



Synthesis, Spectroscopic, Electrochemical and Biological studies of Schiff Base Complexes of Some 3d transition metals derived from 2-aminophenol and 2-hydroxynaphthaldehyde

*V. Gomathi ** R. Selvameena R. Subbalakshmi
*** G. Valarmathy

* PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli-620 002, Tamil Nadu, India.

** PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli-620 002, Tamil Nadu, India.

*** PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli-620 002, Tamil Nadu, India.

ABSTRACT

Metal chelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base has been synthesised by the condensation of 2-aminophenol with 2-hydroxynaphthaldehyde.

The ligand and its complexes are characterised by elemental analysis, molar conductance, magnetic moment, IR, ¹H NMR and electronic spectral data.

From the analytical and spectral data, the stoichiometry has been found to be 1:2 for all the complexes. An octahedral structure has been proposed. The Schiff base and metal complexes were screened for their antimicrobial activities on different species of pathogenic bacteria and fungi and their bio potency has been discussed.

Keywords : Schiff base, Metal complexes, Antibacterial, Antifungal

Introduction

Schiff bases have been used as chelating ligands in the field of coordination chemistry. Several Schiff bases possess anti-inflammatory, allergic inhibitors reducing activity, radical scavenging, analgesic and anti-oxidative action¹. The existence of metal ions bonded to biologically active compounds may enhance their activities². Transition metal complexes with Schiff base ligands have been extensively investigated as catalysts for a large number of organic redox reactions and electrochemical reduction processes. Cyclic voltametry has been a useful tool to investigate the mechanisms of catalysis by Schiff base metal complexes as well as to study the structure reactivity relationships in these compounds. Keeping the above facts in mind and in continuation of our research work³ on transition metal(II) complexes with Schiff base, in the present paper we report the synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base derived from the condensation of 2-hydroxynaphthaldehyde with 2-aminophenol.

Experimental

Materials and Methods

All the reagents used were of AR grade (BDH / E. Merck). Solvents were purified and dried according to the standard procedures. Elemental analysis (C,H,N) were performed using elemental analyser Elementar Vario EL III. Conductivity measurements for the complexes were carried out using Elico conductivity bridge and dip type conductivity cell. IR spectra of the Schiff base and its complexes were recorded in KBr pellets with Perkin Elmer IR RXI Spectrometer in the 4000-400 cm⁻¹ range. The ¹H NMR spectra were recorded on a Bruker 400 MHz FT-PMR Spectrometer (DMSO-d₆). Melting

points were determined using Elico melting point apparatus. The electronic spectra were recorded in Perkin Elmer Lambda 35 spectrometer in the 190-1100 nm range. Cyclic Voltametric measurements for the complexes were measure using Princeton applied Research –Multichannel VersaSTAT-II.

Synthesis of Schiff Base (2HN2AP): To a hot ethanolic solution of 2-aminophenol, (0.002 mol)

2-hydroxynaphthaldehyde (0.002 mol) in ethanol was added. The solution is refluxed for 2 hours. An orange coloured solid mass separated out on cooling was filtered, washed with ethanol and dried over anhydrous CaCl₂ in a desiccator. The purity of the Schiff base was checked by melting point, TLC and spectral data.
(m.p: 230 °C; yield: 83%)

General method for preparation of metal complexes: To a hot magnetically stirred 1, 4-dioxan solution of Schiff base (0.004 mol), an aqueous solution of the corresponding metal (II) acetate (0.002 mol) was added. The reaction mixture was refluxed for 5-6 h. On cooling coloured solid complexes separated. The complexes obtained in each case were filtered and washed with 1,4-dioxan several times to remove excess of the ligand. Finally the complexes were dried in a desiccator.

