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SYNTHESIS AND SPECTROPHOTOMETRIC STUDIES OF METAL (II) COMPLEXES OF HYDRAZONE DERIVATIVES

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ABSTRACT

The hydrazone derivatives of 8-aceto-7-hydroxy-coumarin and their metal complexes were synthesized and characterized. Spectrophotometric study of these compounds have been carried out at the wave length 440 and 570 nm. The structure elucidation has been done by elemental analysis, IR and magnetic studies. The structures of the compounds and their analytical application have been discussed.

Key words: Coumarin, Hydrazone, Metal complex, Spectrophometry.

INTRODUCTION

Coumarins are the best known aromatic lactones[1]. These are naturally occurring compounds and known to have biological activities[2]. Complex forming agents like hydrazone derivatives[3] are becoming of increasing importance in analytical chemistry such as gravimetric, titrimetric and colorimetric measurements. Some coumarin derivatives possessing carboxamide moity are found to have diuretic, analgesic, myorelaxant[4], antifungal[5], and anthelmintic[6] activities. Spectrophotometric study of vanadium complex with n-phenyl-7, 8-diahydroxy coumarin was carried out by some research workers[7].

From the literature survey, it can be concluded that hydroxy coumarins are useful as an analytical reagent. We synthesized some hydrazone derivatives of 4-hydroxy coumarin and their metal complexes and studied their stability constants spectrophometrically.

The complex of Mn (II), Ni (II), Co (II), Cu (II), Zn (II), Cd (II) and Hg (II) with 4-oxo-4H-1-benzobenzyl pyran-3 (carboxaldehyde-4-chlorobenzyl hydrazone) and 4-oxo-4H-1-benzo pyran-3 (carboxaldehyde-4-methylbenzyl hydrazone) have been synthesized and

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characterized[8].

EXPERIMENTAL

Materials and method

All chemicals used in the present work were of A.R. grade. Melting points of compounds were determined in open capillary tubes and are uncorrected. Job's method of continuous variation has been applied for confirming metal-ligand ratio and stability constants. The magnetic measurements were made at room temperature by the Gouy balance method. Infrared spectra were measured in the range 4000-400 cm^{-1} on a Shimadzu FTIR-801 spectrophotometer with KBr pellets.

Spectrophotometric study

The compositions of Cu (II) and Ni (II) chelates with the reagent 8-aceto-7-hydroxy coumarin hydrazone (AHCH) have been determined on the basis of Job's continuous variation method.

Composition of Cu (II) $(AHCH)_2$ complex

0.002 M solution of Cu (II) or Ni (II) was prepared by suitable dilution of the standard solution.

The solution of reagent AHCH (0.002M) was prepared in absolute alcohol or DMF. The solutions of metal salt and the reagent were mixed in varying proportions as under -

Metal ion solution (mL) 1, 2, 3, 4, 5, 6, 7 and 8

Reagent solution (mL) 9, 8, 7, 6, 5, 4, 3 and 2

pH of the solution was adjusted to 4.5. The precipitated complex was extracted with three 5 mL portions of chloroform and final volume of chloroform was made up to 25 mL. The absorbances of chloroform extracts were measured at 440 and 570 nm. The result are tabulated in Tables 1 and 2.

Table 1

Metal ion solution (mL)	Ligand solution (mL)	$\frac{C_M}{C_M + C_L}$	Absorbance Cu (II)		Absorbance Ni (II)	
			440 nm	570 nm	440 nm	570 nm
1	9	0.10	0.033	0.024	0.039	0.023

Cont…

Metal ion solution (mL)	Ligand solution (mL)	$\frac{C_M}{C_M + C_L}$	Absorbance Cu (II)		Absorbance Ni (II)	
			440 nm	570 nm	440 nm	570 nm
2	8	0.20	0.061	0.040	0.061	0.035
3	7	0.30	0.089	0.057	0.082	0.048
4	6	0.40	0.086	0.055	0.078	0.047
5	5	0.50	0.071	0.046	0.065	0.037
6	4	0.60	0.057	0.037	0.050	0.029
7	3	0.70	0.045	0.027	0.036	0.019
8	2	0.80	0.032	0.017	0.025	0.012

Table 2: Elemental analysis of compounds

Chelate with 7-hydroxy-8-aceto coumarin hydrazone						
Mol. Formula	Mol. Wt.	% Elements Calc. (Found)				
		M	C	H	(O)	N
Cu $(C_{11}H_9O_3N_2)_2$	497.5	12.75 (12.76)	53.05 (53.06)	3.60 (3.62)	19.28 (19.29)	11.24 (11.25)
Ni $(C_{11}H_9O_3N_2)_2$	492.71	11.96 (11.96)	53.52 (53.54)	3.64 (3.65)	19.46 (19.47)	11.33 (11.35)

It is evident from the plot (Fig. 1 and 2) that absorbance gradually increases up to molar composition of metal to the reagent and after that it becomes constant indicating 1 : 2 stoichiometry of the complex.

