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Green Chemistry approach towards the synthesis of Anils from 2-hydroxy 3-methoxy benzaldehyde, synthesis of their metal complexes and characterization.

Madhukar A Badgujar*.

Department of Chemistry, Sheth J.N. Paliwala College Pali, Raigad (India)

ABSTRACT

The metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases N-(O-vanilidene)-2,3-dimethylaniline (L^1H) and N-(5-chlorosalicylidene)-2,6-dimethylaniline (L^2H) have been synthesized and characterized. The resulting complexes were characterized by elemental analysis, thermogravimetric analysis, magnetic moment measurements, conductivity measurements, 1H NMR, IR, UV-visible and ESR spectral studies. The metal complexes are coloured, solid and non-hygroscopic in nature. On the basis of electronic spectral analysis and magnetic susceptibility values, geometry of complexes were proposed to be octahedral. The molar conductivity data of complexes suggests their non-electrolytic nature. The ligand and metal complexes have been screened for their microbiological activity. The Schiff bases acts as bidentate monobasic ligands, coordinating through deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes are non-electrolytic in DMSO. The presence of the two coordinated water molecules in these complexes was indicated by IR spectra and thermo gravimetric analysis of the complexes. From the analytical and spectral data the stoichiometry of these complexes have been found to be $[M(L^1)(L^2)(H_2O)_2]$ {where M = Co(II), Ni(II), Cu(II) and Zn(II)}. It has been found that the metal complexes shows octahedral geometry.

Keywords: Schiff bases, Metal complexes

*Corresponding author

INTRODUCTION

The class of the organic compounds, Schiff base [1] which is also known as anil or imine. The chemistry of the carbon-nitrogen double bond plays a vital role in the progresses of chemistry science [1]. It has well been documented that Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activities. Schiff bases have been used extensively as ligands in the field of coordination chemistry [2-8]. The presence of ortho hydroxyl group for instance has been regarded as one of the important elements which favors the existence of intermolecular hydrogen bonding. Due to increasing commercial, medicinal and synthetic applications, studies involving Schiff bases as ligand and their metal complexes are finding importance currently. The aim of this research project is to screen simple and economic methods for preparation of Schiff-bases. Here in the microwave (M.W.) promoted condensation reaction of salicylaldehyde and aryl amines displayed the convenient practicing way for forming a series of Schiff-bases.

The present work also include the synthesis, characterization and antimicrobial study of mixed ligand complexes of Schiff bases derived from salicylaldehyde and the transition metals such as Co(II), Ni(II), Cu(II) and Zn(II).

Experimental

All the chemicals and solvents were of AR grade and were used further without purification. The metal salts used were in their hydrated form.

Synthesis of Anils (Schiff Bases) without Solvent under Microwave Irradiation [14-16]

General Procedure

The Schiff bases were synthesized by mixing equimolar amounts of o-vanillin with appropriate aniline, both dissolved in absolute ethanol. The reaction mixture was refluxed for 5 hours and the precipitate thus formed upon cooling to room temperature was filtered. The solid residue was crystallized from absolute ethanol and dried under reduced pressure.

The ligands N-(O-vanilidene)-2,3-dimethylaniline (L^1H) and N-(5-chlorosalicylidene)-2,6-dimethylaniline (L^2H) were prepared by the microwave-assisted condensations of respective aldehyde and aryl amines in a domestic oven, Midea PJ21B-A 800W. 1 mmol aldehyde with equal mole aryl amines were mixed together at ambient temperature in an Erlenmeyer flask (25 mL). The mixture was subjected to microwave for an optimized time on the "M-High" setting. The crude products were re-crystallized with ethanol.

Preparation of mixed Schiff base complexes

A metal(II) chloride (1.0 mmol.) dissolved in water (2.0 mL) was added slowly with constant stirring to a solution of N-(O-Vanilidene)-2,3-dimethylaniline (L^1H) (1.0 mmol.) and N-(5-chlorosalicylidene)-2,6-dimethylaniline (L^2H) (1.0 mmol.) in ethanol (50 mL). The pH of the solution was slowly raised to obtain the appropriate pH for the formation of the complex by the drop wise addition of 0.1 N sodium hydroxide solution. The resulting mixture was stirred for 2-3 hour. The product was digested on a hot water bath for half an hour. The complex thus formed was filtered out, washed with aqueous alcohol followed by distilled water and dried in vacuum over fused $CaCl_2$. Similarly all the complexes were prepared.

