



Synthesis, Spectral Characterization and Antimicrobial Activities of Unsymmetrical Schiff Base Metal Complexes

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Six new unsymmetrical Schiff base metal complexes of VO²⁺, Ni²⁺ and Cu²⁺ have been synthesized from 2-hydroxynaphthaldehyde, 5-bromo/chlorosalicylaldehyde and *o*-phenylenediamine. Metal ions coordinate in a tetradentate manner with this N₂O₂ donor ligand, which are characterized by elemental analysis, molar conductance, IR and electronic spectral studies. The elemental analysis suggests that the stoichiometry to be 1:1 (metal:ligand). The molar conductivity values suggest that the complexes are non-electrolytic in nature. The ligands (H₂L), in comparison to its metal complexes are screened for its antibacterial activity against two gram negative and two gram positive microorganisms using well diffusion method. The activity data shows that metal complexes have antibacterial activity more than the parent Schiff bases and standard streptomycin because of chelation.

Key Words: Cu(II), Ni(II) and VO(IV) complexes, Spectral studies, Antibacterial activity.

INTRODUCTION

Schiff bases are obtained by the condensation of primary amines with carbonyl compounds^{1,2}. These ligands coordinate to metal ions *via* azomethine nitrogen atom and the resulting transition metal complexes of Schiff bases have been studied extensively^{3,4}. This is because Schiff bases offer opportunities for inducing substrate chirality, enhancing the solubility, tuning the metal centered electronic factor and form stable complexes which also act as catalyst⁵⁻¹⁰. A large number of reports are available on the chemistry and the biocidal activities of transition metal complexes containing hard O or N and soft S donor atoms. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural liability and are sensitive to molecular environment¹¹. The environment around the metal centre "as coordination geometry, number of coordinating ligands and their donor groups" is the key factor for metallo proteins to carry out specific physiological functions¹².

Schiff bases^{13,14} also has been used as biochemical, analytical and antimicrobial agents¹⁵. The metal complexes of ligand containing electron withdrawing group exhibit improved biological activity¹⁶. The biological activity of Ni(II) and Cu(II) complexes of Schiff bases derived from aminothiazole and substituted salicylaldehyde against several species of bacteria and fungi were reported¹⁷. Additionally, vanadium is a biocompatible metal ion used earlier in insulin mimetics and

antitumour agents¹⁸. It is well known that some drugs have greater activity when administered as metal complexes than the free ligands¹⁹.

In the present paper, successful synthesis of unsymmetrical mononuclear Cu(II) Ni(II) and VO(IV) species are chelated by substituted hydroxyaldehydes and *o*-phenylenediamine. Their spectral and antimicrobial activities are discussed.

EXPERIMENTAL

Chemicals used for the preparation of ligands and complexes were purchased from Aldrich and used as such. The purity of ligands and metal complexes were checked by TLC.

The Fourier transform infrared spectrum was recorded in the range 4000-400 cm⁻¹ on a Perkin-Elmer Nicholas FT-IR spectrophotometer with solid KBr disc. The electronic spectra were recorded at 300 K on a Perkin-Elmer Lambda 25 (UV-vis) spectrometer using HPLC grade DMSO as solvent in the range 200-800 nm. Metal and nitrogen estimation was carried out with a Perkin-Elmer 2400 II elemental analyzer. Molar conductivities were measured using an Elico digital conductivity bridge model CM-88 using freshly prepared solutions of complexes in DMSO. All the experiments were performed at room temperature unless otherwise mentioned.

Synthesis of ligands: Schiff base ligands were prepared according to the literature procedure²⁰ with a slight modification. To 1 mM of *o*-phenylenediamine in 30 mL of ethanol,

1 mM of HCl was added and stirred. To this, 1 mM of 5-bromosalicylaldehyde/chlorosalicylaldehyde in 10 mL of ethanol was added and refluxed for 1 h. The solution was allowed to cool and then neutralized with NaOH solution. To this 1 mM of 2-hydroxynaphthalaldehyde dissolved in 15 mL of ethanol was added and refluxed for 1 h. The solution was poured in ice and the schiff base formed as yellow solid was filtered and dried *in vacuo*.

