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Studies of Zn (II) and Cd (II) Metal Complexes with New Schiff's Base N'-(1-(4-hydroxy-2oxo-2H-Chromen-3-yl) Ethylidene) Benzohydride

V. V. Kodgire[1], G. B. Pande[2], M. R. Deshpande[3]

[1]Department of Chemistry, N.S.B, College Nanded, Maharashtra, India

[2]Department of Chemistry, N.S.B, College Nanded, Maharashtra, India

[3]Department of Physics, N.S.B, College Nanded, Maharashtra, India

Abstract: ***Zn (II) and Cd (II) metal complexes of new Schiff's base N'-(1-(4-hydroxy-2oxo-2H-Chromen-3yl)ethylidene) benzohydrideare synthesized by various methods. In present work they are synthesized by reacting methanolic solution of 3-acetyl-4-hydroxy-2Hchromen-2-one and benzohydride with metal chlorides followed by precipitating the complexes by addition of alcoholic ammonia. The metal to ligand ratio for Zinc & Cadmium complexes is 1:1 suggesting monomeric nature. Zn (II) and Cd (II) metal 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 dimethylsulphoxide (DMSO). The complexes were synthesized and characterized by elemental analysis, IR, electronic spectra, molar conductance, TGA and powder XRD.***

Keywords: 3-acetyl-4-hydroxy-2H-chromen-2-one, benzohydrazide, transition metals Zn and Cd

1. Introduction

Schiff's bases are important in the progress of chemistry of coordination compound. In recent years, metal complexes prepared from Schiff's bases have been examined to a great extent as they possess their wide range of applications in numerous scientific areas due to physical and chemical properties. Schiff's base complexes are concentrated to larger extent in study of their catalytic activity in homogeneous and heterogeneous reactions. Schiff bases are very important due to their modified structures, a wide spectrum of biological and industrial application [1-2]. They possess pharmacological activities such as antimicrobial agents [3-7], antidepressant agents [8], antiviral agents [9], anticancer agents [10], fungicidal agents [11], bactericidal agents [12], cytotoxic agents [13], herbicidal agents [14], insecticidal agents [15], antioxidants agents [16], and anti-proliferative agents [17].] 2H-chromen-2-one is also named as 2H-1-Benzopyran-2-one or Coumarin. Coumarins also possess medicinal properties such as anti-bacterial [18], anti-fungal [19], anti-filarial [20] anti-HIV activities [21], anti-coagulants [22], antioxidant [23], antiulcerogenic [24], anti-inflammatory properties [25], selective coronary vasodilators [26] and possess antitumor properties [27]. They are known for stimulating changes in cell growth and also intercellular communication mechanisms [28].

2. Material and Methods

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. The concentration of the solution was around 10-4M. The molar conductance values were interpreted with the help of data given in the literature [29, 30]. Gouy's method was used for the measurement of magnetic susceptibility of the compounds at room temperature. 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.

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 Zn (II) & Cd (II) were soluble in DMSO. Metal chlorides were used as received from S. D. fine chemicals.

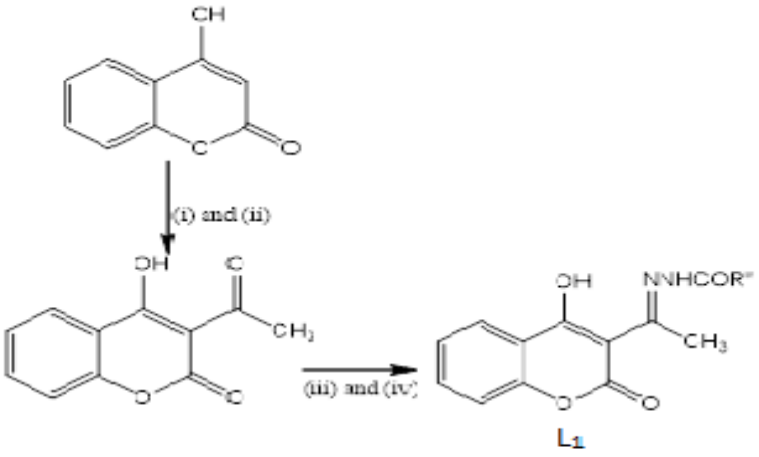
Experimental
General procedure for synthesis of Schiff's bases:
Aryl hydrazides are synthesized by treating aryl ester with hydrazine hydrate as per reported procedure [31]. 3-acetyl-4-hydroxy-2H-chromen-2-one is prepared as per previous reported method [32]. The imines L1 were prepared by adding 3-acetyl-4-hydroxy-chromen-2-one (0.01mole) and benzohydrazide (0.01 moles 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 was checked by M.P. and TLC.

