September 2009 *Volume 4 Issue 3*

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Short Communication

ICAIJ, 4(3), 2009 [133-135]

Determination of stability constant of metal complex of hydrazone derivative by spectrophotometer

Gaurang Jani[1,*], Kartik Vyas[2], Kiran Nimavat[2], Judas Franco[3]

[1]Department of Chemistry, M.N. college, Visnagar, (INDIA)

[2]Department of Chemistry, Govt. Science College, Gandhinagar, (INDIA)

[3]Department of Chemistry, R.A.Shah Bhavan's Science College, Khanpur, Ahmedabad, (INDIA)

E-mail : jani_sunil13@yahoo.com

Received: 11th September, 2009 ; Accepted: 21st September, 2009

ABSTRACT

The stability constant of complexes of metal with 8-aceto-7-hydroxy-coumarin hydrazone was determined by Job's method at Wavelength 440 and 570 nm by keeping metal:ligand ratio is 1:2. The structure elucidation have been done by elemental analysis, IR and Magnetic studies.

KEYWORDS

Coumarin;
Hydrazone;
Metal complex;
Spectrophometric study.

INTRODUCTION

Stability constant of metal complexes have been determined by different methods such as spectroscopy and potentiometry. It is well known that the simplest electroanalytical technique for determination of stability constant is job's method using spectrophotometer.

Coumarin contains the parent nucleus of benzo-α-pyrone. The physico chemical studies[1] of the coumarins with chelating groups at appropriate positions and their metal complexes reveal that the ligands could be used as potential analytical reagents. Coumarins can also be used as fluorescent probes in the study of membrane and protein preparations[2].

Mandakmare and Narwade[3] studied the determination of stability constants of Cu(II) chelates with some substituted coumarins. The conditional stability constant of the complexes was determine from Yoe and Jones mole ratio method[4] and job's continuous variation method.

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 characterized[5].

EXPERIMENTAL

All chemicals used in the present work were of A.R. grade, melting point of compound were determined on open capillary tubes and are uncorrected. Job's method of continuous variation has been applied for confirming metal-ligand ratio and stability constant. The magnetic measurements was made at room temperature by the Gouy balance method[6]. Infra red spectra were measured in the range 4000-400 cm^{-1} on a Schimadzu FT IR-801 spectrophotometer with KBr pellets.

Synthesis of 8 - aceto - 7- hydroxy - coumarin - hydrazone

Ethanolic solution of 7-Hydroxy-8-aceto-coumarin

Short Communication

(20.4 g), Hydrazin hydrate(3.5 ml) and pyridine(1.0 ml) were mixed together in a round-bottomed flask fitted with reflux condenser. The mixture was refluxed on water bath at 135° C for 1 hour, then it was left to cool overnight and then it was neutralized by adding dilute KOH solution. The solid hydrazone obtained was separated and washed with absolute alcohol. Reddish crystalline needles of hydrazone were obtained. Yield: 72%, m.p. : 160 °C.

Synthesis of Bis-(8 - aceto - 7- hydroxy - coumarin - hydrazone)Co(II)complex

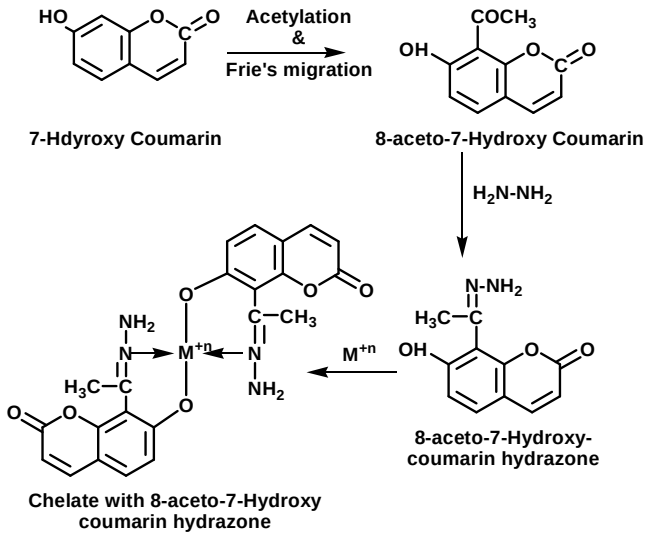
1% ethanolic solution of 7-Hydroxy-8-aceto-coumarin-hydrazone was added dropwise to a warm Cobaltchloride solution maintaining the pH of mixture at 6.5 during the reaction. Brownish pink precipitates were formed. Precipitates thus obtained were washed with warm ethanol. Yield: 52%, m.p. : 262 °C.

SPECTROPHOTOMETRIC STUDY

The composition of Co(II) chelate with the reagent 8-Aceto-7-Hydroxy Coumarin Hydrazone (AHCH) has been determined on the basis of Job's continuous variation method.

