Synthesis and Antimicrobial Study of Complexes of New Schiff's Bases derived from 3-Acetyl-4-Hydroxy-2*H*-Chromen-2-One & Semicarbazide with Cu (II) And Ni (II) Metals

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Abstract: ***Cu (II) and Ni (II) Metal complexes of 3-acetyl-4-hyrdoxy-2H chromen-2-one and semicarbazide are synthesized by various methods. In the present work they are synthesized by reacting methanolic solution of ligand and metal chloride followed by precipitating the complex by addition of alcoholic ammonia. The ligand to metal ratio for copper and nickel complexes is 2: 1 suggesting monomeric nature All the Cu (II) and nickel (II) complexes synthesized are coloured and stable to air and moisture. Most of them decompose at high temperature. They are insoluble in water, common polar and non-polar solvents. The complexes are sparingly soluble in methanol, ethanol, chloroform, dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The complexes were synthesized and characterized by elemental analysis, IR, electronic spectra, molar conductance, TGA and powder XRD. The antimicrobial activities of the ligand and their metal complexes were screened by Agar cup method.***

Keywords: 3-acetyl-4-hyrdoxy-2H chromen-2-one, Semicarbazide, transition metals, antimicrobial activities

1. Introduction

Schiff's bases and their metal complexes has been the subject of intensive research due to their novel structural features, interesting spectral and magnetic properties. They are important because of their application in various fields like food, medical, agricultural, analytical, biological and industrial fields. Applications of Schiff's base ligands and their metal complexes are observed mainly in area of food production [1] dye intermediates and products [2], medicinal [3], analytical chemistry [4], catalysis in chemical transformation [5], antimicrobial activity [6], antiulcer activity [7] in organic electroluminescent (EL) devices [8, 9], in Nonlinear optics (NLO) [10, 11] in electrochemical sensors [12], as liquid crystal [13], and metal corrosion inhibition; [14]. Many metal chelates were reported to possess antitumor and antineoplastic activities [15].

In the present work, we have opted to synthesize ligands (L1) by condensing amines such as hydrazinecarboxamide (semicarbazide) with 3-acetyl-4-hydroxycoumarin (3-acetyl-4-hydroxy-2H-chromen-2-one) LigandL1. (II) &Ni (II) metal complexes synthesized from ligand L1.

2. Materials and Analytical Methods

Chemicals of good quality (AR) grade were used throughout the experimental work. Solvents: Methyl alcohol and Ethyl alcohol and chloroform were used for synthesis of Schiff base and their transition metal complexes. The solvents were purified by distilling over dry calcium oxide. All other solvents the synthesized Schiff base was soluble in methanol and their complexes with Cu (II) & Ni (II) were soluble in DMSO. Therefore their Electronic spectra in this solvent were recorded on SHIMADZU-UV-1601 UV/visible double beam spectrophotometer in the region 200-800 nm using quartz tubes of 1 cm path length. Infrared spectra of the ligands and metal complexes were taken as KBr pellets on Shimadzu spectrometer and some Infrared spectra were recorded as KBr pellets on FTIR-4100 spectrophotometer.

The solution conductivities of the metal complexes in DMSO were measured on digital conductivity bridge at room temperature. The conductivity cell with platinized platinum electrode with a cell constant 1.001 cm-1 was used. Gouy's method was used for the measurement of magnetic susceptibility of the compounds at room temperature.

3. Experimental

Procedure for Preparation of L1 ligand:
3-acetyl-4-hydroxy-2H-chromen-2-one was prepared as per previous reported method [16]. The imines L1 was prepared by adding 3-acetyl-4-hydroxy-chromen-2-one (0.01mole) and semicarbazide (0.01 mole each) in ethanol (50 ml) and refluxing the mixture for 4 hrs. After cooling, the product was crystallized from ethanol. The purity of the ligands waschecked by m. p. and TLC.

Procedure for synthesis of Metal complexes:
0.02 moles (for copper and nickel complexes) of ligand L1 was taken in round bottomed flask containing 30ml of methanol and refluxed for few minutes.0.01 moles of metal salt dissolved in 20ml of methanol was added drop wise in hot solution of ligand. The contents were refluxed for two hours. Solution was cooled and precipitation was not found. Ten percent alcoholic ammonia solution was added drop wise with stirring till precipitation was observed. The pH of precipitation for each complex was noted.