Procedure for synthesis of Metal complexes:
0.01 moles (for Zinc and Cadmium 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. 10% percent alcoholic ammonia solution was added drop wise with stirring till precipitation was observed. The pH of precipitation for each complex was noted.

3. Result and Discussion

Characterization of synthesized ligand L_1: N'-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidene) benzohydrazide (L_1):



(i) AcOH, (ii) $POCl_3$, (iii) R-CONHNH$_2$ (iv)EtOH

R''= (a)C_6H_5-

Color: yellow; Yield: 87%; M.P.:176°C; IR (KBr, cm^{-1}): 3500-2650 (3600, 3280) (broad Phenolic V_{OH}& V_{NH}), 1708 ($V_{C=0}$) of lactone, 1678 ($V_{C=0}$) of aryl hydroxide, 1610 ($V_{C=N}$) of mine. 1545 & 1490 aromatic ($V_{C=C}$), 1360 ($V_{C=0}$) Phenolic OH.) . C, H, N % for $C_{18}H_{14}N_2O_4$. Analytical: C 66.72, H 4.32, and N 8.60; Calculated: C 67.07, H 4.38, and N 8.69

Result and Discussion

On the basis of elemental analysis, metal ligand ratio and thermo gravimetric analysis molecular formulae of the complexes are assigned in table no. 1. Complexes possess different colors than ligand, insoluble in ethanol, chloroform and acetone where as they are sparingly soluble in DMSO /DMF. They decompose at relatively higher temperature (>270°C) indicating good thermal stability at normal conditions.

Table 1: Physical and analytical data

Compound	Molecular formula Formula Wt PH range of precipitation Color M.P.°C M:L ratio 7.5-8 Green 234 1:2	Formula Wt PH range of precipitation Color M.P.°C M:L ratio	PH range of precipitation Color M.P.°C M:L ratio	Color	M.P. °C	Sol^n Cond. μ_v	M:L ratio
[Zn(L_1)Cl] [Cu(C12H10N3O 4)2] 584.00 7.5-8 Dark Green 192 1:2	[Zn($C_{18}H_{13}N_2O_4$)Cl]	422.17	7.0-7.5	Dirty white	>300	17.56	1:1
[Cd(L_1)Cl]	[Cd($C_{18}H_{12}N_2O_4$)Cl]	469.17	7.0-7.5	White	>300	14,66	1:1

Compound	M.F.	Elemental analysis % found (calculated)						
		C	H	N	S	Cl	M	
							Zn	Cd
[Zn(L1)Cl]	[Zn($C_{18}H_{13}N_2O_4$)Cl]	51.18 (51.21)	3.07 (3.10)	6.62 (6.64)	--	8.36 (8.40)	15.45 (15.49)	
[Cd(L1)Cl]	[Cd($C_{18}H_{12}N_2O_4$)Cl]	46.02 (46.08)	2.75 (2.79)	5.94 (5.97)	--	7.52 (7.56)		23.92 (23.96)

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 2. The comparison of IR spectral data of all the complexes and corresponding ligands helps in concluding the bonding pattern of each complex.

