradentate Schiff bases derived from 1,2-diamines and different aldehydes. It is worthwhile to mention here that unsymmetrical Schiff bases of this type are difficult to obtain and not easily isolated. A search of literature reveals that no work has been done on the transition metal complexes of the unsymmetrical Schiff bases derived from Salicylaldehyde, 2-hydroxy-3-methoxy benzaldehyde and ethylenediamine, therefore, it was thought of interest to synthesize unsymmetrical Schiff base formed by the condensation of salicylaldehyde, 2-hydroxy-3-methoxy benzaldehyde and ethylenediamine. The solid complexes of VO(IV), Cr(III), Mn(III), Fe(III) and UO₂(VI) with this ligand have been prepared and characterized by different physicochemical methods.

Materials and methods

All the chemicals and solvents were used of analytical grade. Vanadyl sulphate petahydrate, chromium chloride hexahydrate, anhydrous ferric chloride, uranyl nitrate hexahydrate and ethylene diamine were of Rankem and SD’s fine chemicals and use as supplied. Mn(OAc)₂·H₂O was prepared by the oxidation of Mn(OAc)₂·4H₂O using Christensen’s method.

Synthesis of 2-[(2-(2-hydroxyphenyl) methylidene)amino] ethylidimino] methyl]-6-methoxyphenol (H₂L): To a ethanolic solution of salicylaldehyde (2.4 g, 0.016 mol), 2-hydroxy-3-methoxy benzaldehyde (2.72 g, 0.016 mol) in ethanol was added drop wise with continuous stirring. To this mixture ethylene diamine (1.44 g, 0.016 mol) was added dropwise with continuous stirring and reaction mixture was refluxed on a sand bath for about 4 h. The faint yellow coloured compound formed...
was filtered, washed with ethanol, petroleum ether and then dried in vacuum and crystallized from DMF. Yield: 62%, m.p. 314°C.

δ 12.34 (S, 1H, OH, phenolic), 12.26 (S, 1H, OH, phenolic), 3.83 (S, 3H, Ar-OCH3), 3.76 (m, 4H, CH2), 8.25(s, 2H, CH), 7.04-7.22 (m, 7H, aryl-H).

The schematic representation of the synthesis of ligand H2L is shown in Figure-1.

Synthesis of VO(IV), Cr(III), Mn(III), Fe(III), and UO2(VI) complexes: To a hot DMF-EtOH solution (50:50) (25ml) of ligand (1.0 mmol), a hot ethanolic mixture of the appropriate metal salt (1.0 mmol) was added with continuous stirring. The resulting reaction mixture was heated/reflux for 4-5 h. On cooling to room temperature, the solid complexes were filtered, washed thoroughly with ethanol, DMF and Petroleum ether to remove unreacted ligand and metal salts and dried, (Yield: 65-70%).

