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2, 4-Dihydroxy-5-Bromo- -Phenylacetophenone Thiosemicarbazone (DHB- -PAT) As Analytical Reagent: Studies On Co(II) Chelate

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Abstract: 2, 4-dihydroxy-5-bromo- -phenylaetophenone thiosemicarbazone [DHB- -PAT] has been used for the spectrophotometric determination of Co(II) at pH =8.5. Job's method of continuous variation and Yoe and Jones Mole ratio method show metal: ligand ratio in the complex to be 1:2. The molar absorptivity of complex at 410 nm was found to be 1.17×10^4 lit.mol⁻¹.cm⁻¹ and Sandell's sensitivity was found to be $0.00503 \,\mu$ g/cm².The stability constant determined spectrophotometrically is found to be 1.57×10^9 and Gibb's free energy change for complex formation reaction is calculated to be -12.622 k.cal /mole. The Beer law is obeyed up to 5.89 ppm of Co(II) ion at 410 nm. From TG studies, the energy of activation for both the decomposition steps has been calculated using broido method. They were found to be 13.94 k.cal/mole and 5.67 k.cal/mole respectively. The reagent has been successfully applied for the determination of percentage purity of cobalt from cobalt metal sample.

Keywords: Dihydroxy-5-Bromo- -Phenylacetophenone Thiosemicarbazone (DHB- -PAT) ,Analytical Reagent, Co(II) Chelate.

Introduction

The thiosemicarbazone of aldehydes and ketones in which there is –OH group in ortho position to the carbonyl groups are found to be better chelating agents and they have been exploited to the maximum extent by many workers⁽¹⁻⁶⁾. Many organic reagents like o-hydroxy oximes, oximes, thiosemicarbazones, chalconeoxime, anilides, various heterocyclic compounds have been used for gravimetric and spectrophotometric reagent for Co(II). Spectrophotometric methods have been used to confirm the stoichiometry of the complex and to determine the stability constant of the complex. The stoichiometry was also confirmed by thermo gravimetric analysis.

Experimental

Spectrophotometric measurements were done on Perkin-Elmer Lambada-35 UV-Visible spectrophotometer and all the pH measurement were done on electronic pH-meter (EQ-614). TG analysis was done using "TA-Instrument SDTQ-600".

Synthesis of 2, 4-Dihydroxy-5-Bromo- -Phenylacetophenonethiosemicarbazone

[DHB- -PAT]:

2, 4-dihydroxy- -Phenylacetophenone was prepared from resorcinol, phenyl acetic acid and anhydrous zinc chloride according to the method of H.Nogemi ⁽⁷⁾. The bromination of 2, 4-dihydroxy- -Phenylacetophenone using bromine in glacial acetic acid gives 2, 4-dihydroxy-5-Bromo- -Phenylacetophenone. The reagent was prepared by the reaction of 2, 4-dihydroxy-5-Bromo- -Phenylacetophenone with alcoholic solution of thiosemicarbazide⁽⁸⁾. It was crystallized from absolute alcohol. (M.P. 95 °C)

The thiosemicarbazone reagent under present investigation is characterized by following different analytical techniques.

Elemental analysis: Elemental analysis of the reagent was done using "Carlo-Erba Elemental Analyzer Model 1106". The percentage elements, found are in agreement with its molecular formula. The results are given in the following Table-I.

Table-I

Reagent	%Carbon	%Hydrogen	%Nitrogen	%Sulphur
	[Calc.]	[Calc.]	[Calc.]	[Calc.]
DHBPAT	47.32%	3.66%	10.96%	8.37%
	[47.38%]	[3.71%]	[11.05%]	[8.43%]

TG Studies: The TG study of Chelate was done on "TA-Instrument SDTQ-600".

UV-Visible spectral studies: The UV-Visible spectrum of reagent in ethanol was recorded on Shimadzu UV–1700 Perkin-Elmer Lambada-35 UV-Visible spectrophotometer. Wavelength of maximum absorption was found to be 280 nm that falls in UV region.