The new bands in the regions 514,541 cm^{-1} and 421,428 cm^{-1} observed in the complex spectra may be assigned to stretching of M–O and M–N bond respectively [33-35].

Table 2: Infrared Absorption Frequencies (cm^{-1})N'-(1-(4-hydroxy-2-oxo-2H-chromen-3-yl) ethylidene) benzohydrazide (L_1):

Sr No	Ligand/ Complex	Bond vibrational modes (stretching – v)					
		Lactone	Hydrazide	Azomethine	Enolic	New Peaks	
		(C=O)	(C=O)	(C=N)	(C=O)	M-O	M-N
1	L1	1708	1678	1610	1360	---	---
2	Zn(L1)Cl	1707	1663	1576	1381	514	421
3	Cd(L1)Cl	1709	1664	1574	1386	541	428

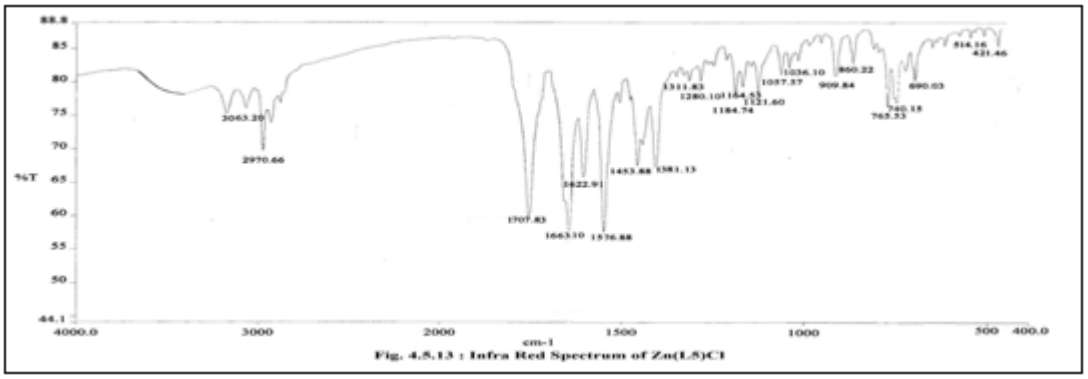


Fig. 4.8.13 : Infra Red Spectrum of Zn(L8)Cl

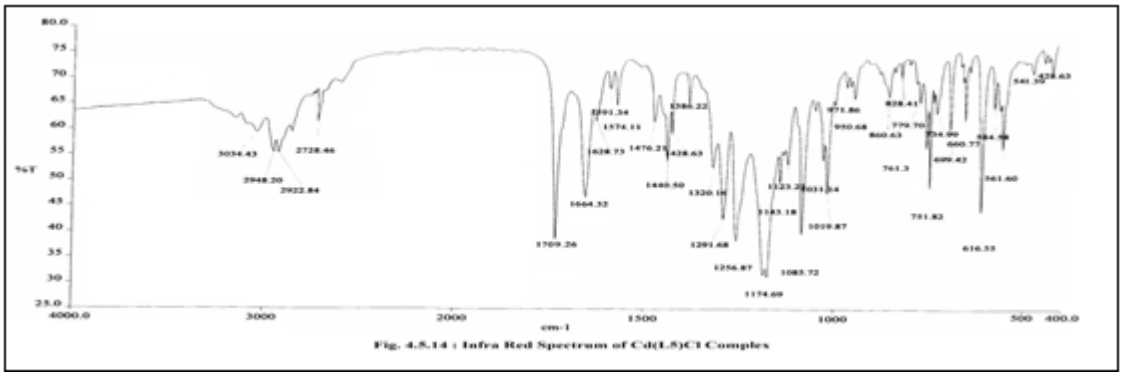


Fig. 4.8.14 : Infra Red Spectrum of Cd(L8)Cl Complex

XRD studies of complexes:

X-ray diffraction technique can be used to determine the crystallinity of the complexes. Thus by matching the pattern recorded for the sample with that in the standard X-ray diffraction pattern, the unknown compound can be identified. The solids can basically be divided in two categories, amorphous and crystalline. In crystalline materials the atomic or molecular spades are ordered in three-dimensional array called lattice, within the solid. This ordering of molecular components is lacking in the non-crystalline materials. The relatively random arrangement of molecules in non-crystalline materials makes them poor coherent scatterer of X-rays, resulting in broad diffused maxima in their diffraction patterns.

