

Synthesis, Spectral Analysis and Antimicrobial Studies of N'-(1-(5-bromo-2-hydroxyphenyl) ethylidene)2-oxo-2H-chromene-3-carbohydrazide

Dr. Mallikarjun Kote

Department of Chemistry B V B College, Bidar-Karnataka

Abstract- The Complexes Such as Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) of Schiff base N'-(1-(5-bromo-2-hydroxyphenyl) ethylidene)2-oxo-2H-chromene-3-carbohydrazide has been synthesized and characterized by various spectral analysis. The complexes were prepared by reacting the ligand and metal chloride of Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) in ethanol to get a series of mononuclear complexes. The complexes were characterized by CHN analysis, conductivity measurements, magnetic susceptibility, IR, NMR, ESR, UV-Vis and X-ray Powder diffraction studies. By these spectral studies it is found that Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes have exhibited octahedral geometry where as the other Zn(II), Cd(II) and Hg(II) complexes have exhibited square pyramidal geometry. The ligand and its metal complexes have been screened for their antimicrobial activities. The prepared ligand shows low activity and its metal complexes shows moderate to good activity.

Key words: Schiff base, Spectral studies, Metal complexes and Antimicrobial activity

I. INTRODUCTION

Coumarins are important and well-known naturally occurring oxygen containing heterocyclic compounds. Coumarin derivatives have great importance for their physiological, photodynamic and bacteriostatic activities¹⁻⁸. 7-hydroxy coumarin is known for its antibiotic and antifungal activities⁹⁻¹⁰. They have several interesting biological activities such as analgesic, anti-inflammatory, antioxidants, antifungal, antiviral, antibacterial and anticoagulant in addition to their well known photosensitizing effect and chemotherapeutics¹¹⁻¹². As a privileged scaffold, coumarins show interesting biological properties, especially for this Anti-HIV, for examples-novobiocin is a coumarin derived antibiotic used as a competitive

inhibitor of the bacteria. The number of transition-metal-catalyzed approaches for assessing coumarins is increasing. However, most of these approaches are focused on mono substituted coumarins only limited applications of transition metal catalyzed reactions¹³⁻¹⁴. Many coumarins compounds, after some suitable structural modification can be used as drugs. Chelating ability of coumarin derivatives have been studied to suggest their use as chelating agents¹⁵.The literature survey reveals that the reaction of 6-bromo-2-oxo-2H-chromen-3-carbohydrazide and 2-hydroxy acetophenone Schiff base has not been reported so far. On the basis of this, we have synthesized ligand and its metal complexes and their coordination behavior were investigated.

II. EXPERIMENTAL

Materials and Methods

The chemicals were purified, acetophenone, hydrazine hydrate, sodium acetate, acetic acid, salicylaldehyde, diethyl melonate, ethyl acetoacetate, distilled alcohol and metal salts were of AR grade.

Preparation of ligand

N'-(1-(5-bromo-2-hydroxyphenyl) ethylidene)2-oxo-2H-chromene-3-carbohydrazide

The Schiff base ligand were prepared by condensation of 2-Oxo-2H-chromene-3-carbohydrazide and 1-(5-bromo-2-hydroxyphenyl) ethanone (1.2ml, 0.01mole) in ethanol was refluxed on water bath for 5-6 hours in presence of few drops of acetic acid. The reaction mixture was cooled to room temperature, the separated Schiff base were filtered and washed with hot alcohol and recrystallized from alcohol to get a pure sample.

The purity of Schiff base was checked by TLC (shown in scheme-I).

Yield: 75%, MP; 270°C, Mol. Wt = 400.90

Preparation of Metal complexes

A solution of 0.01mole of metal chloride in ethanol was mixed with the ethanolic solution of 0.01 mole of ligand and refluxed for 3-4 hours on water both to get clear solution. 0.5gm of excess sodium acetate was added to the reaction mixture to adjust the pH 7-8 of the solution. The reaction mixture was further, refluxed for 2 hours more. The resulting mixture was decomposed by pouring into a 100ml of distilled water with constant stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and then with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccators (yield, 55-75%).

Physical Measurements

Infrared spectra of the ligand and its metal complexes in KBr pellets were recorded in the spectral range 4000 – 350 cm^{-1} with Perkin Elmer Spectrum One FT-IR Spectrometer. $^1\text{H-NMR}$ Spectra were recorded on AMX – 4000 NMR Spectrometer, using TMS as internal standard and DMSO as a solvent. The Electronic Spectra were recorded on a Elico-SL-164 Double BEAM UV-Visible Spectrophotometer in the range of 200 – 1200nm in DMF. X-ray powder diffraction was recorded at central college, Bangalore University, Bangalore. Thermogravimetric Analysis was carried out on a universal V4.5A. Thermal analysis Instrument, up to 1200°C, in nitrogen atmosphere with a heating rate of 10°/minute. Magnetic susceptibility measurements were recorded on Guoy balance method. The Conductance measurements were made on an ELICO-CM-82-conductivity bridge.

