Synthesis and Spectral Characterization of 3-Amino Coumarin based new Schiff base and its Metal Complexes
Shylaja Kotte, Srikanth Goskula, Sreenivas Vasam, V.Ravinder*
Dept of Chemistry, Kakatiya University, Warangal
*Corresponding author: E.mail: k.shylajasatyam@yahoo.in

ABSTRACT
A new series of Mn(II), Cu(II) and Pd(II), complexes have been synthesized by the between carbonyl compound i.e. and 3-amino coumarin. The nature of bonding and geometry of the transition metal complexes as well as ligand have been deduced from elemental analysis, mass, 1H NMR, IR & thermal analysis. The complexes are found to have ML₂ based on elemental, conductance and spectral studies; octahedral geometry was assigned for these complexes. The ligand as a bidentate and co-ordinate through nitrogen atom of azomethine group, oxygen atom of keto group of 3-amino coumarin.

Key Words: Schiff’s base, 3-Amino cumarin, Metal Complexes

1. INTRODUCTION
Coumarin and its derivatives (Schiff’s bases) represent one of the most active classes of compounds possessing a wide spectrum of biological activity. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bio inorganic chemistry.

A Schiff base named after Hugo Schiff is a compound a functional group that contains a carbon-nitrogen double bond with the N-atom connected to an aryl (or) alkyl group not hydrogen. Schiff base is abroad sense heave the general formula R₁ R₂ C=NR₃, were ‘R’ is an organic side chain in this definition Schiff base is a synonymous with azometulne some restrict the term to secondary add mines (Azomethines where the carbon is connected to a H-atom) thus with the general formula RCH=NR. The chain on the nitrogen makes the Schiff base stable amine. Schiff base derived from an aniline. Where R₃ is a phenyl or a substituted phenyl can be called an aniline.

2. MATERIALS AND METHODS
2.1 Reagents and materials: Salicylaldehyde, glycine, sodium acetate, methanol, acetic acid, sodium bicarbonate and required aromatic carbonyl compounds and transitional metal salts.

2.2 Synthesis of 3-Amino coumarin: 1g of 3-acetamido coumarin in 25 ml of acetic acid. And 25 ml of 50% H₂SO₄ heat at 50°C to 60°C for 30 to 45 minutes. This solution is taken in equal volume of cold water. It is neutralized by adding NaHCO₃ filtered this product and recrystallised from dil. Alcohol MP: -130°C

2.3 Synthesis of Schiff base Ligand (3E)-3-(2-chloro benzylidene amino)-2-H-chromene 2-one (CBAC): Amino coumarin (4gms 0.0125 moles) dissolved in methanol (10ml), to this ortho chlorobenzaldehyde (1.75gms, 0.0125moles) dissolved in MeoH (10ml) was added drop wise with constant stirring. Then the where mixture was refluxed for about 8 hrs on a hot plate stirrer. The light brown colour product is separated out. It was washed with MeoH. The product was found to be TLC PURE IN 3:7 ethyl acetate and n- hexane. The ligand CBAC was synthesized by treating 3-aminocoumarin with o-chloro benzaldehyde in 1:1 ratio.

Scheme 1: Synthesis of Schiff base ligand (CBAC)
2.4 Synthesis of Schiff base Mn(II), Cu(II) and Pd(II) complexes:
A general preparation method was used for the synthesis of all the above complexes of new Schiff base ligand i.e. the ligand and corresponding metal salts 2:1 ratio was taken by using methanol solvent refluxed until solid separates out to get solid 3-4 hrs time was taken and recrystallized by the use of different solvents.

3. CHARACTERIZATION
3.1 Characterization of Schiff base ligand:
In the present work, new Schiff base ligands was synthesized by condensation of 3-aminocoumarine with different carbonyl compounds in to methanol this ligands was characterized by elemental, Mass, IR, 1H, 13C NMR, UV-Visible, ESR and spectral analysis. Further the above ligands were utilized in the synthesis of metal complexes of Mn(II), Cu(II) and Pd(II).

a) Mass spectral analysis: The mass spectra of ligands, CBAC, the molecular ion peaks at m/z 283(10%). This data is in good agreement with the respective molecular formula.

b) Infrared spectral analysis: A strong intensity band is appeared in the IR spectra of Schiff base ligand, at 1603 cm⁻¹ which is attributed to νC=O provides a strong evidence for the condensation of Carbonyl compound with the –NH₂ group of 3-amino coumarin. The ligand shown a signal around 1712 cm⁻¹ corresponding to νC=O. The medium intensity band at 1090 cm⁻¹ is assigned to ortho-chlorine (–Cl) of the benzene ring. Aromatic ring stretching frequencies are observed for the ligand at 1451 and 1360 cm⁻¹ and wagging frequency was observed at 3007 cm⁻¹.

