



Synthesis of physico-chemical characterization and antimicrobial activity of Cobalt (II), Nickel (II) and Zinc (II) complexes with new Schiff base ligand of 3-amino coumarin

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Abstract: Metal complexes have been synthesized and characterized with the help of elemental analysis, electrical conductance, I.R, ¹HMR, ¹³CNMR, magnetic susceptibility measurements. Magnetic moment values and electronic spectral values indicates spin free and octahedral structure for cobalt, nickel and zinc complexes with the ligands and their metal complexes show a significant antimicrobial activity against various bacteria.

Keywords : (3E)-3-(2-Chlorobenzylideneamino)-2H-chromene-2-one(CBAC), metal(II) complexes, biological activity, characterization.

1.0. Introduction

A considerable interest is being shown in the phenomenon of metal chelation in biological system. The role of several drugs in relation to metal binding has been established ^[1, 2]. Biological activity of coumarin nucleus and related derivatives has great important effects like antibacterial³, insecticidal⁴, antimutagenic⁵, antithrombotic and vasodilatory⁶. Several reviews summarize advances in various medicinal applications of metal complexes of coumarins^[7,8]. The biological activity of some coumarin derivatives significantly enhances by binding to metal ions ^[9,10]. A broad array of medicinal applications of metal complexes of coumarins has been investigated. It was found that in some cases the metal complexes obtained revealed higher biological activity than their ligands^[11, 12]. Thus, the aim of present work is to synthesize, characterize and study biological activities of transition metal complexes with newly synthesized Schiff base CBAC.

2.0. Materials and Methods

2.1. General Procedures:

All the chemicals used were either of AR or chemically pure grade. The melting points were determined On a Buchi-510 apparatus. Mass spectrum was recorded on a PerkinElmer Hitachi-6L spectrometer and ¹H NMR spectra was recorded in CDCl₃ at room temperature using TMS as internal standard on a Bruker WH 300(400MHz) Varian Gemini-100MHz. IR spectra were recorded using KBr discs in the 4000–200 cm⁻¹ region on a Shimadzu IR-435. U.V- Visible spectra were recorded with Shimadzu U.V-160A. U.V. visible double beam Spectrometer with matched quartz cell of path length 1cm. The elemental analysis was carried out using Perkin-Elmer CHN analyzer. Magnetic susceptibilities of complexes were measured on a Faraday balance CAHN-7550-03 USA at room temperature using Hg[Co(NCS)₄] as calibrant. Diamagnetic correction using Pascal's constants and temperature independent paramagnetic correction were computed. The electrical

conductance measurements were recorded using 10–3M solutions in with dichloro methane at 25C Dig Sun digital conductivity bridge (Model DL-909.) and dip type cell calibrated with KCl solutions. DTA and TGA was carried out using mettle instrument.

2-chloro-benzylidene-3-aminocoumarin (CBAC)

To a 0.05 mole of 3-amino-coumarin dissolved in hot methanol, a 0.05 mole of a methanolic 2-chloro benzaldehyde was added and refluxed for eight hours. Light brown colored compound that separated out was filtered and washed with methanol. The product was found to be TLC pure in 3:7 ethylacetate and n-hexane. Yield 78%; m.p.180 °C; FTIR-(KBr) (in cm⁻¹):1712 (ν C=O), 1603 (ν C=N)1460 cm⁻¹.The mass spectrum of the compound exhibited the characteristic signal at m/z 283.

Metal complexes

A general method was used for the preparation of all the three complexes. A hot methanolic solution of the ligand was added to a methanolic solution of the metal chloride. After complete addition the metal to ligand mole ratio was always kept as 1:2. A distinct and the contents were refluxed on a hot water bath for 5-11 h. The separated Solid complexes were filtered, washed with methanol, petroleum ether and dried in vacuum desiccators over P₂O₅.

Co(II) complex: yield 65%; m.p: 1720 °C ; FTIR (KBr) (in cm⁻¹): 1676 (ν C=O), 1587 (νC=N), 468 (νCo-N), 456 (νCo-o), 312 (νCo-cl), cm⁻¹ (new bands)FTIR; Anal. Calcd for CoC₃₂H₂₀N₂O₄Cl₄: Co, 8.45; C,55.12; H,2.89; N, 4.02; Cl, 7.01 %. Found: Co, 5.73; C, 56.11; H, 2.92; N, 8.15; Cl, 6.91%.