The X-ray patterns of the amorphous materials are quite distinguishable from those of crystalline specimen which give sharply defined diffraction patterns.All calculations were performed by using computerized software program Powder-X developed by Cheng Dang. The data obtained and reciprocal lattice (h, k, l) are listed in the Table no3. On the basis of the results and the support of literature, the complexes with ligands are crystalline in nature due to sharp refluxes shown in table no 4.

Table: 3

Sample Name Zn(L_1)Cl
Crystal system: Monoclinic Lattice Type: P
Lattice Parameter:a= 3.9955 b= 4.1589 c= 5.4089
Lattice Parameter : α= 90 β= 90 γ=115
Radiation: Cu WaveLength: 1.54178
2Theta Start= 5 2Theta End= 25

h	*k*	*l*	2Theta	d	Height
0	0	1	7.369	11.9866	89043.8
-1	1	0	9.03	9.78559	21664.3
-1	1	1	10.759	8.21623	42550.1
0	0	2	11.106	7.96038	25047.6
0	1	0	12.703	6.96325	29964.3
-1	0	0	14.897	5.94195	31495.3
1	0	0	15.305	5.78444	17482.1
0	1	1	16.318	5.42761	21167.4
-1	0	1	21.467	4.13594	41499
1	0	1	22.117	4.01593	25650.6
-1	1	2	22.535	3.94242	18178.2
-1	2	0	23.46	3.78893	33438.9
-2	2	0	24.184	3.67713	41029.1
0	1	2	25.384	3.50596	24468.4
-1	0	2	28.309	3.15	24354.1

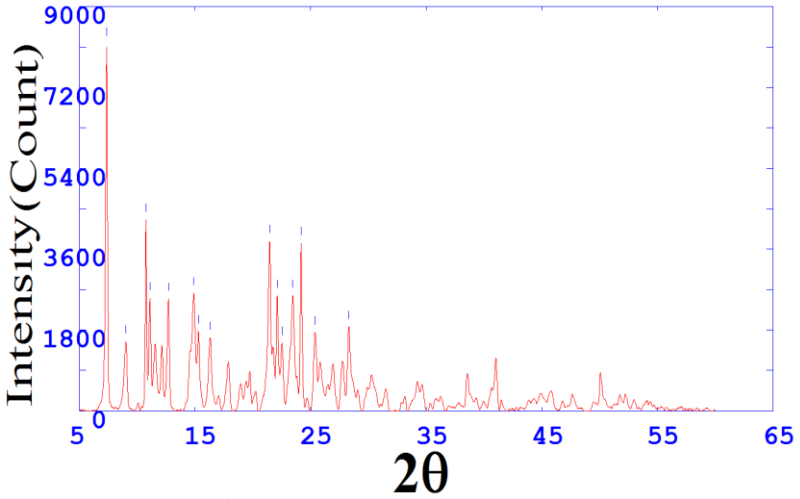


Fig. 4.4.6: XRD Spectrum of $Zn(L_5)_2$

Table 5

Sample Name $Cd(L_1)Cl$
Crystal system: Monoclinic Lattice Type: P
Lattice Parameter: a= 4.2568 b= 4.9168 c= 5.4089
Lattice Parameter : α= 90 β= 90 γ=145
Radiation: Cu WaveLength: 1.54178
2Theta Start= 5 2Theta End= 30