Physical measurements: Elemental analyses for C, H and N were obtained using Carlo Erba 1108 analyser in micro analytical laboratory, CDRI, Lucknow. IR spectra were recorded on a Bruker alpha IR spectrophotometer. 1H NMR spectrum of ligand was obtained using a Bruker Auaance-II 400 NMR spectrophotometer in a mixed solvent (DMSO+CdCl3) at SAIF Punjab University, Chandigarh. The Electronic spectra of the complexes were recorded on Cary-60 UV spectrophotometer. Magnetic Susceptibility was measured at room temperature by Sherwood magnetic Susceptibility balance (MK-1). The solid state D.C. electrical conductivity of compounds was measured by Zentech Electrometer in the analytical laboratory, CDRI, Lucknow. IR spectra were compared with ligand in order to determine the coordination sites that may involve in complexation. The IR spectrum of the free ligand shows a medium broad band at 2990 cm⁻¹ due to intramolecular hydrogen bonded phenolic ν OH group. The absence of this band in the spectra of complexes indicates the breaking of hydrogen bond and coordination of phenolic oxygen to the metal after deprotonation. It is further supported by a upward shift in ν (C=O) (1258-1278 cm⁻¹) in all spectra of complexes. The IR spectrum of ligand shows a strong band at 3453–3433, 1534–1487, 878–834 and 787–741 assignable to (O-H) , (OCO) modes. A band at 660 cm⁻¹ due to (V=O) vibrations. A band at 1348 cm⁻¹ due to ν (C=NH) stretch. On complexation this band shifted to lower frequency side in all complexes by 4-20 cm⁻¹ indicating participation of azomethine nitrogen in complex formation. Non involvement of amido oxygen in coordination of the acetate group in Mn(III) complexes is confirmed due to difference between the two bands (Δν > 191 cm⁻¹) appeared at 1618 and 1426 cm⁻¹ which are as signable to νasym (OCO) and νsym (OCO) modes. A band at 660 cm⁻¹ due to δ(O-C=O) which is confirmed a diagnostic band for a monodendate ligand. The coordinated water molecule in VO(IV), Cr(III), Fe(III) and Mn(III) complexes are indicated by the appearance of bands at 3453–3433, 1534–1487, 878–834 and 787–741 assignable to γ(O-H), δ(O-H),  pρ (H2O) and  pρw (H2O) modes respectively. The UO2(VI) complex show bands around 956, 978, 956 cm⁻¹ due to νasym (O=U=O) vibrations. The VO(IV) complex show bands at around 982 cm⁻¹ due to ν (V=O) vibrations.

Results and discussion

All the metal complexes are colored solids, non-hygroscopic, air stable and insoluble in common organic solvents but sparingly soluble in DMF and DMSO respectively. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes.

IR spectra: The IR spectra of the complexes have been compared with ligand in order to determine the coordination sites that may involve in complexation. The IR spectrum of the free ligand shows a medium broad band at 2990 cm⁻¹ due to intramolecular hydrogen bonded phenolic ν OH group. The absence of this band in the spectra of complexes indicates the breaking of hydrogen bond and coordination of phenolic oxygen to the metal after deprotonation. It is further supported by a upward shift in ν (C=O) (1258-1278 cm⁻¹) in all spectra of complexes. The IR spectrum of ligand shows a strong band at 3453–3433, 1534–1487, 878–834 and 787–741 assignable to (O-H) , (OCO) and (O-C=O) modes. A band at 660 cm⁻¹ due to (V=O) vibrations. A band at 1348 cm⁻¹ due to ν (C=NH) stretch. On complexation this band shifted to lower frequency side in all complexes by 4-20 cm⁻¹ indicating participation of azomethine nitrogen in complex formation. Non involvement of amido oxygen in coordination of the acetate group in Mn(III) complexes is confirmed due to difference between the two bands (Δν > 191 cm⁻¹) appeared at 1618 and 1426 cm⁻¹ which are as signable to νasym (OCO) and νsym (OCO) modes. A band at 660 cm⁻¹ due to δ(O-C=O) which is confirmed a diagnostic band for a monodendate ligand. The coordinated water molecule in VO(IV), Cr(III), Fe(III) and Mn(III) complexes are indicated by the appearance of bands at 3453–3433, 1534–1487, 878–834 and 787–741 assignable to γ(O-H), δ(O-H), ρ (H2O) and ρw (H2O) modes respectively. The UO2(VI) complex show bands around 956, 978, 956 cm⁻¹ due to νasym (O=U=O) vibrations. The VO(IV) complex show bands at around 982 cm⁻¹ due to ν (V=O) vibrations.

Biological Activity: The ligand and its complexes were tested against the bacterial species E. coli, S. abony, S. aureus and B. subtilis by disc diffusion method. The concentration of compounds was used for testing was 1µg/ml in DMSO and used as control. In a typical procedure a well was made on the agar medium incubated with microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated at 37°C for 24h. During this period the test solution diffused and the growth of microorganisms was affected. The antibacterial activity of compound was evaluated by studying the zone of growth inhibition against test microorganisms. The procedure was performed in separate plates for each microorganism.