1H-NMR Spectral Studies: The NMR spectrum of the reagent was taken in DMSO. The NMR spectrum was recorded on a BRUKER AVANCE II 400 NMR spectrometer using TMS as reference, Assignment of signals to different protons is given in the following Table-II.

Table-II

Reagent	-CH ₂ singlet	-NH ₂ singlet	Aromatic Proton Multiplate	-CSNH- singlet	Phenolic -OH Singlet
DHBPAT	= 3.48	= 4.25	= 6.5-8.0	= 11.13	=12.62

Result and Discussion

Antibacterial activity of reagent and chelate:

Thiosemicarbazones being chelating agent's shows good antibacterial activity ⁽⁹⁻¹¹⁾ by hinder the growth of bacteria by chelating the metal ions which are present in trace in biological fluids. The antibacterial properties of the above compound are studied by using "Broth Dilution Method" ^(12, 13).

The results are given in Table-III and Table-IV.

STANDARD DRUGS	E.Colli / gram –ve / microgram/ml	S.Aures / gram +ve / microgram/ml
GENTAMYCINE	0.05	0.25
AMPICILINE	100	250
CHLORAMPHENICOL	50	50
CIPROFLOXACIN	25	50
NORFLOXACIN	10	10

Table-III

Table-IV

SAMPLE	E.Colli / gram –ve / / microgram/ml /	S.Aures / gram+ve / / microgram/ml /
DHBPAT	200	250
Co(II) - DHBPAT	125	200

From above result we can conclude that,

DHB- -PAT reagent shows poor activity against E.coli (Gram-ve) bacteria while shows same activity for S.Aureus (Gram+ve) bacteria like "Ampicilline drug".

Co(II)-DHB- -PAT chelate shows weak activity against E.coli (Gram-ve) bacteria than S.aureus (Gram+ve) bacteria, which is more than "Ampicilline drug".

Spectrophotometric study of Co(II)-DHB- -PAT

5 mg of chelate was dissolved in 25ml of 50% ethanol and absorption of the solution was measured between 340nm-800nm.Spectra of complex shows shoulder band at 410 nm, and this wave length was selected for further spectrophtometric work. pH study of chelate from pH=6.0 - 9.0 was done using ammonia and ammoniumchloride buffer and maximum absorbance was observed at pH=8.5. Hence this pH was selected for further spectrophtometer work.

0.002M metal soln. in varying proportion was mixed with 4.0ml 0.01M ligand soln and pH was maintained 8.5 and diluted to 25ml with (50% v/v) aqueous ethanol. Absorbance of this solution was measured at 410 nm against ligand blank. Absorbance were plotted against concentration of Co(II).It was found that Beer's law was obeyed up to 5.89 ppm of Co(II). Molar absorptivity and Sandell's sensitivity⁽¹⁴⁾ were found to be 1.17 x10⁴ lit.mol⁻¹.cm⁻¹and 0.00503µg/cm² respectively. Job's method ⁽¹⁵⁾ and Mole ratio method ⁽¹⁶⁾ was used to determine the stoichiometry of the complex. It was found to be 1:2[M: L]. Stability constant was calculated using the formula;

$$K = \frac{1 - \alpha}{4 \alpha^3 C^2}$$
, where $\alpha = \frac{Em - Es}{Em}$

Where, = degree of dissociation

- Em = maximum absorbance found from graph.
- Es = absorbance at the stoichiometric molar-ratio of the metal to reagent in complex.
- C = concentration of complex

The Average stability constant from two method is 1.57×10^9 and Gibb's free energy change for complex formation reaction was calculated using the formula $G^\circ = -RTlnK_s$ and found to be -12.622 K.Cal.mol⁻¹ at 27° C.

