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THERMOGRAVIMETRIC AND ANDDNA CLEAVAGE STUDIES OF SOME LIGANDS AND ITS METAL COMPLESES

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ABSTRACT

The Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) complexes of Schiff base *N'*-(1-(5-bromo-2-hydroxyphenyl)ethylidene)2-oxo-2H-chromene-3-carbohydrazide
Has been synthesized and characterized by various spectral techniques. 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. By these 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 DNA Cleavage activities. The prepared ligand shows low activity and its metal complexes shows moderate to good activity.

Key words: Schiff base, Thermal studies, Metal complexes and DNA Cleavage

INTRODUCTION

Coumarins are important and well-known naturally occurring oxygen containing heterocyclic compounds. Coumarin derivatives have great importance for their physiological, photodynamic and bacteriostatic activities[1-8]. 7-hydroxy coumarin is known for its antibiotic and antifungal activities[9-10].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 chemotherapeutics[11-12]. 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 reactions[13-14]. 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 agents[15].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 for. On the basis of this, we have synthesized ligand and its metal complexes and their coordination behavior were investigated.

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 recrystalized 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%) [15-20].

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. The stoichiometry of all the complexes confirmed by spectrophotometric method. The values measures in DMF solution fall in the range 12 – 20 Ohm^{-1} cm^2mol^{-1}. These observed values of the molar conductance are well within the expected range for non-electrolytic nature[20-25].

Thermogravimetric Analysis of Fe (III) complex.

The thermal decomposition studies of the Fe(III) complex has been carried out. In the thermagram of the complex ($Fe(C_8H_{12}N_2O_4)Br.Cl_2.H_2O$),the loss of coordinated water molecule($-H_2O$) and chlorine atom($-1/2Cl_2$) observed at 243.33^0C is indicated by an inflexion in the curve at 243.33^0C, 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 357.92^0C with weight loss of 39.01% which correspond to the $–C_{10}H_5N_2O_2$ species. This practical weight loss of 388.88% the third inflection occurred at 546.75^0C with weight loss of 12.92% which account for the weight loss of –HCl species. This accordance with the theoretical weight loss of 12.86% Thereafter the complex showed gradual decomposition upto 1050^0C and onwards. The weight of the residue corresponds to the formation of Fe_2O.[25-30] The decomposition of ($Fe(C_8H_{12}N_2O_4)Br.Cl_2.H_2O$).

Thermal decomposition of Fe(III) complex

Complex	Stage	Peak Temp. TG (^{0}C)	Loss of Mass (%)		Probable Assignments
			Practical	Theoretical	
$(Fe(C1_8H_{12}N_2O_4)Br.Cl_2.H_2O)$	-	-	-	-	$[Fe(C_8H_{12}N_2O_4)Br.Cl_2.H_2O]$
	I	243.33	10.042	10.037	$\downarrow$ $-H_2O$, $-1/2Cl_2$

	II	357.92	39.01	38.88	$[Fe(C_8H_{12}N_2O_4)Br.Cl.]$ ↓ $[C_{10}H_5N_2O_2]$ $[Fe(C_8H_7O_2)Br.Cl.]$ ↓ -HCl $[Fe(C_8H_6O_2)Br]$ ↓ $(C_8H_6O)Br$ Fe_2O
	III	546.75	12.92	12.86	

DNA CLEAVAGE STUDIES

The DNA cleavage activity of Schiff's base, and their Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) complexes were studied by agarose gel electrophoresis method[31]. The gel after electrophoresis clearly revealed that, all the metal complexes have acted on DNA and shows the complete cleavage Mn(II) and Mn(II) appears to bind DNA, due to which the DNA band has significantly shifted its position. It also has shown disrupt band, may be because of partial cleavage. So, Mn(II) analysis is inconclusive. As there was molecular weight difference between the control and the treated DNA samples[32]. This shows that, the control DNA alone does not show any apparent cleavage where as Schiff's base, L^1=HMOHAD and their complexes shown. The results indicated the important role of metal in these isolated DNA cleavage reactions. However, the nature of reactive intermediates involved in the DNA cleavage by the complexes has not been clear. As the compounds were observed to cleave the DNA, it can be concluded that the compounds inhibits the growth of the pathogenic organism by cleaving the genome[33-34].

Gel electrophoresis pictures of Schiff's base ligands and their Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(III) complexes. Photograph showing the effects of transition metal complexes on DNA of Calf-thymus. Lane M (DNA marker), Lane C (Untreated DNA).