Figure-1: Schematic representation of synthesis of Ligand (H2L)
Electronic Spectra: The electronic spectrum of VO(IV) complex shows bands at 922, 521 and 392 nm corresponding to transitions d_{xy}(b_2)→d_{x^2-y^2}(e_g), d_{xy}(b_1)→d_{x^2-y^2}(b_2^*) and d_{xy}(b_2)→d_{x^2-y^2}(a_1^*) respectively towards square pyramidal geometry of complex.\(^\text{18}\) The Cr(III) complex shows absorption at 620, 484 and 290 nm due to \(4A_2g (F)→T_{2g} (F)\), \(4A_2g (F)→T_{1g} (F)\) and \(4A_2g (F)→T_{2g} (P)\) transitions, indicating an octahedral environment around the Cr(III) ion.\(^\text{19}\) The value of various ligand field parameters are found to be \(D_q=1634.5 \text{ cm}^{-1}\), \(\beta= 0.564\) and % covalency= 44.6. The observed B value is considerably lower than that of the free ion value suggesting a considerable amount of covalent character in the metal -ligand bond. The Mn(III) complex exhibits bands at 735, 632, 522 and 364 nm due to \(5B_1→5B_2\), \(5B_1→5A_1\) and \(5B_1→5E\) and LMCT, transitions, corresponding to square pyramidal geometry of complex.\(^\text{20}\) The Fe(III) complex shows bands at 768, 652 and 449 nm due to \(6A_1g→6T_{1g}\), \(6A_1g→6T_{2g}\) and \(6A_1g→6E_g\) transitions respectively in an octahedral field.

Magnetic properties: The VO(IV), Cr(III), Mn(III) and Fe(III) complexes exhibit magnetic moments of 1.53, 3.48, 4.75 and 5.76 B.M respectively and these values are close to the reported data for these complexes.\(^\text{21}\) The UO\(_2\)(VI) complex is found to be diamagnetic as expected from its electronic configuration.

Electrical conductivity measurements: The temperature dependence of the solid state conductivity (\(\sigma\)) of the synthesized ligand and its complexes in their compressed pellet form (5 ton cm\(^{-2}\)) was measured in the temperature range (313–403 K). The electrical conductivity (\(\sigma\)) was found to vary according to the relation \(\sigma = \sigma_0 \exp (-Ea/kT)\). Where: \(\sigma_0\) is a constant, \(Ea\) is the activation energy of electrical conduction, \(T\) is the absolute temperature and \(k\) is Boltzmann constant. The values of electrical conductivity of the ligand and its complexes increases with increases temperature and plots of log\(\sigma\) vs 1/T are found to be linear over studied temperature range indicating their semiconducting nature.\(^\text{23, 24}\) The value of electrical conductance lies in the range 4.56 x 10\(^{-11}\) to 6.67 x 10\(^{-3}\) ohm\(^{-1}\).

Thermogravimetric study: Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies to know the presence of water molecules in these complexes as well as to know their decomposition pattern. The Cr(III), Mn(III) and Fe(III) complexes show three stage decomposition pattern whereas VO(IV) and UO\(_2\)(VI) complexes indicate two stage decomposition patterns. The VO(IV), Cr(III) Mn(III) and Fe(III) complexes show elimination of one lattice water molecule in the temperature range 80-125°C. The Cr(III) and Fe(III) complexes exhibits loss of one water molecule takes place between 140-225°C which indicates the presence of this water as coordinated water molecule in the complexes [% wt. loss, obs./calcd. VO(IV): 3.92/3.58; Cr(III): 3.96/3.62; Mn(III): 3.39/3.56; Fe(III): 3.87/3.59 for lattice water and Cr(III): 3.78/3.62; Mn(III): 3.36/3.46; Fe(III): 3.91/3.59]. In the TG curve of UO\(_2\)(VI) complex, there is no weight loss upto 160°C and this rules out the presence of any water molecule in the complex. After the loss of water molecule, a continuous and rapid weight loss has been observed above 250°C which may be due to the thermal degradation of free part of the ligand along with some other side chain present in the complexes. A gradual weight loss observed above ~420°C due to the degradation of actual coordination part of the ligand and TG curves attain a horizontal level above 650°C suggesting the formation of final decomposition product as respective stable metal oxides [% residue, obs./calcd. VO\(_2\)= 20.85/20.69; CrO\(_2\)= 15.68/15.31; MnO\(_2\)= 14.24/13.25; FeO\(_2\)= 16.25/15.99; and U\(_2\)O\(_3\)=43.98/43.66]. The half decomposition temperature of the compounds decreases in the order: \(\text{UO}_2(\text{VI}) > \text{Mn(III)} > \text{Cr (III)} > \text{Fe (III)} > \text{VO (IV)} > \text{H}_2\text{L}\). The metal oxide has been inferred to be the final product by aerial oxidation of the complexes.