Results and discussion

Analytical data: The analytical data obtained for the ligand and complexes (Table-1) agree very well with the proposed molecular formulae and also indicates the formation of 1:2 (M:L) complexes of general formula of [M(2HN2AP-H)₂(H₂O)₂] [M= Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺]

Table-1

Physical Characteristics and analytical data of Schiff base and the complexes

S. No	Schiff base & Complexes	Molecular Formula	Colour	Elemental analysis % Found (Calcd)			Metal % Found (Calcd)	M.Pt °C	Yield %	Molar Conductance ohm ⁻¹ cm ² mol ⁻¹	Magnetic moment B.M
				C	H	N					

1	2HN2AP	C ₁₇ H ₁₃ NO ₂	Orange	77.70 (77.57)	4.50 (4.94)	4.56 (5.32)	-	230	87	-	-
2	[Mn(2HN2AP-H)(H ₂ O) ₂]	MnC ₃₄ H ₂₈ N ₂ O ₆	Pale yellow	66.17 (66.34)	4.98 (4.55)	4.11 (4.55)	10.03 (10.80)	300	82	7.35	5.15
3	[Co(2HN2AP-H) ₂ (H ₂ O) ₂]	CoC ₃₄ H ₂₈ N ₂ O ₆	Dark brown	65.18 (65.92)	3.86 (4.52)	4.91 (4.52)	20.49 (21.50)	305	75	1.57	3.92
4	[Ni(2HN2AP-H) ₂ (H ₂ O) ₂]	Ni C ₃₄ H ₂₈ N ₂ O ₆	Yellow	65.00 (65.95)	5.01 (4.53)	5.05 (4.53)	12.98 (13.70)	310	80	7.86	3.37
5	[Cu(2HN2AP-H) ₂ (H ₂ O) ₂]	CuC ₃₄ H ₂₈ N ₂ O ₆	Dark green	66.50 (65.43)	3.97 (4.49)	5.16 (4.49)	12.56 (12.10)	305	68	6.98	1.65
6	[Zn(2HN2AP-H) ₂ (H ₂ O) ₂]	Zn C ₃₄ H ₂₈ N ₂ O ₆	Pale Yellow	66.41 (65.24)	4.80 (4.48)	4.92 (4.48)	10.90 (11.09)	310	63	9.83	dia

Conductance and magnetic susceptibility measurements: The molar conductance of the complexes was determined at a concentration 1x10⁻³M in DMF (Table-1). All the complexes showed very low molar conductance values 1.57-9.83 ohm⁻¹ cm² mol⁻¹ which indicates that the complexes are non electrolytic in nature⁴. The observed magnetic moment value of 5.15 B.M, 3.92 B.M, 3.37 B.M and 1.65 B.M for the Mn(II), Co(II), Ni(II) and Cu(II) complexes suggests octahedral¹³ geometry. The Zn(II) complex is found to be diamagnetic.

IR Spectra: The important IR spectral bands of the ligand and its metal complexes are given in Table-2. A strong band observed in the free ligand at 1602 cm⁻¹, is characteristic of

azomethine (-CH = N) group⁵. This band shifts to higher frequency by 36-112cm⁻¹ after complexation except for Ni(II) complex where the band shifts to lower frequency by 18 cm⁻¹, indicating the coordination of azomethine nitrogen to metal ion. This is further confirmed by the appearance of the new band at 538-640 cm⁻¹ due to ν(M-N) band. A medium intensity band at 3401 cm⁻¹ in the free ligand due to ν(OH) was absent in the complexes, indicating deprotonation of the Schiff base prior to the coordination. The appearance of new band in the range 3422-3451 cm⁻¹ is due to C-O mode. This is further confirmed by the appearance of the new band in the range 456-490 cm⁻¹ due to ν(M-O) in the metal complexes⁶.

Table-2
Infra red and Electronic Absorption Spectral data of Schiff base and the complexes

S. No	Schiff base & Complexes	IR in (cm ⁻¹)				UV-Vis in (cm ⁻¹)
		ν(OH)	ν(>C=N)	ν(M-O)	ν(M-N)	
1	2HN2AP	3401	1602	-	-	30853, 30115, 21186, 21174
2	[Mn(2HN2AP-H)(H ₂ O) ₂]	3451	1709	490	640	31657, 28890
3	[Co(2HN2AP-H) ₂ (H ₂ O) ₂]	3414	1638	490	615	21439
4	[Ni(2HN2AP-H) ₂ (H ₂ O) ₂]	3432	1599	476	582	30857, 22199, 20534
5	[Cu(2HN2AP-H) ₂ (H ₂ O) ₂]	3422	1714	456	538	29756, 22174
6	[Zn(2HN2AP-H) ₂ (H ₂ O) ₂]	3428	1712	470	541	30518