Effect of diverse ion:

Interference due to associated ions was examined in the determination of 5.89 ppm of Co(II) at pH=8.5 using the reagent DHB- α -PAT. The tolerance limit was taken as the amount of foreign ion required to cause $\pm 2\%$ error in the absorbance. How many excess could be tolerated is shown in bracket. Many anions like F⁻, Cl⁻, Br⁻, NO₃⁻, and SO₄⁻² do not interfere in the determination of cobalt at pH=8.5, even when they are present in 50-fold excess. Thiourea (20), thiosulphate (18), oxalate (4), thiocyanate (18), tetraborate (15) can be tolerated. A 30-fold excess of Zn(II), Sr(II), Ca(II), Mg(II), Cd(II), Al(III), Na(I), K(I), Ba(II) and Zr(IV), do not interfere.

Thermo gravimetric analysis:

Thermo gravimetric analysis of cobalt chelate was done on "TA-Instrument SDTQ-600". A definite quantity of chelate was taken in an alumina crucible and was put on a hanger of microbalance and crucible was kept in a furnace. The temperature of the furnace was raised from 30° C to 900° C in a programmed manner at the heating rate of 10° C/min.

From thermo gravimetric analysis of the Co(II) chelate, it was found that there is no mass loss up to 130°C, indicating that the chelate can be dried safely without decomposition at 110°C. Loss in mass above 130°C is due to decomposition of chelate and loss of ligand molecules. Mass of final residue corresponds to Co_3O_4 is in accordance with the formula ($C_{15}H_{13}O_2N_3SBr$) ₂Co. The observed loss and mass expected as per formula of chelate in which M: L ratio is 1:2 in the complex. Broido method⁽¹²⁾ was applied to TG thermo grams of Co(II) chelate obtained with heating rate 10°C/min. Activation Energy Ea was calculated using this method for thermal decomposition of chelates. The value of 'Ea' was found to be 13.94 and 5.67 k.cal/mole for first and second decomposition step respectively.

IR Spectra:

Examination of IR spectra of the chelate shows the weak band around 3394 cm⁻¹ in comparison of ligand molecule , which shows that during chelate formation, the hydrogen of 2- hydroxy group is lost and oxygen forms covalent bond with metal whereas 4- hydroxy group does not take part in complex formation . The bands of aliphatic C-H stretching and aromatic C-H stretching are observed at nearly same position in reagent as well as in cobalt complex. The band due to C=N stretching which is observed at 1618 cm⁻¹ in ligand is shifted to around 1593 cm⁻¹ in complex. This may be due to coordination of cobalt metal through nitrogen. Thus, in the chelates, metal is covalently bonded with oxygen and co-ordinately bonded with nitrogen.

Determination Of Percentage Purity Of Cobalt From Cobalt Metal Sample:

Preanalysed sample of cobalt metal, was weighed exactly (0.2760 gm) and dissolved in 5 ml concentrated nitric acid by heating on a sand-bath. Excess nitric acid was evaporated and 2-3 ml concentrated hydrochloric acid is added and evaporated. The solution was diluted to 1000 ml (stock solution) with double distilled water in a volumetric flask. From this stock solution, 25.0 ml solution was taken and again diluted with double distilled water to 100 ml (1ml = $69\mu g$). The stock solution was used after standardization with EDTA⁽¹⁷⁾ and percentage of cobalt was determined (average of determinations) it was found to be 99.63% cobalt (II). Complexation behavior of Co(II) present in 1.0ml and 2.0ml of diluted solution was studied with excess of reagent at pH= 8.5 by making final volume 25ml with 50% aqueous ethanol and the absorbances of above solutions were measured at 410nm using ligand blank. Absorbance values obtained were plotted in Beer's law plot.

Absorbance	ppm of Co(II) taken	ppm of Co(II) found	percentage of Co(II) obtained	%Error
0.566	2.76	2.750	99.27	-0.36%
1.088	5.52	5.475	98.84	-0.79%

%	of	Cobalt in	cobalt	metal	sample = 99.63%	
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(Beer's law plot)

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