Ni(II) complex: yield 80%; m.p. 1620 °C ; FTIR (KBr) (in cm⁻¹): 1721 (ν C=O), 1604 (νC=N), 522(ν Ni-N),450(νNi-O),319 (νNi-Cl) cm⁻¹ Anal. Calcd for NiC₃₂H₂₀N₂O₄Cl₄: Ni, 2.79; N, 7.80; Cl, 9.89 %. Found: Ni, 8.04; C, 52.75; H, 2.75; N, 7.71; Cl, 9.75%.

Zn(II) complex: yield 70%; FTIR (KBr) (in cm⁻¹): 1696(ν C=O), 1585 (ν C=N), 521 (νZn-N), 466 (νZn-o), 318 cm⁻¹ (νZn-Cl), (new bands);

Anal. Calcd for Zn C₃₂H₂₀N₂O₄Cl₂: Zn 9.25; C, 54.06; H, 2.86; N, 3.96; %.⁽¹³⁾

3.0. Results and Discussion:

The reaction of 3-aminocoumarin (AC) with 2-chlorobenzaldehyde (CB) resulted in 2-chloro benzylidene-3 aminocoumarin (CBAC) in 75% yield which was purified by TLC. Elemental analysis indicates that the ligand, CBAC, has the molecular formula C₁₆H₁₀NO₂Cl. The mass spectrum shows parent peak at m/e 283 which is consistent with the molecular formula. The NMR spectrum of the ligand reveals the presence of –CH proton of the coumarin moiety at δ6.34. The ring protons of the coumarin are identified in the region of δ7.12 to δ7.38. The CH–proton of the azomethine group is appearing at δ8.35.

3.1. Characterization of metal complexes

The complexes are found to be stable under atmospheric conditions. They are soluble in methanol and DMSO. The analytical data show metal to ligand ratio of 1:2 in Ni(II) and Co(II),

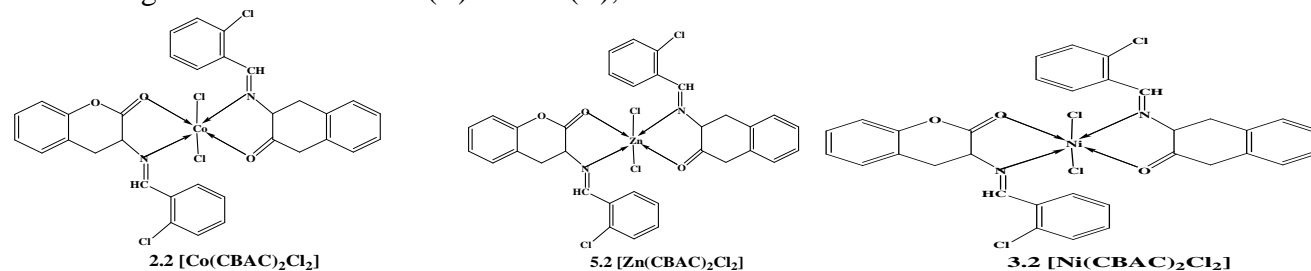


Fig. 1: Structure of Co (II), Zn & Ni (II) complexes

4.0: Biological activity:

Table 1. Preliminary antibacterial screening of new Schiff base ligands against four different bacteria: Zones of inhibitions of ligands against four different bacteria

S. No.	Ligands	Conc. (µg/ml)	Zone of inhibition (mm)			
			MTCC-619	MTCC-96	MTCC-722	MTCC-109
STD.	Streptomycin	40 units	15	13	20	20
1.	CBAC	1000	10	09	-	-

The investigated compounds were categorized into four classes according to their anti bacterial activity (zone of inhibition) and the number of bacteria. Class-I: Active on all four strains, Class-

Table 2. Preliminary antibacterial screening of Co(II), Ni(II), and Zn(II) complexes against four different bacteria: Zones of inhibitions of Co(II) complexes against four different bacteria.