¹H NMR Spectra: ¹H NMR Spectra of free ligand and its Zn(II) complex were recorded in DMSO-d₆. The multiplet which extends from δ = 6.7-7.9 ppm and δ = 6.9-8.8 ppm corresponds to the aromatic protons of Schiff base and metal complexes respectively. The coordination of the azomethine nitrogen is inferred by the upfield shifting of the -CH = N proton signal from 8.5 ppm in the ligand to 8.9-9.4 ppm in the complexes. The presence of peaks at δ = 15.67 ppm and δ = 10.31 ppm indicates the presence of two different hydroxyl protons in the Schiff base. The deprotonation of hydroxyl proton and coordination through oxygen⁷ is inferred by the disappearance of peak at δ = 15.79 ppm. The existence of peak at δ = 10.45 ppm indicates the presence of phenolic oxygen in the metal complexes. The IR spectra of the entire metal complexes exhibited bands in the range (3776-3792 cm⁻¹) which indicates the presence of coordinated water molecules.

Electronic Spectra

The electronic spectra of the Schiff base and its metal complexes were recorded in DMSO and given in Table-2. The Schiff base is orange in colour and shows four absorption bands at 30853 cm⁻¹, 30115cm⁻¹, 21186 cm⁻¹ and 21174 cm⁻¹. The Mn(II) complex shows two bands 31657 cm⁻¹ and 28890 cm⁻¹ which may be due to M → L charge transfer transition and ⁶A_{1g} → ⁴T_{2g}(D) transitions respectively. The Co(II) complex exhibits high energy band at 21439 cm⁻¹ which is assigned to the transition ⁴T_{1g}(F) → ⁴T_{1g}(P) for a high spin octahedral geometry. The Ni(II) complex is yellow in colour, exhibits three absorption bands at 30857cm⁻¹, 22199 cm⁻¹ and 20534 cm⁻¹. The band at 30857 cm⁻¹ may be attributed to L → M charge-transfer transition. The bands in the region 22199 cm⁻¹ and 20534 cm⁻¹ can be assigned to ³A_{2g}(F) → ³T_{1g}(P) transition. The Cu(II) complex exhibits two absorption bands at 29756 cm⁻¹ and 22174 cm⁻¹ may be due to the promotion of an electron or the transfer of a hole from ²E_g → ²T_{2g} transition. The Zn(II) complex exhibits three absorption bands at 30518 cm⁻¹ due

to the ligand-metal⁸ charge transfer transitions. The Zn(II) complex is found to be diamagnetic as expected.

Cyclic Voltammetry: Electrochemical cyclic voltammetry measurements were performed at room temperature in an air-tight three electrode cell by using Glassy carbon electrode with 0.071 cm² surface area as a working electrode, a platinum wire served as the counter electrode and a Ag/AgCl in a saturated KCl solution as reference electrode. The electrochemical reaction was charged with 10 ml DMF solution of all the complexes (1x10⁻⁴M) and tetrabutyl ammonium perchlorate (0.1M) as supporting electrolyte⁹. Measurements were made over a potential range between -1.3 V to +1.3 V for Mn(II), Co(II) and Ni(II) complexes with a scan rate of 0.1 vs⁻¹. The general reaction involved in redox process is assigned to one electron transfer of the metal centre. The observed cyclic voltammograms are characterised as reversible. The ratio of anodic to cathodic peak current ip_a/ip_c = 1 corresponds to a simple one electron process.

