



2, 4-Dihydroxy-5-Bromo [2'Methyl] Propiophenone Thiosemicarbazone [DHBMP] as an Analytical Reagent: Studies on Co(II) Chelate

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ABSTRACT

Co(II) was determined spectrophotometrically after complexing with 2, 4-Dihydroxy-5-Bromo [2'Methyl] Propiophenone thiosemicarbazone [DHBMP] at room temperature at pH 9.0 in 50% (V/V) aqueous ethanol at 410nm. Beer's law was obeyed up to 9.43 ppm of Co(II). Molar absorptivity and Sandell's sensitivity were found to be $2.487 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and $0.0237 \mu\text{g/cm}^2$ respectively. Composition of chelate was determined using Job's method of continuous variation and Yoe and Jones mole ratio method which was found to be 1:2 (M:L). The stability constant determined spectrophotometrically was found to be 2.73×10^{10} . Gibb's free energy change for complex formation reaction was also calculated and found to be $-14.324 \text{ k cal/mol}$. From TGA, the energy of activation was calculated using Broido method and found to be 8.48 k cal/mol for 1st and 10.08 k cal/mol for 2nd step decomposition. Study of antibacterial activity of reagent and Co (II)-DHBMP complex was also done using Broth Dilution Method. The reagent has been satisfactorily applied for the determination of percentage purity of cobalt from cobalt metal sample.

Keywords: Spectroscopic determination, Propiophenone thiosemicarbazone, DHBMP.

INTRODUCTION

Organic reagent have been known for the detection and determination of transition metal ion due to its sensitivity, specificity and the greater convenience in use. By the work of Werner [1] in the field of coordination chemistry, It has become possible to determine the concentration of metal ions present in traces. The organic chelating agents are used as gravimetric reagent, as a spectrophotometric reagent and in solvent extraction.

The thiosemicarbazone of aldehydes and ketones are found to be better chelating agents and they have been exploited to the maximum extent by many workers [2-12].

Many organic reagents like o-hydroxy oximes, oximes, thiosemicarbazones, chalcone oxime, 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. Here we have synthesized a reagent [DHBMP] for spectroscopic determination of Co (II).

MATERIALS AND METHODS

Co (II)-metal solution: A stock solution of cobalt (II) (0.05M) was prepared by dissolving 2.9743 gm of cobalt chloride (A.R. Grade) was dissolved in double distilled water with little free acid and dilute to 250ml. It was standardised with EDTA [13]. Solutions of other ions were prepared by dissolving their salts (A.R) in deionized water.

Synthesis of Reagent [DHBMP]: 2, 4 dihydroxy [2' methyl] propiophenone (DHMP) was prepared from resorcinol, phenyl acetic acid and anhydrous zinc chloride according to the method of H.Nogemi [14]. 2, 4-dihydroxy-5-bromo [2' methyl] Propiophenone (DHBMP) was prepared from 2, 4 dihydroxy [2' methyl] propiophenone (DHMP) and bromine in glacial acetic acid. It was crystallized from ethanol. The reagent was prepared by the reaction of 2, 4-dihydroxy-5-bromo [2' methyl] propiophenone with alcoholic solution of thiosemicarbazide [14]. The reagent was crystallized from absolute alcohol having m. p. 123°C.

RESULTS AND DISCUSSION

Characterization of Reagent: 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 1.

Table-I: Elemental analysis of reagent DHBMP

Reagent	%Carbon [Calc.]	%Hydrogen [Calc.]	%Nitrogen [Calc.]	%Sulphur [Calc.]
DHBMP	39.80% [39.77%]	4.18% [4.25%]	12.58% [12.65%]	9.61% [9.65%]

TG Studies: The Thermo Gravimetric study of chelate was done on "Mettler-Instrument STAR SW11.00". 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 50°C to 900°C in a programmed manner at the heating rate of 10°C min⁻¹.