h	*k*	*l*	2Theta	d	Height
0	0	1	8.937	9.88638	12697.2
-1	1	0	9.487	9.315	18366.4
0	1	0	11.4	7.75544	16641.9
-1	0	0	12.226	7.2337	31369.1
0	1	1	12.75	6.93748	19923.9
-1	0	1	14.731	6.00868	73434.2
1	0	1	15.817	5.5986	34261.7
0	0	2	16.075	5.50929	9312.3
-1	2	1	19.521	4.54372	6202.7
0	1	2	22.094	4.02006	18302.8
-1	0	2	24.512	3.62873	18402
-2	1	0	25.118	3.5425	10714.3
-2	2	0	25.552	3.48327	16255
1	1	0	26.71	3.33491	26647.5
-2	1	1	27.104	3.28727	18093.1
-2	2	1	28.39	3.14119	17550.6
0	2	0	28.73	3.10478	5599.1

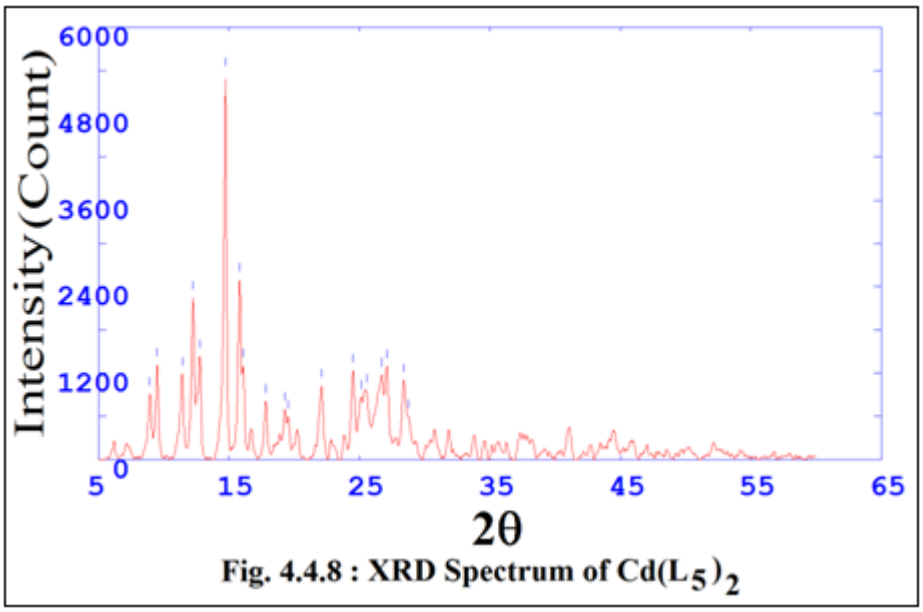
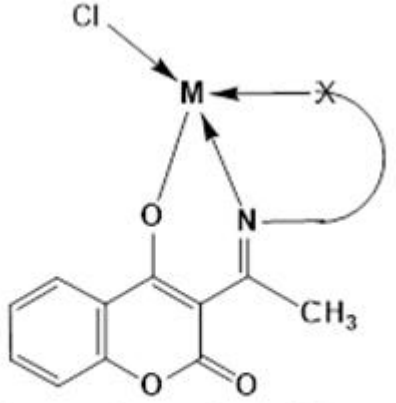


Fig. 4.4.8 : XRD Spectrum of $Cd(L_5)_2$

On the basis of elemental analysis, conductivity, magnetic susceptibility the Zinc (II) and Cd (II) complexes of present work may be assigned as monomeric structure with tetrahedral geometry

4. Conclusion

Hence on the basis of elemental analysis, IR spectra, conductivity measurement data, following tetrahedral structures are proposed for Zn (II) and Cd (II) complexes.



Monomeric tetrahedral Structure of Zn(II) and Cd(II)Complexes with Ligand L_1 Where X= O

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