Synthesis of complexes: The mono nuclear copper(II) Schiff base complex was prepared by refluxing 0.3217 g of copper(II) perchlorate hexahydrate with 0.2670 g of ligand in 30 mL of ethanol for 2.5 h. The solution was cooled, filtered and left in a Petri dish to allow the solvent to evaporate slowly. The green colour complex formed was washed with ethanol to remove the unreacted ligand²¹. The same procedure was adopted for the synthesis of other complexes.

Analytical, colour and spectral data of ligands and their metal complexes

Ligand H₂L¹: Yellow powder. Yield (%): 85. m.p. 146 °C. IR (KBr, ν_{\max} , cm^{-1}) 3421(-OH), 1615 (HC=N), 1365 (phenolic C-O). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 319, 366, 444. Anal. calcd. (%) for C₂₄H₁₈N₂O₂Br; C, 64.5; H, 4.03; N, 6.27. Found (%): C, 64.7; H, 4.05; N, 6.28.

Ligand H₂L²: Reddish yellow powder. Yield (%): 80. m.p. 123 °C. IR (KBr, ν_{\max} , cm^{-1}) 3432 (-OH), 1619 (HC=N), 1366 (phenolic C-O). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 317, 369, 445. Anal. calcd. (%) for C₂₄H₁₈N₂O₂Cl; C, 71.7. H, 4.48; N, 6.97. Found (%): C, 71.5; H, 4.5; N, 6.96.

[Cu(C₂₄H₁₆N₂O₂Br)]: Green colour. Yield (%): 53. m.p. > 180 °C. IR (KBr, ν_{\max} , cm^{-1}): 1617 (HC=N), 1365 (phenolic C-O), 538 (Cu-O), 463 (Cu-N). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 267, 318, 365, 445, 541. Anal. calcd. (%) for [Cu(C₂₄H₁₆N₂O₂Br)]; C, 56.76; H, 3.15; N, 13.5; Cu, 12.5. Found (%): C, 56.78; H, 3.17; N, 13.3; Cu, 12.3.

[Ni(C₂₄H₁₆N₂O₂Br)]: Green colour. Yield (%): 46.5. m.p. > 170 °C. IR (KBr, ν_{\max} , cm^{-1}): 1597 (HC=N), 1465 (phenolic C-O), 449 (Ni-O), 440 (Ni-N). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 277, 321, 375, 451, 500. Anal. calcd. (%) for [Ni(C₂₄H₁₆N₂O₂Br)]; C, 57.29; H, 3.18; N, 6.36; Ni, 11.6. Found (%): C, 57.27; H, 3.15; N, 6.38; Ni, 11.4.

[VO(C₂₄H₁₆N₂O₂Br)]: Dark blue colour. Yield (%): 57.2. m.p. > 180 °C. IR (KBr, ν_{\max} , cm^{-1}): 1616 (HC=N), 1460 (phenolic C-O), 460 (V-O), 425 (V-N), 961 (V=O). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 268, 320, 365, 444, 480. Anal. calcd. (%) for [VO(C₂₄H₁₆N₂O₂Br)]; C, 55.28; H, 3.07; N, 5.37; VO, 12.87. Found (%): C, 55.25; H, 3.1; N, 5.35; VO, 12.88.

[Cu(C₂₄H₁₆N₂O₂Cl)]: Dark green colour. Yield (%): 59.7. m.p. > 180 °C. IR (KBr, ν_{\max} , cm^{-1}): 1617 (HC=N), 1365 (phenolic C-O), 538 (Cu-O), 463 (Cu-N). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 267, 318, 365, 445, 541. Anal. calcd. (%) for [Cu(C₂₄H₁₆N₂O₂Cl)]; C, 62.17; H, 3.45; N, 6.04; Cu, 13.7. Found (%): C, 62.2; H, 3.48; N, 6.1; Cu, 13.5.