S. No.	Co(II) complexes (1000 µg/ml)	Zone of inhibition (mm)			
		MTCC-619	MTCC-96	MTCC-722	MTCC-109
1	[Co (CBAC) ₂ C]	15	13	13	08
2	[Ni (CBAC) ₂ Cl ₂]	16	14	15	10
3	[Zn (CBAC) ₂ Cl ₂]	17	15	17	14

The new Schiff base metal complexes show more increased activity than corresponding ligand

Ni(II) and (Zn) complexes. The presence of two chlorides per every divalent is also evidenced by analytical data. The molar conductance measurements The molar conductance values for the Schiff base Co(II), Ni(II) and (Zn) complexes (10⁻³M) are determined in dichloromethane. These values are found to be low (10.5-15.6 ohm⁻¹cm²mol⁻¹) indicating non-electrolytic nature of the complexes and also indicating that all ligands are placed in coordination sphere. There was sharp modification between the IR spectra of the metal Complexes and the ligands. The IR spectra of the complexes indicate two distinct patterns of metal binding by CBAC. In these complexes, the ligand behaves as a neutral bidentate ON donor, binding to metal ions through the azomethine nitrogen and the oxygen of nitro group¹⁸. The room temperature magnetic moments reflect the paramagnetic nature of all the complexes. These values are consistent with a spin free configuration.⁽¹⁴⁻¹⁷⁾

because the chelation reduces the polarity of metal ion due to the partial sharing of its positive charge

with the donor groups of ligands. Such chelation increases the leophophilic character of the metal complexes which is necessary to cross the permeability barrier of cells resulting in

interference with normal process of bacteria. The trend of growth inhibition against all the four types of bacteria is found to be in the order Ni>Co>Zn.⁽¹⁸⁻²¹⁾