The metal estimations were carried out by standard Methods [11-19]. Elemental analysis was performed at SAIF, IIT Bombay, Mumbai. The conductance was measured in DMSO solvent on an Equiptronic EQ-660 conductivity meter. The magnetic susceptibility measurements at room temperature were made on Gouy balance using $HgCo(NCS)_4$ as calibrant. The IR spectra of ligands and their complexes were recorded on a Shimadzu FTIR – 8400S spectrometer in KBr pellets in the range of 4000-350 cm^{-1} . UV-Visible spectra were recorded on a Jasco V-530 UV-Visible spectrometer in the range 200-1100 nm. Electron spin resonance spectra of Cu(II) complex in polycrystalline state was recorded on Varian E-112x-band ESR spectrometer using TCNE as 'g' marker ($g=2.0027$) at room temperature. Thermal analysis of the metal complexes was carried out using Mettler Toledo Star^e SW 7.01 thermal analyzer in an inert atmosphere of nitrogen.

RESULTS AND DISCUSSION

The elemental analysis shown in the Table 1 indicates that, all the metal complexes have 1:1:1 stoichiometry with respect to L¹H: L²H: M {where M = Co(II), Ni(II), Cu(II) and Zn(II)} and are dark colored amorphous substances, soluble in DMF and DMSO. The molar conductance values (0.010 - 0.016 ohm⁻¹ mol⁻¹ cm²) of 10⁻³ M solution in DMSO indicate that the metal complexes are non-electrolytic in nature.

Table1: Analytical, magnetic susceptibility measurements and molar conductance data of the ligands and their complexes.

Ligand / Complex, Ligand / Complex, Molecular Formula	Mol. Wt.	Analysis % Found (Calculated)				μ_{eff} BM.	λ_m Ohm ¹ cm ² mol ⁻¹
		C	H	N	M		
L ¹ H C ₁₆ H ₁₈ NO ₂	256.32	74.75 (80.75)	7.05 (6.71)	5.42 (6.21)	-	-	-
L ² H C ₁₆ H ₁₈ NO ₂ Cl	291.77	68.07 (69.36)	5.09 (5.39)	5.18 (5.39)	-	-	-
[Co(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₃₆ ClN ₂ O ₄ Co	607.02	62.23 (62.34)	4.61 (5.41)	4.89 (4.85)	10.50 (10.20)	5.10	0.016
[Ni(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₃₆ ClN ₂ O ₄ Ni	606.78	62.16 (62.37)	5.20 (5.41)	4.49 (4.85)	10.25 (10.16)	3.20	0.011
[Cu(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₃₆ ClN ₂ O ₄ Cu	611.64	61.51 (61.85)	5.23 (5.36)	4.61 (4.81)	10.11 (10.51)	1.80	0.013
[Zn(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₃₆ ClN ₂ O ₄ Zn	613.48	61.20 (61.65)	5.12 (5.35)	4.89 (4.79)	10.95 (11.19)	-	0.010