Antimicrobial activity: Antibacterial and antifungal activity of Schiff base and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been tested by disc diffusion technique¹⁰. The antimicrobial activity results for ligand and all complexes are given in Table-3. The various gram positive and gram negative bacterial organisms such as gram positive bacteria *Staphylococcus aureus* and *Bacillus subtilis*, gram negative bacteria *E. Coli* and *Pseudomonas aeruginosa* and fungi *Candida albicans* and *Aspergillus niger* are used to find out the antimicrobial activity (Table-3). The test was carried out in DMSO solution at a concentration of 100 ppm. Results were compared with standard drug Ciprofloxacin for bacteria and Nystatin for fungi at the same concentration. All the complexes show better antibacterial and antifungal activity when compared to the Schiff base. However the Cu(II) complex is highly active when compared to Schiff base and other metal complexes.

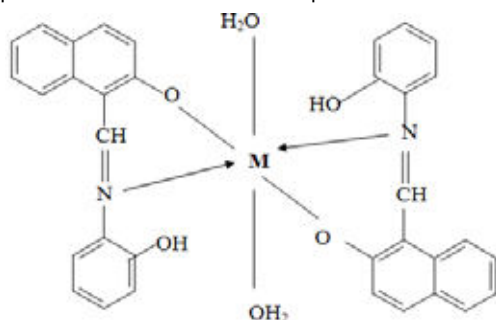
Table 3
Antimicrobial Activity of Schiff base and complexes

S.No	Antimicrobial activity of the and complexes	Staphylococcus aureus	Bascillus substilis	E.Coli	Pseudomonas aeruginosa	Candida albicans	Aspergillus niger
1	2HN2AP	++	++	++	++	++	-
2	[Mn(2HN2AP-H)(H ₂ O) ₂]	+++	++	++	+++	++	+
3	[Co(2HN2AP-H) ₂ (H ₂ O) ₂]	++	+++	++	+++	++	+
4	[Ni(2HN2AP-H) ₂ (H ₂ O) ₂]	+++	++	++	++	++	+
5	[Cu(2HN2AP-H) ₂ (H ₂ O) ₂]	+++	+++	++	+++	++	+
6	[Zn(2HN2AP-H) ₂ (H ₂ O) ₂]	+++	++	++	+++	++	+

Standard= Ciprofloxacin 5 µg/ disc for bacteria; Nystatin= 100 units/disc for fungi. Highly active = +++ (inhibition zone > 15mm); Moderately active = ++ (inhibition zone >10mm); Slightly active= + (inhibition zone > 5mm); Inactive = - (<5 mm)

Conclusion: Based on the conductance measurements, magnetic susceptibility measurements, elemental analysis, infrared spectra, ¹H NMR and electronic spectra, the probable structure of the complexes proposed in the present work is given in Figure 1.

Proposed structure of the metal complex



M= Mn(II),Co(II), Ni(II),Cu(II) and Zn(II)

Acknowledgements

We acknowledge to the University Grants Commission, Hyderabad, India, for the financial support and also thank the Management, Seethalakshmi Ramaswami College, Tiruchirappalli, Tamil Nadu, India for providing laboratory facilities.

REFERENCES

1. L. Hadjipavlu, J.dimitra, A.Athina & geronikaki, Drug Des Discovery., | 1998,15,199-206 | Chem Abstr.,129,148934 (1998) | 2. E. Canpolat & M. Kaya, | J.Coord. Chem., 2004,57,1217. | 3. V.Gomathi and R.Selvameena., Asian | J. Chem.,2013,25(4),2083-2086 | 4. W.J.Geary, Coord.Chem. Rev., | 1971,7,81. | 5. R. Ramesh, K. Natarajan., Synth. | React., Met-Org. Chem., 1996,26,47. | 6. Carlin RL, Transition Metal | Chemistry., 2nd edn, Marcel Decker: | New York.1965 | 7. V.L. Chavan and B.H. Mehta, Asian J. | Chem., 2010,22(8) 5976-5980. | 8. Lever ABP. Inorganic Electronic | Spectroscopy, Elsevier Amsterdam, | 1984. | 9. Mabbot, J of chemical Education., | 1983,60,252-706., | 10. F. Simoncini, R. Rangone & | C.Calanni, Farnance Ed. | Prat.,23(10),559. | Chem. Abstr., 1968,69,109851. |