III. RESULTS AND DISCUSSION

Nature and Stoichiometry

All the complexes are colored in nature and were sparingly soluble in common organic solvents but soluble in DMF, DMSO and acetonitrile. The analytical data indicates that the complexes are agree well with 1:1 metal to ligand stoichiometry for Fe(III), Zn(II), Cd(II) and Hg(II) and 1:2 for Cu(II), Co(II),

Ni(II) and Mn(II) complexes shown in Table 1. The stoichiometry of all the complexes confirmed by spectrophotometric method. The observed molar conductance Table 1 values measures in DMF solution fall in the range 12 – 20 $\text{Ohm}^{-1} \text{cm}^2\text{mol}^{-1}$. These observed values of the molar conductance are well within the expected range for non-electrolytic nature¹⁶.

Infrared Spectra

The significant IR bands for the ligand *N'*-(1-(5-bromo-2-hydroxyphenyl) ethylidene)-2-oxo-2H-chromene-3-carbohydrazide as well as for its metal complexes and their tentative assignments are compiled and represented Table 2. The broad band observed at 3462 cm^{-1} in the IR spectra of the ligand assigned to $\nu_{(\text{OH})}$, which were found to have disappeared in all their respective complexes, there by indicating the involvement of phenolic oxygen is bonding with metal ions through deprotonation. The band $\nu_{(\text{NH})}$ observed at 3180 cm^{-1} in ligand and complexes $\nu_{(\text{NH})}$ observed at 3180 – 3196 cm^{-1} respectively. A strong sharp band observed at 1667 cm^{-1} is assigned to coumarin ring $\nu_{(\text{C}=\text{O})}$, which was shifted to 9 – 32 cm^{-1} in all complexes, indicates the involvement of coumarin ring carboxyl in complexation with metal ion, the band at 1627 cm^{-1} is assigned to the azomethine $\nu_{(\text{C}=\text{N})}$ group, lowering of $\nu_{(\text{C}=\text{N})}$ 8-20 cm^{-1} in the complexes as compared to its ligand, is due to reduction of double bond character carbon-nitrogen bond of the azomethine group¹⁷. The band observed at 1241 cm^{-1} , of the ligand is attributed to phenolic $\nu_{(\text{C}-\text{O})}$ in view of previous observations¹⁸. This band is shifted to higher frequency and is found in the region 1241 – 1267 cm^{-1} (16-30 cm^{-1}) for the complexes. Thus, this further confirms the involvement of $\nu_{(\text{C}-\text{O}-\text{C})}$ in the complex formation. The low frequency skeletal vibrations due to $\nu_{(\text{M}-\text{O})}$ and $\nu_{(\text{M}-\text{N})}$ stretching provide direct evidence for complexation. In the present investigation the bands in the 525 – 521 cm^{-1} region for $\nu_{(\text{M}-\text{O})}$ and 480 – 457 cm^{-1} region for $\nu_{(\text{M}-\text{N})}$ vibration respectively. The bands due to $\nu_{(\text{M}-\text{Cl})}$ were observed in the 323 – 320 cm^{-1} region and are characteristics of chlorine atom in Zn(II), Cd(II) and Hg(II) complexes is further confirmed by quantitative chloride estimation.

Magnetic movement and Electronic spectra of the complexes

Copper (II) complex

The complexes having temperature independent magnetic moments in the range of 1.75 – 2.2 B.M. agreeable to the spin only value. These complexes are mononuclear having no major spin-spin interactions, however no compromise can be set between the magnitude of the distortion and other variable factors. The Cu(II) complexes with this behavior indicate marked spin-exchange and strong coupling interaction between Cu(II) atoms. As the spin only value for a single unpaired electron is 1.73 B.M. The slight excess over this value for the Cu(II) complexes can be attributed to spin orbital coupling. The observed magnetic moment values for the present Cu(II) complexes is 1.94 B.M.¹⁹. This value is expected for one electron system and is in the normal range of Cu(II) complex system. As the spin only values for a single unpaired electron is 1.73 B.M. The slight excess over this value found for the Cu(II) complex can be attributed to spin orbital coupling. In view of the above observations the magnetic moment values for the present Cu(II) complexes, suggest the distorted octahedral geometry around Cu(II) ions. Electronic spectra of Cu(II) complexes exhibit a broad, low intensity shoulder band. The 2E_g and ${}^2T_{2g}$ states of octahedral Cu(II) ion (d^9) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transition viz., ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$, to remain unresolved in the spectra. It is concluded that all three transition lie within the single broad band in the region 24500 – 31000 cm^{-1} , have been assigned to charge transfer bands from ligand to metal. The observation favor distorted octahedral geometry around Cu(II) complexes. A broad asymmetric band in the region 12495 – 16605 cm^{-1} , the symmetry being on the lower energy side²⁰. The broadness of the band may be due to dynamic John-Teller distortion. The band maxima observed for the present Cu(II) complexes is at 12095 – 16400 cm^{-1} , 12205 – 16425 cm^{-1} and 12300 – 16260 cm^{-1} suggest that the complex displays coordination number six. In addition, we have observed a high intensity band around 15065 cm^{-1} that can be attributed to the ligand- metal charge transfer transition.