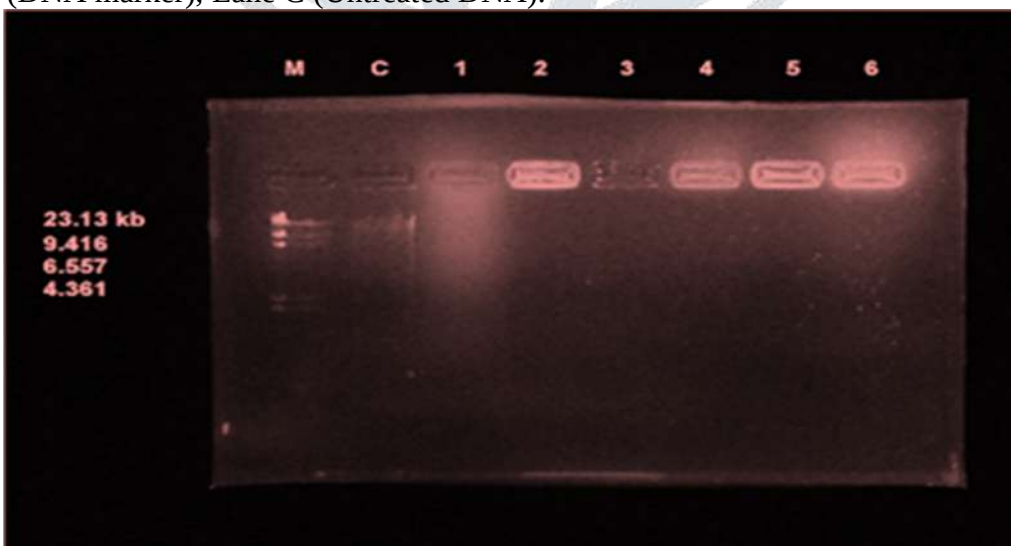
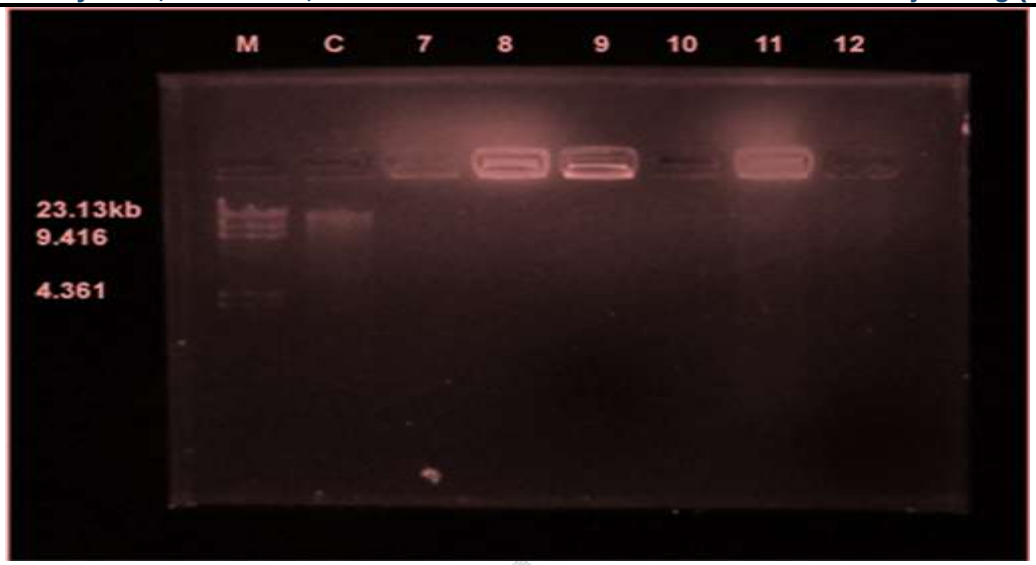


Figure-3. Lane 1 (ligand, L^1), Lane 2 (L^1 Cu(II)), Lane 3 (L^4), Lane 4 (L^4 Co(II)), Lane 5 (L^6), Lane 6 (L^6 Mn(II).



CONCLUSION

The Schiff's base ligands **L^4, L^5**and**L^6**behaved as a hexadentate ligand and their complexes are isolated in solid state possess 1:1 (M: L) stoichiometry and these are all non-electrolytic behavior of the complexes. The DNA cleavage studies of ligands and its metal complexes that reveals that theresults indicated the important role of metal in these isolated DNA cleavage reactions. However, the nature of reactive intermediates involved in the DNA cleavage by the complexes has not been clear. As the compounds were observed to cleave the DNA, it can be concluded that the compounds inhibits the growth of the pathogenic organism by cleaving the genome.

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