Synthesis, Characterization, Fluorescence, Electrochemical and Biological Studies on Co(II), Ni (II) and Cu(II) complexes of N-4-methoxyphenyl (2,4-dihydroxyacetophenylideneimine)

S.Amala, S.Santhi, R.Suganya

Abstract— The Co(II), Ni(II) and Cu(II) complexes of resacetophenone-anisidine Schiff base have been synthesized, characterized and their electrochemical, fluorescence and biological behaviour have also been reported. The complexes have been characterized on the basis of metal estimation studies, molar conductance measurements, magnetic susceptibility measurements, IR, UV-visible, EPR spectral studies and thermal analysis. Analytical data revealed that there is a formation of 1:2 metal : ligand complex. Based on the various data, an octahedral geometry has been suggested for Co(II) complex, square planar geometry has been suggested for Cu(II) and Ni(II) complexes. A tentative structure has been proposed to the complexes. The redox property of the complexes have been examined by using cyclic voltammetry. Fluorescence property of the complexes have been studied and the complexes are found to have remarkably high fluorescence behavior compared to the ligand. The complexes have been screened against bacterial and fungal pathogens. The activities of the complexes are higher than the ligand towards most of the pathogens studied.

Index Terms— antimicrobial, cyclic voltammetry, fluorescence, Schiff base.

I. INTRODUCTION

The coordination chemistry of Schiff base ligand possess considerable attention due to their ability to form complexes with interesting structures[1], biological activities[2] and oxygen carrying capability[3]. In the present study the Co(II), Ni(II) and Cu(II) complexes of N-4-methoxyphenyl-(2,4-dihydroxyacetophenylideneimine) are synthesized and characterized. The redox property of the complexes has been examined by using cyclic voltammetry. Fluorescence property of the complexes were studied. Both the ligand and complexes are screened against bacterial and fungal pathogens.

II. EXPERIMENTAL

2.1 Materials and Methods

IR spectra were recorded in KBr medium using FT-IR spectrophotometer (model : Shimadzu IR affinity).

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R.Suganya, PG and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli 620 002, Tamil Nadu, India, 8870160026 Measurements were performed on powder samples at 298K. Thermal analysis was carried out by using the instrument (NETZSCH STA 409 C/CD) from 303K to 1673K at the heating rate of 10K/min under nitrogen gas. Electron paramagnetic reasonance spectra at room temperature, were recorded on a Bruker EMX plus spectrometer with 100 KHz field modulation. The EPR spectra in liquid nitrogen JES FA200 ESR temperature were recorded using spectrometer. The UV-spectra of the ligand and complexes were taken using Perkin Elmer Spectrometer provided with quarts cells using DMSO as a solvent. The electrical conductivity of the complexes isolated were measured in 10^{-3} M solution of DMSO using a Elico conductivity bridge and a dip type conductivity cells. The metal estimation has been done by colorimetric method (copper and nickel) and pyrolytic method (cobalt). The magnetic susceptibility were determined by using Gouv Balance at room temperature.Electrochemical cyclic voltammetry measurements were performed at room temperature in an air tight three electrode cell by using glassy carbon electrode 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 reactions were carried out using tetrabutylammonium perchlorate (0.11M) as a supporting electrolyte with scan rate 0.2V/s.The fluorescence measurement were carried out in a quartz cell, in a Jasco Spectro Fluorimeter model FP-8200 at room temperature with the same concentration of 10^{-4} M in DMSO.

2.2 Preparation of complexes

The ligand N-4-methoxyphenyl-(2,4-dihydroxyacetophenylideneimine) has been synthesized and characterized by various spectral studies and its structure was established by single crystal XRD analysis by the authors in their previous article[4]. The above mentioned ligand(0.2 mmol) and the metal salt (0.1mmol) (cobalt acetate, Nickel chloride & copper chloride) were taken in 100 ml of ethanol and refluxed for 6 hours. The complex formed was filtered washed with water and dried.The complexes are soluble in DMF and DMSO.