Evaluation of stability constants

$$ML_n = M + nL \quad \ldots(1)$$

$$C(1-\alpha) \quad C(n.c\,\alpha)^n$$

$$K_s = c(1-\alpha)/c[n.c\,\alpha]^n \quad \ldots(2)$$

Taking n = 2 in this case, the equation reduces to -

$$K_s = 1-\alpha/4\,c^2\,\alpha^2 \quad \text{Where } \alpha = (E_M-E_S)/E_M \quad \ldots(3)$$

E_M = Maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines.

E_S = Absorbance at the stoichiometry molar ratio of the metal to reagent in complex.

Calculation of stability constant

The stability constants were calculated from the relation (3).

The standard free energy change, ΔG^0, for the formation reaction of complex has been calculated at 25^0C using the formula $\Delta G^0 = -RT \ln K$

Job's Method	E_M	E_S	α	K_S	ΔG^0 (kcal/mole)
Cu (II)	0.093	0.089	0.043	3.59×10^8	-11.74
Ni (II)	0.087	0.082	0.057	2.357×10^8	-11.41

$Cu(II)(AHCH)_2$

Metal solution : 0.002 M

Ligand solution : 0.002 M

Final volume of chloroform extract : 25 mL

Wavelengths : 440 nm, 570 nm.

pH : 4.5 for Cu (II) and 5.5 for Ni (II)

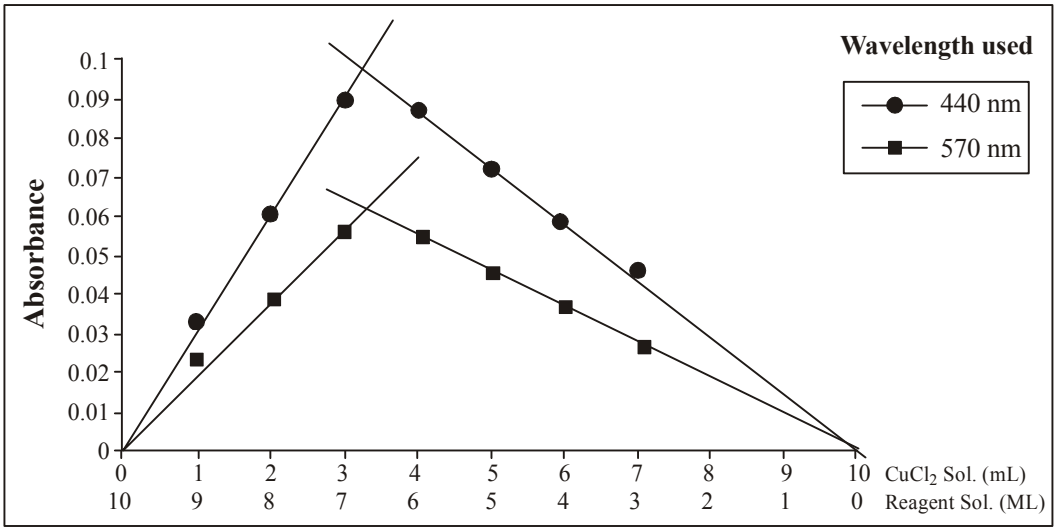
RESULTS AND DISCUSSION

All the compounds gave satisfactory elemental analysis and the results are in close agreement with the calculated values.

These solids do not melt sharply and undergo decomposition above 260^0C temperature. The chelates described here were also investigated for their magnetic susceptibility. The metal chelate of Cu (II) is paramagnetic and the metal chelate of Ni (II) is diamagnetic in nature and having octahedral geometries.