[Ni(C₂₄H₁₆N₂O₂Cl)]: Green colour. Yield (%): 48.3. m.p. > 170 °C. IR (KBr, ν_{\max} , cm^{-1}): 1597 (HC=N), 1465 (phenolic C-O), 449 (Ni-O), 440 (Ni-N). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 277, 321, 375, 451, 500. Anal. calcd. (%) for [Ni(C₂₄H₁₆N₂O₂Cl)]; C, 62.8; H, 3.49; N, 6.1; Ni, 12.8. Found (%): C, 62.6; H, 3.44; N, 6.2; Ni, 12.

[VO(C₂₄H₁₆N₂O₂Cl)]: Light green colour. Yield (%): 54.8. m.p. > 180 °C. IR (KBr, ν_{\max} , cm^{-1}): 1616 (HC=N), 1460

(phenolic C-O), 460 (V-O), 425 (V-N), 961 (V=O). UV-Visible spectrum in DMSO [λ_{\max} (nm)]; 268, 320, 365, 444, 480. Anal. calcd. (%) (IV) (C₂₄H₁₆N₂O₂Br); C, 61.7; H, 3.43; N, 6.0; VO, 14.35. Found (%): C, 62.0; H, 3.5; N, 6.2; VO, 14.41.

Antibacterial activity: The *in vitro* antibacterial activity of the ligand and the complexes were tested against the bacteria *Bacillus subtilis* (gram +ve), *Staphylococcus aureus* (gram +ve), *Escherichia coli* (gram -ve) and *Klebsiella pneumoniae* (gram -ve) by well diffusion method using nutrient agar as the medium. Streptomycin was used as standard. The stock solution (10⁻² mol L⁻¹) was prepared by dissolving the compound in DMF. In a typical procedure, a well was made on the agar medium inoculated with microorganisms in a Petri plate. The well was filled with test solution and the plate was incubated for 24 h at 35 °C. During the period, the test solution diffused and the growth of inoculated microorganisms was affected. The inhibition zone was developed and the concentration was noted.

RESULTS AND DISCUSSION

All the complexes are coloured, non-hygroscopic and stable in air. The metal complexes are soluble in DMF and DMSO, while they are insoluble in other common organic solvents. The results of elemental analyses are in good agreement with those required by the proposed formulae.

Molar conductance measurements: The molar conductivities of complexes are measured in DMSO solution. The observed molar conductance of complexes in 10⁻³ molar solution is in the range 25-30 ohm⁻¹ cm² mol⁻¹, which are consistent with the non-electrolytic nature of all the complexes²².

FT-IR spectra: The comparison of IR spectra of ligands and its metal complexes indicate that the ligands are principally coordinated to metal ion in two ways, thus acting as a tetradentate ligand. The band appearing at *ca.* 1615 cm⁻¹ due to azomethine is shifted to a lower frequency by *ca.* 10-20 cm⁻¹ in complexes, indicating the participation of azomethine nitrogen in interaction with metal ion²³⁻²⁵. A broad band appearing at 3421 cm⁻¹ assigned to $\nu(\text{OH})$ in ligand is no longer found in the spectra of metal complexes but instead a new band appeared at *ca.* 1365 cm⁻¹, indicating deprotonation and coordination of hydroxyl oxygen with the metal ion. The oxovanadium(IV) complexes exhibit an intense band at 981 cm⁻¹, which has been assigned to $\nu(\text{V}=\text{O})$ stretching frequency²⁶.

Further, the coordination of ligand with metal ions was shown by the appearance of new weak low frequency bands at 463 and 530 cm⁻¹. These are assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ vibrations, respectively²⁷, thus confirming the participation of hydroxyl oxygen and azomethine nitrogen in coordination.