Composition of Co(II) $(AHCH)_2$ complex by Job's continuous variation method

A 0.002 M solution of Co(II) was prepared by suitable dilution of the standard solution.



Scheme 1 : Stepwise preparation of hydrazone and their chelates

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

Metal ion solution : 1 2 3 4 5 6 7 8
Reagent solution : 9 8 7 6 5 4 3 2

pH of the solution was adjusted to 6.5 the precipitated complex was extracted with three 5ml portion of chloroform and final volume of chloroform to 25 ml. The absorbance of chloroform extracts were measured at 440 and 570 nm. The result are tabulated in TABLE 1.

TABLE 1

Metal ion solution ml	Ligand solution ml	Cm/Cm+CL	Absorbance(Co(II))	
			440nm	570nm
1	9	0.10	0.242	0.132
2	8	0.20	0.303	0.173
3	7	0.30	0.366	0.215
4	6	0.40	0.350	0.212
5	5	0.50	0.290	0.174
6	4	0.60	0.232	0.135
7	3	0.70	0.180	0.105
8	2	0.80	0.135	0.072

It is evident from the graph 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 constant

$MLn = M+nL$

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

$Ks = c(1-\alpha)/c[n.c\ \alpha]^n$

Taking n = 2 in this case the equation reduce to

$Ks = 1- \alpha/4\ c^2\ \alpha^2$ Where $\alpha = (Em-Es)/Em$

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

Es = absorbance at the stoichiometry molar ratio of the metal to reagent in complex.

Calculation of Stability constant

The stability constant is calculated from the above relation.

The standard free energy change ΔG^0 for the formation reaction of complex has been calculated at 25

C^0 using the formula $\Delta G^0 = -RTLnK$

Method Job's	Em	Es	α	Ks	ΔG^0
Co(II)	0.390	0.380	0.0256	$8.53x10^8$	-12.107kcal/mole

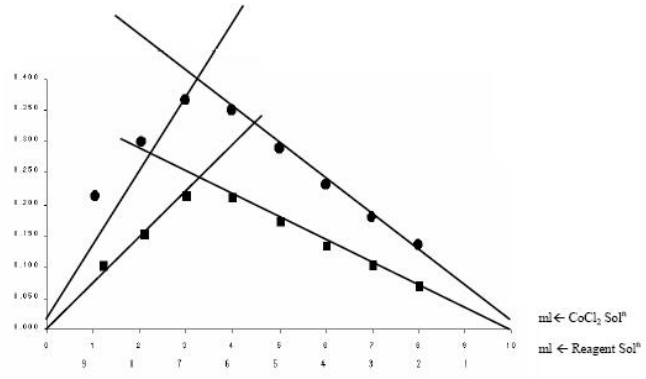
$Co(II)(AHCH)_2$
Metal solution : 0.002M
Ligand solution : 0.002M
Final volume of Chloroform extract : 25ml
Wavelength : 440nm, 570nm.
pH : 6.5

RESULT AND DISCUSSION

All the compounds gave satisfactory elemental analysis values and are close with the calculated value (TABLE 2)

TABLE 2 : Elemental data of compounds

Chelate with 8-aceto-7-hydroxy coumarin hydrazone							
Mol. Formula	Mol. Wt.	% of Elements					μ_{eff} in B.M.
		M	C	H	(O)	N	
$C_{11}H_{10}O_3N_2$	218.00	-	60.50 (60.53)	40.52 (40.55)	21.55 (21.58)	12.82 (12.87)	-
$Co(C_{11}H_9O_3N_2)_2$	492.94	Co 12.11 (12.11)	53.47 (53.46)	3.67 (3.64)	19.46 (19.44)	11.32 (11.44)	2.03 (paramegnetic)



Wavelength used λ= ● 440 nm λ= ■ 570 nm

JOB's Method For Bis[7-hydroxy-8-aceto coumarin hydrazone] Cobalt (II)complex

The solids do not melt sharply and under go decomposition above 260^0 C temperature The chelates described here are also investigated for their magnetic susceptibility. The metal chelate of Co(II) is paramagnetic in nature and having low spin tetrahedral geometry.

Most of the band appeared in the spectra of corresponding ligand are observed at similar position in the IR spectra of metal complexes. The broad band between 3600-3200 cm^{-1} in ligand is disappeared in spectra of metal complex. This shows that H, of O-H group is involved in chelate formation with metal.

One new band in infra red spectra appears at 560-580cm^{-1} which probably due to M-O,M-N band[7].

Job's method of continuous variation could be made applicable and this study revealed that the chelate of Co(II) is formed with metal ligand molar ratio 1:2.

CONCLUSION

The spectral study, Spectrophotometric study and magnetic study of these metal complex of hydrazone reveals that the metal complex is having low spin tetrahedral geometry and the metal ligand Ratio is 1:2. The ligand can be good analytical reagent for some metal ions.

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