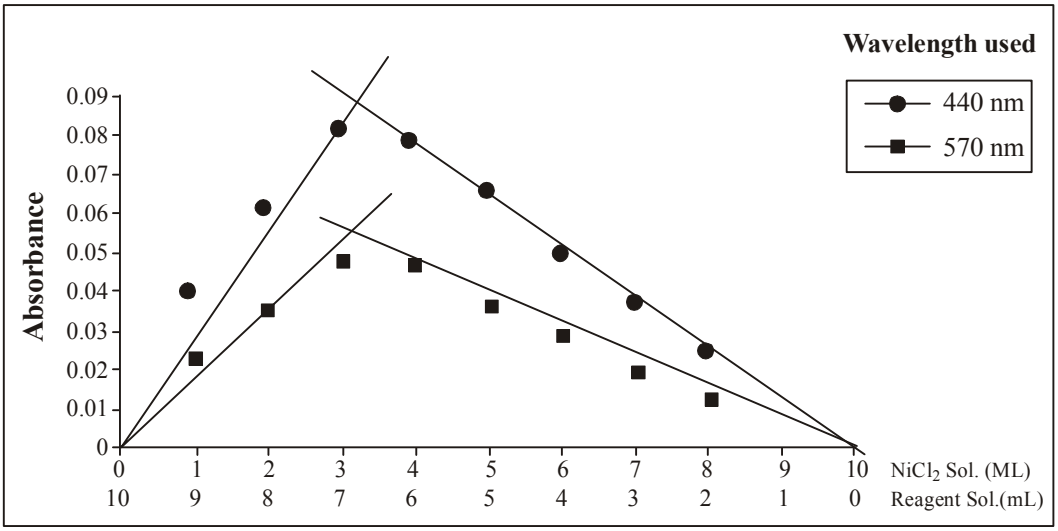
Most of the bands appearing in the spectrum of corresponding ligand were observed at similar position in the IR spectra of metal complexes also. The broad band between 3600-3200 cm^{-1} in ligand disappeared in spectra of metal complex .This shows that of O-H group is involved in chelate formation with metal. One new band in infrared appears at 560-580

cm^{-1}, which is probably due to M-O, M-N band. Job's method of continuous variation revealed that the chelates of Cu (II) and Ni (II) are formed with metal ligand molar ratio 1 : 2.



Metal : Ligand ratio = 1 : 2

Fig. 1: Job's method for bis[7-hydroxy-8-aceto coumarin hydrazone] copper (II)

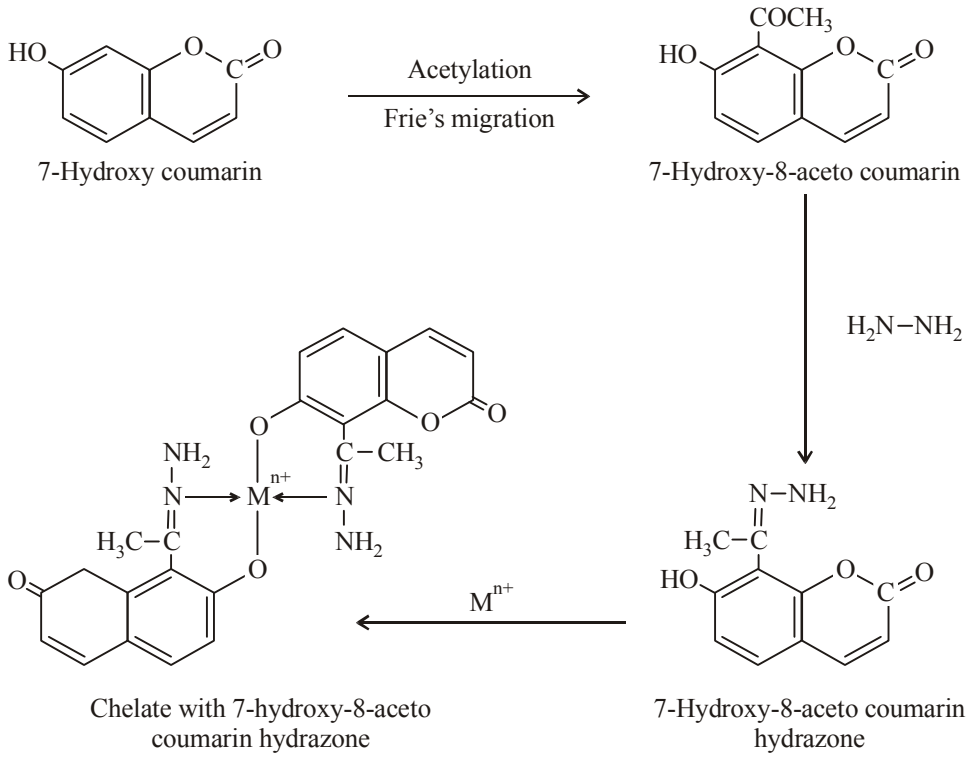


Metal : Ligand ratio = 1 : 2

Fig. 2: Job's method for bis[7-hydroxy-8-aceto coumarin hydrazone] nickel (II)

Scheme 1

Stepwise preparation of hydrazone and their chelates (Schematic)



CONCLUSION

Spectrophotometric and magnetic studies of these metal complexes of hydrazone reveal that these metal complexes are having octahedral geometries and the metal ligand ratio is 1 : 2. The ligand can prove to be a good analytical reagent for some metal ions like copper and nickel..

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