Powder XRD study: The X-ray diffractogram of VO(IV) complex has been recorded as representative system (Figure-2). The complex shows sharp crystalline peaks indicating its crystalline phase. The X-ray diffraction patterns of the complex with respect to their prominent peaks have been indexed by using appropriate methodology and use of computer program (Powd Mult, Version 2.3). The above index method also yielded miller indices (h,k,l) values, unit cell parameters and volume of unit cell. The indexing is confirmed on the basis of correction obtained between observed and calculated values. The unit cell lattice parameter of VO(IV) complex are \(a = 18.3604\text{Å}, b = 12.063\text{Å}, c = 8.7769\text{Å}, \alpha = 98.342^\circ, \beta = 110.203^\circ, \gamma = 94.858^\circ\). Volume (\(V\)) = 1041.82 Å\(^3\) belongs to Triclinic system.

Biological Activity: The Schiff base and its complexes were screened for their antibacterial study against \(E.\ coli, S.\ abony, S.\ aureus\) and \(B.\ subtilis\) by disc diffusion method.\(^\text{25}\) The results for antibacterial study are interpreted by measuring the zones of inhibition of growth of the bacterial culture. The results show that ligand \(\text{H}_2\text{L}\) and VO(IV), Cr(III), Mn(III), Fe(III) complexes show bacteriostatic behavior towards all the bacterial strains. The VO(IV), Cr(III), Mn(III) and UO\(_2\)(VI) complexes exhibit moderate bactericidal activity against all the microbes. This may be due to the less permeation to the cells and tissues. Fe(III) complex shows good activity against \(E.\ coli\) and \(S.\ aureus\), whereas moderate activity against the \(S.\ abony\) and \(B.\ subtilis\). In general the results reveal that, the activity of the ligand was found to be enhanced on complexation with metal ions. It has been often observed that the metal complexes show enhanced antibacterial activity as compared to the free ligand against the same microorganism under identical experimental conditions, this is due to complexation.\(^\text{26}\) This may be explained by chelation theory, according to which chelation or complexation reduces the polarity of central metal atom because of partial sharing of its positive charge with the donor group within the whole chelate ring system. This chelation increases the lipophilic nature of the central atom, which favors the permeation of the complexes through the lipid layer of the cell membrane and results in enhancement of activity.
Unsymmetrical Schiff base and its complexes were prepared and characterized using microanalytical, electronic and vibrational spectral analysis. IR spectral data demonstrates the ligand act as dibasic tetradentate, coordinating via phenolic oxygen and azomethine nitrogen atoms as illustrate in Fig.1. Magnetic and electronic spectral studies reveal square pyramidal structure for Mn(III) and VO(IV) complexes, whereas octahedral geometry for Cr(III), Fe(III) and UO$_2$(VI) complexes. Thermal study revealed that complexes are thermally stable. The solid-state D.C. conductivity of complexes indicate their semiconducting behaviour. Powder XRD analysis suggests crystalline phase and triclinic crystal system to VO(IV) complex. The complexes are biologically active and showed enhanced antimicrobial activities compared to the free ligand.

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