2.2.1. [Co(NMPDHAPI)₂(H₂O)₂]: Yield: 85%, M.p. 305°C. m.w(g/mol): 607; Metal percentage found (calcd.): 9.84(9.71); IR (Solid state, cm⁻¹): v(O-H) 3431; v(-C=N-) 1596; v(C-O) 1247; v(M-O) 616; v(M-N) 522; UV (In DMSO, λ_{max} /nm): 201, 228 & 276 (Intra ligand charge transfer transitions); 475 (⁴T_{1g}(F) \rightarrow ⁴T_{2g}(F); Conductivity in DMSO(Λ_{M}): 16 ohm⁻¹cm²mol⁻¹.

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2.2.2. $[Ni(NMPDHAPI)_2]$: Yield:82%, M.p.302°C m.w(g/mol): 571; Metal percentage found (calcd.): 10.93(10.28); IR (Solid state, cm⁻¹): v(O-H) 3437; v(-C=N-) 1597; v(C-O) 1226; v(M-O) 612; v(M-N) 531; UV (In DMSO, λ_{max} /nm): 280, 319 & 361 (Intra ligand charge transfer transitions) ; 536 (${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$); Conductivity in DMSO(Λ_{m}): 20 ohm⁻¹cm²mol⁻¹.

2.2.3. [*Cu*(*NMPDHAPI*)₂]: Yield: 86%, M.p.306°C m.w(g/mol): 576; Metal percentage found (calcd.): 10.31(11.04); IR (Solid state, cm⁻¹): v(O-H) 3439; v(-C=N-) 1601; v(C-O) 1249; v(M-O) 602; v(M-N) 516; UV (In DMSO, λ_{max} /nm): 208, 226 & 274(Intra ligand charge transfer transitions) 508(²B_{1g} \rightarrow ²E_g; ²B_{1g} \rightarrow ²B_{2g} and ²B_{1g} \rightarrow ²A_{1g}); Conductivity in DMSO(Λ_{M}): 23 ohm⁻¹cm²mol⁻¹.

2.4Antimicrobial activities

Antimicrobial activities of the ligand and their metal complexes have been studied by disc diffusion method using nutrient agar as medium.

III. RESULTS AND DISCUSSION 3.1 Characterisation of complexes of NMPDHAPI 3.1.1. FT-IR spectra

The stretching vibrations of the azomethine groups appearing at 1587.73cm⁻¹ in the free ligand is shifted to 1596-1601cm⁻¹ in the complexes. This shows involvement of nitrogen of the azomethine in coordination with metal[5]. The coordination of nitrogen to the metal may be further confirmed by the presence of new band at 522.31cm⁻¹ in Co(II) complex; 531.26cm⁻¹ in Ni(II) complex and 561.77cm⁻¹ in Cu(II) complex corresponding to M-N bond which is absent in the ligand [6,7]. The another coordination site is phenolic oxygen present in the ortho position to the imine group. This is evidenced by the appearance of new band corresponding to metal-oxygen bond at 616.12cm-1 in Co(II) complex; 612.24cm⁻¹ in Ni(II) complex and 602.16cm⁻¹ in Cu(II) complex[8,9]. The C-O stretching vibration of phenolic group is observed at 1249.09cm⁻¹ in the ligand. This band is shifted to lower frequency in the complexes indicating coordination of phenolic oxygen to the metal[10].

3.1.2. Electronic spectra and magnetic susceptibility

The electronic spectra of the Co(II) complex exhibit four spin allowed transition at 475nm, 276nm, 228 nm 201nm. The band at 475nm assignable to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ transitions[11] and the magnetic moment of 4.78 BM is in conformity with octahedral arrangement around Co(II) ion[12]. The Ni(II) complex shows four absorption bands at 536nm, 361nm, 319nm and 280nm. The band at 536nm which may be assigned to the transitions from ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ [13] corresponding to the square planar geometry around Ni(II) and it is diamagnetic[14]. The Cu(II) complex exhibits four bands at 508nm, 274nm, 226 nm and 208nm. The band at 508nm is attributed to ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$; ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and

 ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions[15] of Cu(II) square planar geometry. The magnetic moment of 1.18 BM confirms the square planar geometry[16] around Cu(II).