The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The precipitate of complex formed was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40–600°C) and dried in vacuum desiccators over calcium chloride.

4. Result and Discussion

Data of 2-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidene) hydrazinecarboxamide L1:

Color: yellow; Yield: 88%; M. P.230°C; IRIR (KBr, cm-1): 3500-2600 (3464, 3293, 3154) (broad Phenolic VOH, VNH2), 1708 (VC=0) of lactone, 1666 (VC=0) of sermicarbazide, 1606 (Vc=N) of imine, 1538 & 1490 aromatic (VC=C), 1366 (VC-0) Phenolic 0H.).

The color, meting/decomposition temperature, conductivity measurement and elemental analysis of Cu (II), Ni (II) synthesized from ligand L1 are shown in the table

Table 1: Physical &Analytical data

Compound	Molecular formula	Formula Wt	PH range of precipitation	Color	M. P. °C	M: L ratio
[cu (L1) 2]	[Cu (C12H10N3O4) 2]	584.00	7.5-8	Dark Green	192	1: 2
[Ni (L1) 2]	[Ni (C12H10N3O4) 2]	579.14	7.5-8	Green	234	1: 2

Table 2: Elemental analysis data

Compound	M. F	Elemental analysis found (calculate)						
		%C	%H	%N	%Cl	%S	%Cu	%Ni
[cu (L1) 2]	[Cu (C12H10N3O4) 2]	49.32 (49.36)	3.40 (3.45)	14.36 (14.39)	---	---	10.84 (10.88)	
[Ni (L1) 2]	[Ni (C12H10N3O4) 2]	49.75 (49.77)	3.43 (3.48)	14.48 (14.51)		---	--- -	10.09 (10.13)

Infrared Spectra:

Infrared spectral study of metal complexes was recorded for examination of bonding pattern in the synthesized complexes. The assignments to each bonding mode are supported by literature values. Important absorption bands are presented in Table No 3 and spectra are revealed in Table No3. The comparison of IR spectral data of all the complexes and corresponding ligands helps in concluding the bonding pattern of each complex.

Table 3: Infrared Absorption Frequencies (cm-1) of 2-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidene) hydrazinecarboxamide (L1) complexes

Sr No	Ligand/ Complex	Bond vibrational modes (stretching-v)					
		Lactone	Hydrazide	Azomethine	Enolic	Newpeaks.	
		(C=O)	(C=O)	(C=N)	(C=O)	M-O	M-N
1	L1	1708	1666	1606	1366	---	---
2	Cu (L1) 2	1708	1657	1583	1378	555	427
3	Ni (L1) 2	1710	1652	1589	1477	540	424

Electronic Spectra:

The electronic absorption spectra of each Cu (II) complexes showed a broad in the range of (625 to 610 nm) 16000-16394 cm-1, (810 to 790 nm) 12345-12658 cm-1 and a charge transfer band (370 to 350 nm) 27027-28571cm-1. These observed bands may assigned to transition 2Eg→2T2g. These values fall within the range of many distorted octahedral Cu (II) complexes reported earlier [17-19].

The electronic spectra of Ni (II) complexes studied in the present investigation exhibit a regular pattern of absorption bands in three regions as expected for octahedral geometry. V1 = 11236-11494 cm-1, V2 = 16233-16393 cm-1 and V3 = 27777 cm-1. These observed bands may be assigned to three spin allowed transition 3A2g→3T2g, 3A2g→3Tlg (F) and 3A2g→3Tlg (F) charge transfer band respectively which are characteristic of distorted octahedral field [20,]. The electronic spectra of these complexes are given in Table No 4 and their spectral data are presented in Table no 4.

Table 4: Electronic Absorption Spectral Data of Cu (II) &Ni (II) complexes

Complex	Absorption Maxima cm-1 (nm),		
	V_1	V_2	V_3
Cu (L1) 2	12345 (810)	16130 (620)	28571 (350)
Ni (L1) 2	11494 (870)	16393 (610)	27777 (360)

Antibacterial Activity

Antibacterial activity was tested by Agarcup method

Test suspensions of Gram positive and Gram negative bacteria. The test complexes have been subjected to in vitro screening by Agar cup method against Gram positive and Gram negative bacterial strain. Nutrient Agar was prepared & sterilized at 1.5 psi for 15 min in the autoclave. It was cooled below 450C & seeded with turbid suspension of test bacteria a separately prepared from 24 hours old slant cultures. Every time 3% Inoculates was made. The bacterial cultures selected were two types Gram negative cultures e. g. E. coli, Salmonella typhi, two Gram positive cultures staphylococcus aureus, Bacillus subtilis. There preparation were then poured separately in sterile petriplates under aseptic condition and allowed to solidify. Then the plates were shifted to incubator at 370 C and incubated for 24 hours. After incubate on plates were observed for the zone of inhibition of bacterial growth ground the Agar cup measurement of inhibition zone.