Electronic spectra and Magnetic moment

The electronic spectral studies of Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases L¹H and L²H were carried out in DMSO solution (1x 10⁻³M). The absorption spectrum of the Co(II) complex shows bands at ~ 9363 cm⁻¹ and ~ 18868 cm⁻¹ attributed to ⁴T_{1g}(F) → ⁴T_{2g}(F) (ν₁) and ⁴T_{1g}(F) → ⁴T_{1g}(P) (ν₃) transitions respectively in an octahedral field [20]. The spectral parameters²¹ of Co(II) complex are as follows : Dq = 1036, B¹ = 715, β = 0.736 and β⁰ = 26.4%. The reduction of Racah parameter from the free ion value 971 cm⁻¹ and β⁰ value of 26.4% testify the presence of considerable covalence in the complex [22]. The Co(II) complex has magnetic moment 5.10 BM also suggest an octahedral geometry. Ni(II) complex exhibits two electronic spectral bands at ~ 10356 cm⁻¹ and ~ 16260 cm⁻¹ which can be assigned to ³A_{2g}(F) → ³T_{2g}(F) (ν₁) and ³A_{2g}(F) → ³T_{1g}(F) (ν₂) transitions in an octahedral field [9]. The transition due to ³A_{2g}(F) → ³T_{1g}(P) (ν₃) was completely obscured by the intense intra ligand transition band. The ν₂: ν₁ ratio is 1.57 is in the usual range reported for the octahedral Ni(II) complexes [23]. The spectral parameters [21] of the Ni(II) complex are as follows : Dq = 1035, B¹ = 739, β = 0.717 and β⁰ = 28.2%. The reduction of Racah parameter from the free ion value 1030 cm⁻¹ and β⁰ value of 28.2% confirms the presence of considerable covalence in the complex [21]. The Ni(II) complex has magnetic moment 3.20 BM also suggest an octahedral geometry. The Cu(II) complex exhibit broad band centered at ~ 14700 cm⁻¹ mainly due to ²E_g → ²T_{2g} transition suggesting the distorted octahedral geometry [4]. The observed magnetic moment value for Cu(II) complex is 1.80 BM suggestive of distorted octahedral nature for the complex. Zn(II) complex does not exhibit any characteristic d-d transitions and is also found to be diamagnetic in nature.

UV-Vis spectra and magnetic properties

The electronic spectrum was measured at room temperature in methanol (10⁻⁴ M) for the dark green complex bis(o-vanillinato)- triethylglycoldiiminecopper(II) (1), and it exhibited two absorption bands. The bands at 370 nm (ε = 9101 L mol⁻¹ cm⁻¹) and 472 nm (ε = 1556 L mol⁻¹ cm⁻¹) have been assigned to π to π*

Infrared spectra

The IR spectrum of (1) displays a strong absorption at 1636 cm^{-1} which is assigned to a C=N stretching mode in the Schiff base. A band observed at 1450 cm^{-1} is due to $\nu(\text{C}=\text{O})$ of the phenolic group of the title complex. The important infrared frequencies exhibited by the ligands L^1H and L^2H and their mixed ligand complexes are given in the Table 2. Infrared spectra of the schiff bases show a broad band centered around 3430-3450 cm^{-1} due to the phenolic hydroxyl group in free ligands which disappeared in their complexes indicating probably the coordination through phenolic oxygen moiety. A medium intensity bands around 1278-1283 cm^{-1} due to phenolic $\nu(\text{C}=\text{O})$ group of the ligands is shifted to higher region in their complexes indicating the coordination through the phenolic oxygen atom [24]. The IR spectra of the ligands exhibit a strong bands at 1614-1622 cm^{-1} due to $\nu(\text{C}=\text{N})$ (azomethine) which has been seen shifted towards lower region in the spectra of complexes indicating the participation of the azomethine group in the complex formation [24]. The spectra of the complexes show a broad diffused bands in the region 3100-3700 cm^{-1} , strong bands at 1535-1538 cm^{-1} and weak intensity bands at 815-832 cm^{-1} due to $\nu(\text{OH})$, $\delta(\text{OH})$ and $\rho_r(\text{OH})$ respectively of coordinated water molecules [25]. The coordination through nitrogen of azomethine and oxygen of (C-O) group of ligands are further evidenced by the appearance in the complexes of non-ligand bands around 600-610 cm^{-1} and 439-450 cm^{-1} , are due to M-O and M-N bonds respectively [25]

Table 2: Characteristic IR bands of the ligand L^1H and L^2H and their mixed ligand complexes

Schiff base / Complex	IR bands (cm^{-1})							
	ν_{OH}	ν_{OH} (H_2O)	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{C}=\text{O}}$	δ_{OH} (H_2O)	ρ_{rOH} (H_2O)	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
L^1H	3450	-	1614	1278	-	-	-	-
L^2H	3430	-	1622	1283	-	-	-	--
$[\text{Co}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3150- 3650	1603	1308	1535	832	600	439
$[\text{Ni}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3100- 3700	1605	1311	1536	827	610	490
$[\text{Cu}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3350- 3650	1607	1305	1538	815	592	461
$[\text{Zn}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$	-	3350- 3660	1602	1314	1537	826	600	450