3.1.3. EPR spectra

In the EPR spectrum of $[Cu(NMPDHAPI)_2]$ complex at 300K shows one intense absorption band in the

high field region and is isotropic due to tumbling motion of the molecules. In liquid nitrogen temperature the [Cu(NMPDHAPI)₂] shows well defined peaks. The g tensor values of Cu(II) complex can be used to derive the ground state. In square planar complexes the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ${}^{2}B_{1g}$ as the ground state with $g_{\parallel} > g_{\perp}$. for [Cu(NMPDHAPI)₂], In our case g_{\parallel} > g_{\perp} (2.35 > 2.02). g_{\parallel} > g_{\perp} indicates that the unpaired electron is predominantly present in $d_x^2 - y^2$ orbital[17] rather than d_z^2 . As a result the screening effect by the d_z^2 electrons is to a greater extent leading to elongation (Jahn teller distortion) finally detachment of two orbitals from the metal ion, resulting in square planor geometry. The epr spectra of the complex is shown in fig. 1.

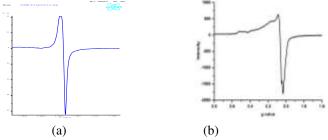


Fig. 1. (a) EPR Spectra of [Cu(NMPDHAPI)₂] at room T (b) EPR Spectra of [Cu(NMPDHAPI)₂] at LNT

3.1.4 Conductance measurements

The molar conductance of the complexes were found to be below 30 ohm^{-1} cm² mol⁻¹. This indicates the non-electrolytic nature of the complexes[18].

3.1.5 Metal estimation studies

The values obtained are in good agreement with the values calculated for the proposed structure of the complexes.

3.1.6 Thermal Analysis

In thermo gravimetric analysis of $[Co(NMPDHAPI)_2(H_2O)_2]$, the first weight loss noticed in the temperature range $110-145^{\circ}C$ (observed 6.39%, calculated 5.93%) is consistent with the elimination of two coordinated water molecules. The second weight loss is in the 220-340°C (observed 39.42%, temperature range of calculated 42.34%) is due to the decomposition of one molecule of ligand NMPDHAPI. The third weight loss is in the temperature range of $420-525^{\circ}C$ (observed 44.02%, calculated 42.34%) is corresponds to the decomposition of second molecule of ligand NMPDHAPI. The weight loss continues beyond this temperature and finally attains a constant mass corresponding to cobalt oxide(observed 11.36%, calculated 12.36%). The TGA/DTA curve is given fig. 2.

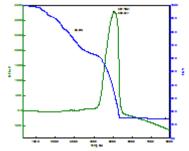


Fig. 2. TGA/DTA curve of [Co(NMPDHAPI)₂(H₂O)₂] 3.1.7 Cyclic voltammetry

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The voltammogram of cyclic $[Co(NMPDHAPI)_2(H_2O)_2]$ shows one cathodic peak at E_{Pc} =0.32V and its associated anodic peak at E_{Pa} =0.58V. This couple is found to be quasi-reversible as the peak separation between the anodic and cathodic peak potential is greater than 120mV. The ratio between anodic and cathodic currents suggests the process to be simple quasi-reversible one electron transfer process[19]. The voltammogram of [Ni(NMPDHAPI)₂] also shows one cathodic peak and one anodic peak. The cathodic peak is observed at $E_{Pc} = 1.20V$ and anodic peak is noted at $E_{Pa} = 1.39V$. This couple is found to be quasi-reversible and ratio between anodic and cathodic current suggests the process to be simple one-electron transfer. The voltammogram of [Cu(NMPDHAPI)₂] shows no cathodic peak and has only cathodic peak at E_{Pc} = -0.46V at suggesting the process to be irreversible[20]. The cyclic voltammograms are given in fig. 3.

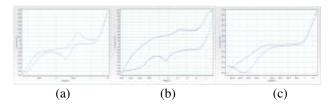


Fig.3 (a) Cyclic voltammogram of [Co(NMPDHAPI)₂(H₂O)₂] (b) Cyclic voltammogram of [Ni(NMPDHAPI)₂] (c) Cyclic voltammogram of [Cu(NMPDHAPI)₂]

3.2 Fluorescence spectra

The fluorescence spectra of ligand and its complexes were shown in Fig. 4. The emission spectra of the ligand NMPDHAPI shows a maxima at 386nm with intensity of 105 a.u.. The Co(II), Ni(II) and Cu(II) complexes showed enhancement of fluorescence intensity with the blue shift of about 6nm to 26nm. The enhancement in fluorescence intensity may be attributed to the complex formation between the metal ion and the ligand. The formed complex may be a rigid chelate system leading to chelation – enhanced fluorescence effect (CHEF)[21]. The CHEF effect diminished the PET process in the ligand.