The zones of inhibition found around each dies were measured by means of calipers. The end point was taken as the complete inhibition of growth as it appeared to the unaided eye. The diameter of zones were recorded and reported as resistant or sensitive to each microbial tested. The complexes have been tested for their antibacterial activity with the help of pour plate method. Results are shown in the following table No 5.

Table 5: Antibacterial Activity:

Compound	Zone of inhibition (diameter in mm)			
	E. coli	*S. typhi*	*S. aureus*	*B. subtills*
penicillin	26	20	23	15
(L_1)	12	-	9	8
Cu $(L_1)_2$	20	9	17	9
Ni $(L_1)_2$	18	8	13	7

Antifungal Activity:
Antifungal activity was carried out by poison plate method. The medium was potato Dextrose Agar.

Contents of potato Dextrose Agar:
200gm Potato, 20gm Glucose, 30gm Agar, 1000 ml Distilled water.38

Procedure:
The medium was prepared and sterilized at 10 psi in autoclave for 15 minutes. Then the compound to be tasted in added to the sterile medium in aseptic condition so as to get final concentration on 1%. A plate with ethanol was prepared as blank i. e. called negative control similarly a plate with 1%. Gresiofulvin was prepared as standard reference plate i. e. called positive control.

Aspergillus Aigar, penicillium chrysogenum, fusarium moneliforme, Asprgillus flavus were selected as test fungal cultures. They were allowed to grow on slant and spores were scraped with the help of michrome wire loop to form suspension. The fungal suspension was inoculated on the plate's prepared using compounds with the help of michrome wire loop. The plates were cubated at room temperature for 48 hours.

After incubation plates were observed for the growth of inoculated fungi. Results were recorded in Table No 6

Table 6: Antifungal Activities

Compound	Growth of fungi			
	A. niger	*P. chrysogenum*	*F. moneliforme*	*A. flavus*
Gresiofulvin	-	-	-	-
(L_1)	+	++	++	+
Cu $(L_1)_2$	-	-	-	-
Ni $(L_1)_2$	-	+	-	+

Moderate growth (++), Reduced growth (+) and No growth (-) of fungi.

Anti-bacterial activity: all Schiff's bases have shown lesser activity against Staphylococcus aureus, Escherichia coli, Bacillus substiis, Salmonella typhi compared with penicillin taken as standard.

The decreasing order of antibacterial activity for Ligand complexes in the order of Cu (II) >Ni (II).

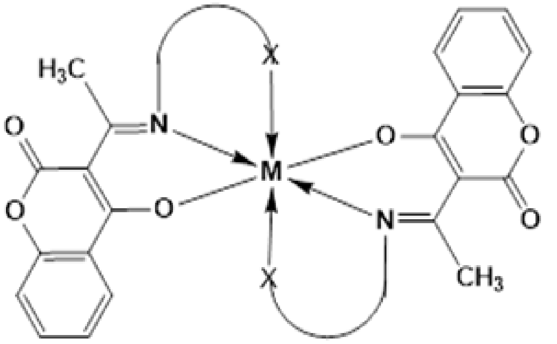
Anti-fungal activity: Anti-fungal activity observed against various species like A. niger, P. chrysogenum, F. moneliforme and A. flavus compared with Grisiofulvin taken as standard.

The metal complexes and their corresponding ligand show anti-fungal activity It means compounds are reactive as anti-fungal agents. The decreasing order of anti-fungal activity for ligand complexes.

5. Conclusion

Hence on the basis of elemental analysis, IR spectra, UV, spectra, magnetic moment data, conductivity measurement data, following octahedral structures are proposed for Cu (II) & Ni (II).

Structure



Structure I: Monomeric octahedral Structure of Cu(II), andNi(II) Complexes with Ligand L_1
Where X= O

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