Thermogravimetric analysis

The dynamic TGA with the percentage mass loss at different steps have been recorded. The elimination of lattice and coordinated water molecules take place in the first step. The Co(II), Ni(II), Cu(II) and Zn(II) complexes lose their weight in the temperature range $\sim 135\text{-}270^\circ\text{C}$, $135\text{-}250^\circ\text{C}$, $120\text{-}250^\circ\text{C}$ and $135\text{-}280^\circ\text{C}$ respectively corresponding to two coordinated water molecules with an endothermic peak in DTA curve²⁰⁻²². After the total loss of water, the organic moiety decomposes on further increment of temperature. The complete decomposition of ligands occurs at $\sim 450\text{-}650^\circ\text{C}$ and the observed residue corresponds to the respective oxide [26]. The occurrence of endothermic peak and elimination of the water molecules at comparatively higher temperature unambiguously confirm our earlier observation based upon the IR spectrum that the water molecules are coordinated in the metal complexes.

ESR spectra

The ESR spectrum of the powder sample of the Cu(II) complex was recorded at room temperature. The observed value for the $[\text{Cu}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})_2]$ complex are $g_{\parallel} = 2.14$, $g_{\perp} = 2.08$ and $G = 1.75$. The observed g_{\parallel}

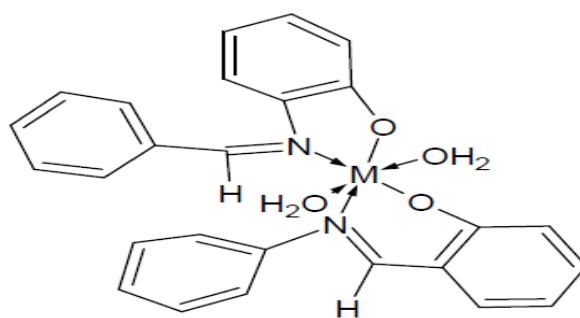
value is less than 2.3 in agreement with the covalent character of the metal – ligand bond²². The trend $g_{||} > g_{\perp} > g_e$ (2.0023) observed for this complex shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of Cu(II) ion and the spectral features are characteristic of axial symmetry; tetragonal elongated structure may be assumed for this Cu(II) complex [22].

Antimicrobial activity

Synthesized Schiff bases and their corresponding mixed ligand metal complexes were screened against *E.coli*, *S.aureus*, *B.subtilis*, and *S.typhi* to assess their potential as antimicrobial agent by Disc Diffusion method. The zones of inhibition based upon zone size around the discs were measured. The measured zone of inhibition against the growth of various microorganisms is listed in Table 3. It is found that the metal complexes have higher antimicrobial activity than the free ligand. Hence complexation increases the antimicrobial activity [23-27]. Such increased activity of the metal complexes can also be explained on the basis of ‘Chelation theory [27].

Table 3: Antimicrobial activity data of synthesized compounds

Schiff base / complex	Zone of inhibition (mm)			
	S.aureus	B.subtilis	E.coli	S.yphi
L ₁ H	0.0	2.5	0.0	0.0
L ₆ H	2.6	2.4	0.0	2.5
[Co(L ¹)(L ²)(H ₂ O) ₂]	6.5	7.5	4.7	4.5
[Ni(L ¹)(L ²)(H ₂ O) ₂]	9.0	8.5	6.5	4.2
[Cu(L ¹)(L ²)(H ₂ O) ₂]	8.7	5.8	6.8	5.1
[Zn(L ¹)(L ²)(H ₂ O) ₂]	9.8	7.3	8.5	5.7



Proposed structure of the complex

CONCLUSION

The elemental analysis, magnetic susceptibility, electronic, IR and ESR spectral observations suggest the octahedral geometry for the Co(II), Ni(II), Cu(II) and Zn(II) complexes and exhibit coordination number six. The Schiff's bases do show some antimicrobial activity to certain extent but their complexes exhibit comparatively greater amount of activity against the microorganism and in the study as indicated by the above result. Further research can be carried out to test the toxicity of the complexes in animals and human being, these complexes can be considered as antipathogenic agents against such kind of bacterial infections. Hence elaborate further study is suggested.

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