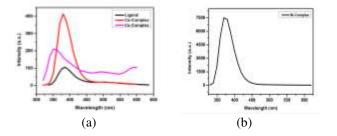


Fig.4 – (a) Fluorescence spectra of NMPDHAPI, $[Co(NMPDHAPI)_2(H_2O)_2]$ & $[Cu(NMPDHAPI)_2]$ (b) Fluorescence spectra of $[Ni(NMPDHAPI)_2]$.

On the basis of all the above findings it is concluded that the cobalt complex is formed by coordination through the azomethine group and ortho phenolic group (deprotonated) of the ligand. Two water molecules are also coordinated to the metal leading to octahedral geometry. In the nickel and copper complexes, coordination to the metal ions occurs through nitrogen of the azomethine group and oxygen of the phenolic group (deprotonated) in the ortho position leading to square planar geometry. The tentative structure of the complexes are given in the Fig. 5.

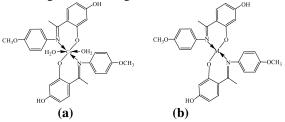


Fig.5.(a)Co(NMPDHAPI)₂(H₂O)₂ (b) $[M(NMPDHAPI)_2]$, M=Ni(II) and Cu(II)

3.3 Antimicrobial activities

Antimicrobial activities of NMPDHAPI and their complexes are given in Table 1. The complexes are found to be more sensitive than ligand towards almost all pathogens studied, which can be explained on the basis of overtone's concept and chelation theory[22]. The maximum sensitiveness of the cobalt and nickel complexes is observed with the fungal pathogen candida albicans. The copper complex shows the considerable activity against the bacterial pathogen Klebsiella aerogens. The antimicrobial activity images are shown in Fig. 6.



Fig. 6. (a) Activity against K. aerogenes and (b) Activity against C.Albicans {S.S.S.37 = NMPDHAPI, S.S.S.38 = [Cu(NMPDHAPI)₂], S.S.S.39= [Co(NMPDHAPI)₂(H₂O)₂], S.S.S.40 = [Ni(NMPDHAPI)₂] }

Table 1 Antimicrobial activity of the ligand and its complexes.

	Zone of Inhibition in mm				
Compound /Complex	Gram positive	Gram negative		Fungi	
	SA	EC	KA	CA	AN
NMPDHAPI	14	10	20	16	14
[Co(NMPDHAPI)	16	12	20	20	12
$_{2}(H_{2}O)_{2}]$	10	16	21	22	18
[Ni(NMPDHAPI) ₂]	20	10	22	18	14
[Cu(NMPDHAPI) ₂]	35	38	30	32	35
Standard					

SA = S.aureus; EC = E.coli; KA = K.aerogenes; CA = C.albicans; AN = A.niger; Standard = Ciprofloxacin 5µg / disc for bacteria;

Nystatin 100 units / disc for fungi. Solvent = DMSO.

IV. CONCLUSION

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The ligand NMPDHAPI has been complexed with Cobalt(II), Nickel (II) and Copper (II). Analytical data revealed that there is formation of 1:2 (metal to ligand) complex. The molar conductance data indicated the non-electrolytic behaviour of the complexes. The IR spectral data suggests the coordination of deprotonated phenolic group and >C=N group with Co(II), Ni(II) and Cu(II). The UV-Vis spectral data and magnetic susceptibility values for Co(II), Ni(II) and Cu(II) complexes are indicative of octahedral geometry around Co(II), square planar geometry around Ni(II) and Cu(II) complexes.A tentative structure has been assigned to all the metal chelates. Fluorescence emission with high intensity infers the fluorescent nature of the compounds and their application in fluorescent sensors. The complexes are found to possess remarkable biopotency compared to the uncomplexed ligand.

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