Cobalt (II) complex

In octahedral Co(II) complexes the ground state is ${}^4T_{1g}$ and a large orbital contribution to the magnetic moment values for various Co(II) complexes are in the

range 4.12-4.70 B.M. and 4.7-5.20 B.M. for tetrahedral and octahedral complexes respectively. In present investigation the observed magnetic moment values is in the range 4.79 B.M.²¹, which indicates octahedral geometry for these Co(II) complexes. This is due to partial quenching of orbital contribution to the magnetic moment. Electronic spectra of Co(II) complex exhibits three bands in the region 9628-10250 cm^{-1} , 14612-15285 $^{-1}$ and 20733- 26854 cm^{-1} due to the transition. ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) = 9628-10250 cm^{-1} , ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) = 14612-15285 cm^{-1} and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) = 20833-26854 cm^{-1} These transitions suggest octahedral geometry. The region at 25550-26970 cm^{-1} refers to the charge transfer band. These transitions suggest octahedral geometry for the Co(II) complexes. These assignments are in good agreement with the reported values²².

Nickel (II) complex

Ni(II) complexes exhibits the magnetic moment value of 2.95 which are well within the range of expected value for octahedral geometry around the central metal ion²¹. Electronic spectra of Ni(II) complexes in octahedral coordination is ${}^3A_{2g}$, the Ni(II) complexes show three transition in an octahedral field, viz., ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; ν_1 7470- 8100 cm^{-1} , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$; ν_2 16500-17000 cm^{-1} ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$; ν_3 24814 -25000 cm^{-1} . The observed transition bands lie well within in the range of reported values. There values indicate considerable covalent character and support the octahedral geometry for the Ni(II) complex²³.

Manganese (II) complex

The observed magnetic moment values for Mn(II) complex of the ligand is in the range 5.70 B.M. The electronic spectra of Mn(II) complex shows three transition, which corresponds to the following transitions, ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$; ν_1 =15632-16500 cm^{-1} , ${}^6A_{1g} \rightarrow {}^4E_g(4D)$; ν_2 = 17523-18500 cm^{-1} , ${}^6A_{1g} \rightarrow {}^4T_{1g}(4D)$; ν_3 = 21753-22600 cm^{-1} These values indicate considerable covalent character and support the octahedral geometry²⁴. Hence under the present study octahedral geometry is suggested for Mn(II) complex.

Iron (III) complex

The observed magnetic moment value for Fe(III) complex of the ligand is about 5.73 B.M. which is well

within the range of expected for octahedral geometry²¹. The absorption spectra of high-spin Fe(III) complexes have been measured with difficulty. The ground state of high spin octahedral coordinated Fe (III) complexes is ${}^6A_{1g}$. A very sharp band at 25000cm^{-1} is due to the transitions to the accidentally degenerate ${}^4A_{1g}$ and 4E_g levels. The difficulty in assigning the transitions for high-spin Fe (III) complexes is mainly due to the charge transfer absorption which occurs at the lower energy in Fe (III) complexes, and often most of the d-d transitions are observed. The electronic spectrum exhibits three transition bands which are assigned to the following transitions; ${}^6A_{1g} \rightarrow {}^4T_{1g}(G); \nu_1=12471-12880\text{cm}^{-1}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G); \nu_2=16220-16540\text{cm}^{-1}$, ${}^6A_{1g} \rightarrow {}^4E_g(G); \nu_3= 23784 -24112\text{cm}^{-1}$. These values suggest the considerable covalent character and support the octahedral geometry²⁵.