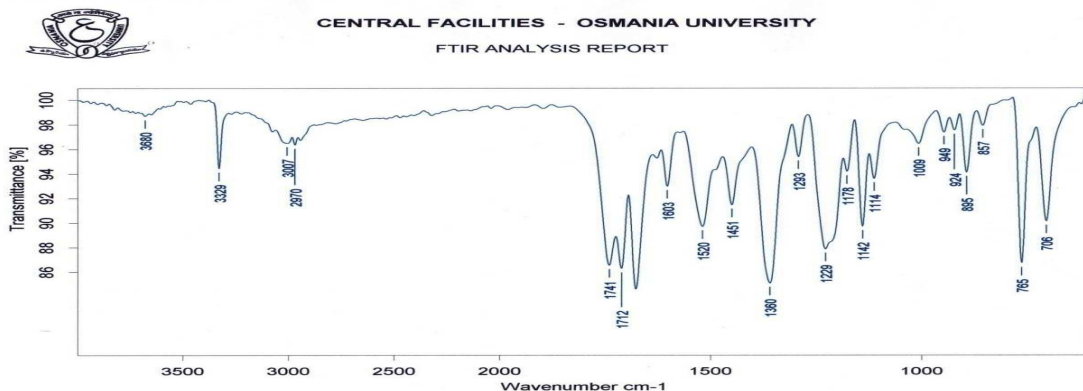


Fig.3.1.3 IR Spectrum of CBAC

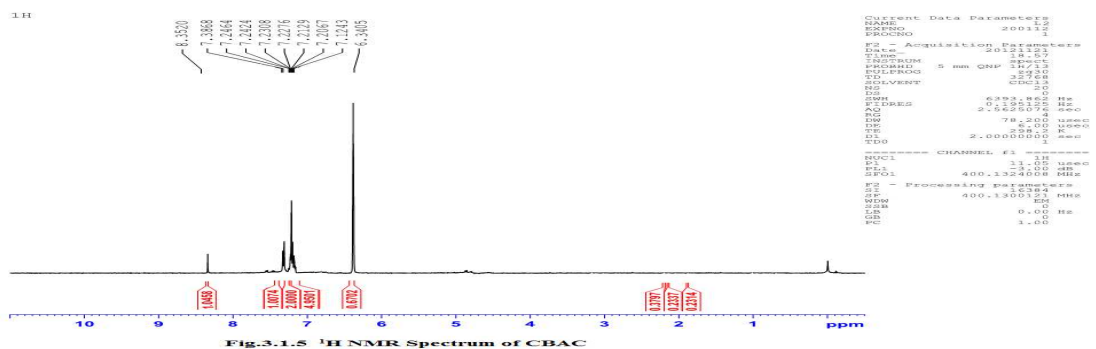


Fig.3.1.5 ¹H NMR Spectrum of CBAC

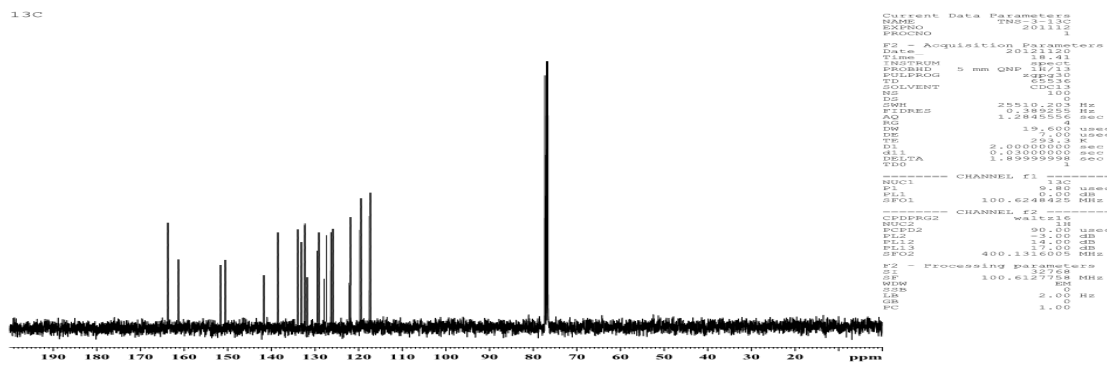


Fig.3.1.7 ¹³C NMR Spectrum of CBAC

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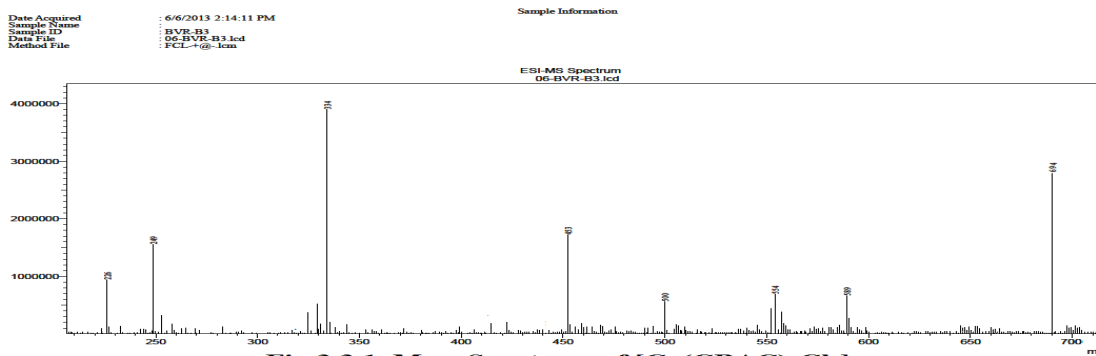


Fig.3.3.1 Mass Spectrum of [Co(CBAC)₂Cl₂]

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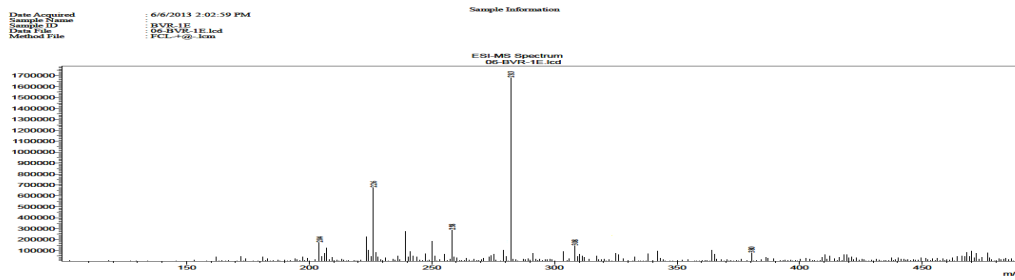


Fig.3.1.1 Mass Spectrum of CBAC



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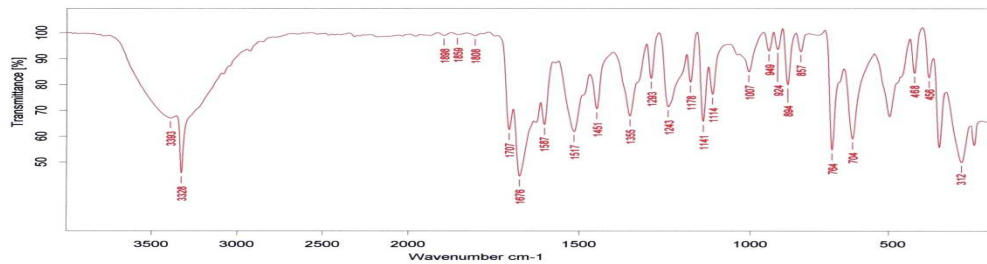
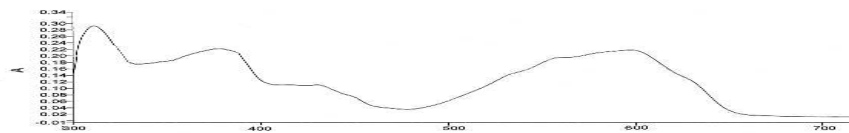