Electronic spectra: The electronic spectra of ligands and its complexes have been taken in DMSO between 200-800 nm. The Schiff base ligands exhibit two bands at 250 and 310 nm. The bands are due to the transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of -C=N group in the ligand structure^{28,29}. In addition, the mononuclear complexes show a new band around at 440 nm which is assigned to ligand-metal charge transfer transition³⁰.

The bands of very low intensity in visible region are assigned to *d-d* transition. The copper(II) complex exhibits a characteristic shoulder at 541 nm is attributed to square planar geometry of copper(II) complex^{31,32}.

TABLE-I
ANTIMICROBIAL ACTIVITY DATA OF LIGANDS AND ITS METAL COMPLEXES

Compound	Antimicrobial activity (%) (diameter of zones in mm)											
	<i>B. subtilis</i>			<i>S. aureus</i>			<i>K. pneumoniae</i>			<i>E. coli</i>		
	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Napopdbrsal	10	14	16	11	14	16	11	15	18	10	14	18
Napopdclsal	12	15	17	14	16	18	12	18	19	11	12	20
[Cu(Napopdbrsal)]	12	15	20	12	14	18	12	15	18	10	12	16
[Ni(Napopdbrsal)]	11	13	18	12	13	17	11	16	19	11	14	17
[VO(Napopdbrsal)]	11	13	16	10	14	17	11	14	17	10	13	16
[Cu(Napopdclsal)]	13	17	22	13	16	20	13	19	20	12	13	19
[Ni(Napopdclsal)]	12	15	19	12	14	18	12	15	19	12	13	18
[VO(Napopdclsal)]	12	15	17	12	13	17	11	14	18	11	13	18

The nickel complex shows *d-d* bands below 500 nm which suggests a square planar geometry around nickel(II)³³. The electronic spectrum of vanadium(IV) complex shows intense absorption bands at 485 and 510 nm, suggesting a square pyramidal environment³⁴.

Antibacterial activity: The gram +ve and gram -ve bacterial strains used to test the biological activity of ligand and complexes were *Bacillus subtilis* (gram +ve), *Staphylococcus aureus* (gram +ve), *Escherichia coli* (gram -ve) and *Klebsiella pneumoniae* (gram -ve).

From the Table-1, it is concluded that all the metal complexes exhibit moderate and higher antimicrobial activity than the free ligand. The activity increases with increase of concentration of test solution containing new complexes. On comparing the biological activity of Schiff bases and its metal complexes with standard (streptomycin), the following results are obtained: The free ligands and its metal complexes show positive effects towards *Escherichia coli*. The ligands and copper(II) complexes show higher antibacterial activity against both negative bacterias because of effective chelation that is more stable. Copper (II) and oxovanadium(IV) complexes have higher biological activity than the nickel(II) complexes.

From the above results it is concluded that metal complexes have higher antimicrobial activity than the free ligand because of chelation. On chelation^{35,36}, the polarity of metal ion is reduced to a greater extent due to the overlap of ligand orbital and partial sharing of the positive charge of metal ion with donor groups. It increases the delocalization of π -electrons over the whole chelate ring and enhances the lipophilicity of the complex. The increased lipophilicity enhances the penetration of complexes into lipid membranes and blocking of metal binding sites on the enzymes of microorganisms.

Conclusion

In this report, coordination chemistry of Schiff base ligands, obtained from the reaction of naphthaldehyde, 5-bromo/chlorosalicylaldehyde and *o*-phenylenediamine is discussed. Cu(II), Ni(II) and VO(IV) complexes have been synthesized and characterized by spectral and analytical data. Based on these data, a square planar geometry has been assigned to the complexes except VO(IV) complex which has square pyramidal geometry. The metal complexes have higher antimicrobial activity than the ligands. Further, the biological activity of the complexes are found to follow the order Cu(II) > VO(IV) > Ni(II) > ligand > standard streptomycin.

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