${}^1\text{H}$ NMR Spectra

Spectrum of ${}^1\text{HNMR}$ is DMSO- d_6 solvent used. In ligand N' -(1-(5-bromo-2-hydroxyphenyl)ethylidene)2-oxo-2H-chromene-3-carbohydrazide showed the sharp peak at δ 10.12 (S, 1H) due to OH at 2-position of phenyl ring of 1-(5-bromo-2-hydroxyphenyl)ethanone moiety has resonated, but in the case of Zn(II) complex which has been disappeared indicating the involvement of phenolic oxygen in the coordination *via*, deprotonation²⁶. A single large peak showed at δ 2.55 (S, 3H, CH_3) due to protons of the azomethine group in ligand but in case of Zn (II) complex the peak observed at δ 2.50 (S, 3H, CH_3)²⁷. The Eight aromatic protons due to coumarine and phenyl rings have resonated in region δ 6.97- 7.80 (m, 8H, Ar-H) as a multiplet, in Zn (II) complex the eight aromatic protons have been observed in the region δ 6.87-7.78 (m, 8H, Ar-H) as a multiplet. The Zn(II) complex suggests coordination of the phenolic OH with metal ion.

X-ray powder diffraction studies

X-ray powder diffraction pattern for Hg(II) complex has characterized with a view to find the type of crystal system the XRD data given the table the diffractogram of Hg(II) complex consists of ten reflections in the range of 13-70 (2θ value) with maxima at $2\theta = 15.31^\circ$ The interplanar spacing(d) has been

calculated from the position of intense peaks using Bragg's equation $n\lambda = 2d \sin \theta$ $d = 1.5406 / \lambda \sin \theta$ The observed and calculated values of d are quite consistent (Table 4) The unit cell calculations have been carried out for the cubic system, the set of $h^2 + k^2 + l^2$ values of the complex were found to be 1,2,3, 5, 6, 7, 9,10, 12 and 16 which corresponds to the planes and presence of forbidden number (7) confirms the hexagonal or tetragonal symmetry from the above results the unit cell constants for hexagonal system were found to be $a=b=c = 15.456 \text{ \AA}$ for the Hg(II) complex of the ligand the complex showed broad peak indicates amorphous nature²⁸⁻²⁹.

Thermogravimetric Analysis of Fe (III) complex.

The thermal decomposition studies of the Fe(III) complex has been carried out. In the thermogram of the complex $(\text{Fe}(\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4)\text{Br}.\text{Cl}_2.\text{H}_2\text{O})$, the loss of coordinated water molecule ($-\text{H}_2\text{O}$) and chlorine atom ($-1/2\text{Cl}_2$) observed at 243.33°C is indicated by an inflexion in the curve at 243.33°C , with the weight loss of 10.042%, this practical weight loss is in agreement with the theoretical weight loss of 10.37% The resultant intermediate complex underwent further degradation and gave another break at 357.92°C with weight loss of 39.01% which correspond to the $-\text{C}_{10}\text{H}_5\text{N}_2\text{O}_2$ species. This practical weight loss of 38.88% the third inflection occurred at 546.75°C with weight loss of 12.92% which account for the weight loss of $-\text{HCl}$ species. This accordance with the theoretical weight loss of 12.86% Thereafter the complex showed gradual decomposition upto 1050°C and onwards. The weight of the residue corresponds to the formation of Fe_2O_3 .³⁰ The decomposition of $(\text{Fe}(\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4) \text{Br}.\text{Cl}_2.\text{H}_2\text{O})$ is given in Table 5.

Antibacterial activity

The antibacterial activity results revealed that the ligand and its complexes shown weak to good activity (Table 6). The ligand and its Cu(II), Hg(II), Ni(II) complexes shows weakly active with the zone of inhibition 10-13 mm against the both organisms when compared to the standard drug streptomycin. The Mn(II), Co(II), Cd(II) shows active and moderate activity as compared to its ligand with zone of inhibition 15-17 mm and 18-20 when compared to the standard drug streptomycin³¹⁻³².

Antifungal Activity

The antifungal activity, results revealed that the ligand and its Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) complexes have exhibited weak to good activity (Table 6). The ligand and its Co(II), Fe(III) complexes shows weak activity with zone of inhibition, the Cu(II), Ni(II), Mn(II), Zn(II), Cd(II), Hg(II) shows moderate activity as compared to its ligand with the zone of inhibition 15-17mm, to good activity with the zone of inhibition of 18-20mm when compared to the standard drug clotrimazole³³.

IV.

CONCLUSION

The elemental analysis, magnetic susceptibility, electronic spectra, IR, ¹H NMR, ESR spectra and thermal data observations projects the following structures for these complexes where in Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) are exhibit six coordinated octahedral geometry and whereas Zn(II), Cd(II) and Hg(II) are exhibit four coordinated tetrahedral geometry.

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