Fig.3.3.5 IR Spectrum of [Co(CBAC)₂Cl₂]



Peak No.	Position (nm)	Intensity	Type
1	629.0	0.2093	Peak
2	427.4	0.1021	Peak
3	373.5	0.3275	Peak
4	305.5	0.3275	Peak

Fig.3.3.7 Electronic spectrum of [Co(CBAC)₂Cl₂]



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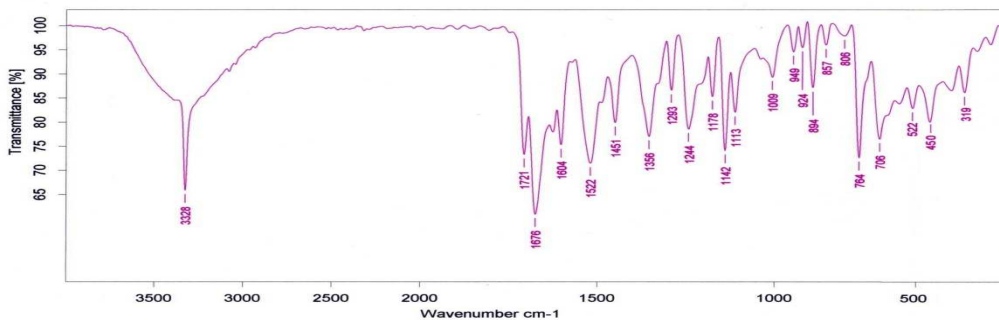


Fig.3.4.5 IR Spectrum of [Ni(CBAC)₂Cl₂]

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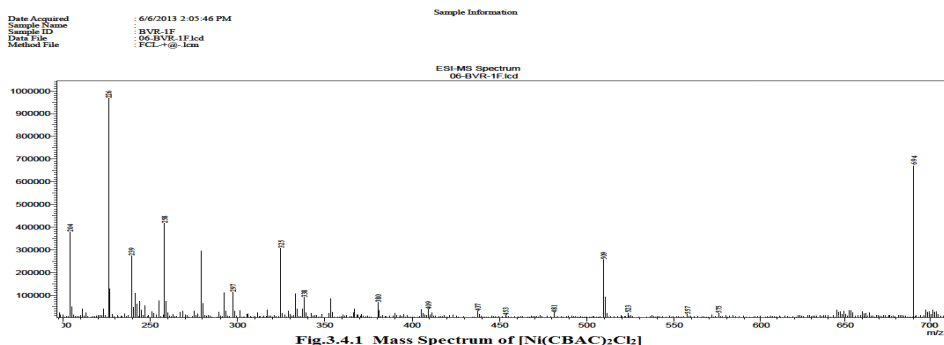


Fig.3.4.1 Mass Spectrum of [Ni(CBAC)₂Cl₂]

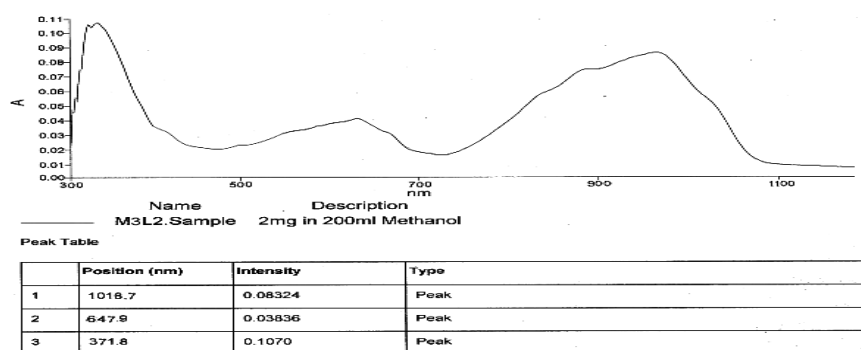


Fig.3.4.7 Electronic spectrum of $[\text{Ni}(\text{CBAC})_2\text{Cl}_2]$

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