c) 1H NMR spectral analysis: In the 1H NMR spectra of Schiff base ligand, the integral intensities of each signal are found to agree with the number of different types of protons present. In the spectra of the ligand, a singlet signal is appeared for CH=N proton (1H) in the range of 8.35δ. This supports the formation of a Schiff base by the condensation of carbonyl compound with 3-aminocoumarin. This fact is also supported by the appearance of peaks around 9.98 δ corresponding to aldehydic proton. The ligand was shown a singlet peak in the of 6.62-6.34 ppm which is due to olefinic proton of lactone ring in coumarin. In the spectra of ligand a multiplet has been observed in the range of 7.12-7.38 ppm which was assigned to the aromatic protons.

3.1 Characterization of Mn(II), Cu(II) and Pd(II) complexes:

a) Mass spectral analysis: The mass spectra of Schiff base Mn(II), Cu(II) and Pd(II) complexes have been recorded. All the spectra exhibit parent peaks due to molecular ions (M+). The proposed molecular formulae of these complexes were confirmed by comparing their molecular formula weights with m/z values. The molecular ion peaks at m/z (M⁺) 690 [for Mn(II)], 699 [for Cu(II)] , 742 [for Pd(II)]. The mass spectra supports the molecular formula of M(II) complexes. These values are in good agreement with the respective molecular formulae.

b) Infrared spectral analysis: The IR spectra of Schiff base complexes was studied by comparing with the IR spectra of free ligands to know the binding modes of metal and ligand. In the IR spectra of the Schiff base ligand, a high intensity νC=O band was observed in the range of 1603 cm⁻¹. This band is shifted towards lower side and observed at about 1590 cm⁻¹ for Mn(II), 1589 cm⁻¹ for Cu(II) and 1591 cm⁻¹ for Pd(II) complexes. This downward shift shows the coordination of azomethine nitrogen to the central metal ion. This fact is further supported by the appearance of a medium intensity band in the region of 685–695 cm⁻¹ assignable to νM=N vibration and 446-455 cm⁻¹ is due to νM=O. A band present in the range of 314-316 cm⁻¹ in the spectra of the Mn(II) and Cu(II) complexes indicates the presence of two chlorides in trans position around metal centre.

In the spectra of ligand the uC=O band of coumarin is observed at 1712 cm⁻¹. This was shifted to downwards and observed at 1681-1700 cm⁻¹ and supported by the appearance of new band in the range of 446-455 cm which is due to νM=O. This clearly indicates the coordination of lactonyl oxygen to M(II) ion. All the characteristic bands due to the aromatic rings were also present in the expected regions in all the Schiff base M (II) complexes.

c) 1H NMR spectral analysis: To study the binding nature of Schiff base ligands to the Pd (II) ion, 1H NMR spectra of the Schiff base Pd (II) complex was compared with those of the Schiff base ligand. In the ligand signal due to CH=N protons appeared in the range of 8.94-8.82 ppm. This signal has been shifted to downfield and appeared at 9.12-9.34 ppm indicating the coordination of nitrogen atom of CH=N group to Pd (II) ion. No appreciable change is seen in the peak positions corresponding to aromatic protons.
d) **ESR Analysis:** The ESR spectra of Cu(II) complex in solid state have been recorded at room temperature and the bonding parameters are calculated using approximations of Kneubuhl. The spectra of all the Cu(II) complexes contain two clear peaks at room temperature. One of the two peaks is an intense absorption peak at high field and other a less intense peak at low field. The $g_{||}$, $g_{\perp}$, $g_{\text{ave}}$, and G is calculated for the two peaks as described in literature. The $g_{||}$ and $g_{\perp}$ values calculated are useful in distinguishing the coordination environment around the Cu(II) ion. As an example the tetragonal distortions in octahedral geometry can occur either by compression or by elongation. In the case of $g_{\perp} > g_{||}$ distortions occur by compression and in the case of $g_{||} > g_{\perp}$ by elongation. In conformity with this the $g$ values of the complexes are fairly consistent. The $g_{||}$ values are from 2.196–2.225 while $g_{\perp}$ values are from 2.036–2.085.

d) **Structures of the complexes:** Octahedral structure was assigned to Mn(II), Cu(II) complexes and square planner for Pd(II) complex based on elemental and spectral data.

**Conclusion:** On the basis of analytical and spectral data, octahedral geometry has been tentatively proposed for all of Schiff base M (II) complexes. The Mn(II), Cu(II) compounds were found to have non-electrolytic nature where as Pd(II) complex in non-electrolytic nature. Octahedral structure was assigned to Mn(II), Cu(II) complexes and square planner for Pd(II) complex based on elemental and spectral data.

![Proposed Structures of Metal Complexes](image-url)