From thermo gravimetric analysis of the Co (II) chelate, it was found that there is no mass loss up to 160°C, indicating that the chelate can be dried safely without decomposition at 160°C. Loss in mass above 160°C is due to decomposition of chelate and loss of ligand molecules. Mass of final residue corresponds to Co₃O₄ is in accordance with the formula (C₁₁H₁₃O₂N₃SBr)₂ Co. The observed loss and mass expected as per formula of chelate in which M: L ratio is 1:2 in the complex. Broido method [18] was applied to TG of Co(II) chelate obtained with heating rate 10°C min⁻¹. Activation Energy Ea was calculated using this method for thermal decomposition of chelates. The value of 'Ea' was found to be 8.48 and 10.08 k cal/mole for first and second decomposition step respectively.

UV-Visible spectral studies: The UV-Visible spectrum of the reagent in ethanol was recorded on Perkin-Elmer Lambda-35 UV-Visible spectrophotometer. Wavelengths of maximum absorptions were found to be 222, 268 and 337 nm that fall in UV region.

FT-IR Spectral studies: FT-IR spectrum of the reagent and its chelate was recorded on "Simadzu 8400-S spectrophotometer" in KBr pallet. Absorption bands observed are shown in table 2.

Table-2: FT-IR Spectral studies of reagent DHBMP and Co (II)-DHBMP

Reagent	$\nu_{\text{O-H}}$ stretching	$\nu_{\text{C=N}}$ stretching	$\nu_{\text{C-H}}$ stretching	$\nu_{\text{C=S}}$ stretching	$\nu_{\text{C-Br}}$ stretching	$\nu_{\text{N-N}}$ stretching
DHBMP	3384cm ⁻¹	1618cm ⁻¹	2875-2972cm ⁻¹	1273cm ⁻¹	650cm ⁻¹	1136cm ⁻¹
Co(II)-DHBMP	3375cm ⁻¹	1560cm ⁻¹	2829-2980 cm ⁻¹	1292cm ⁻¹	669cm ⁻¹	1148cm ⁻¹

Examination of IR spectra of the chelate shows the weak band around 3384 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 (II) complex. The band due to C=N stretching which is observed at 1618 cm⁻¹ in ligand is shifted to around 1560 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.

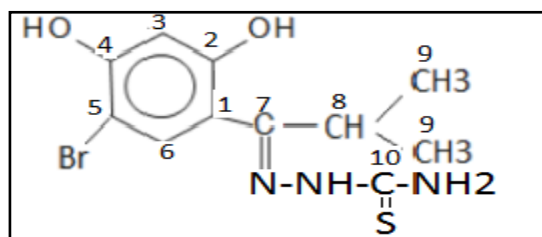
¹H and ¹³C NMR Spectral Studies: The NMR spectrum of the reagent was taken in CDCl₃. The NMR spectrum was recorded on a BRUKER AVANCE II 400 NMR spectrometer using TMS as reference, Assignment of signals to different protons and carbons are given in tables 3, 4.

Table-3: ¹H-NMR

Reagent	-CH ₃ Alkyl group	Methine proton	Phenolic (-OH)	-NH ₂ Proton	-CSNH Proton	Aromatic Proton
DHBMP	Doublet $\delta = 1.30$	Multiplet $\delta = 2.20$	Singlet $\delta = 13.51, 13.32$	Singlet $\delta = 4.17$	Singlet $\delta = 12.72$	Multiplet $\delta = 6.4$ to 8.00

Table-4: ¹³C-NMR

Assignment	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Chemical shift(δ) In ppm	113.70	155.66	103.67	155.66	99.38	130.39	161.58	55.31	44.01	201.87



2, 4-Dihydroxy-5-Bromo-[2' methyl]-propiophenone thiosemicarbazone [DHBMP]

Spectrophotometric study of Co (II) –DHBMP: 5 mg of chelate was dissolved in 25ml of (50% v/v) aqueous ethanol and the absorption was recorded in the range of 340 -800 nm. It was observed that the absorbance of the coloured solution of the chelate increase continuously towards the shorter wavelength. The spectra of chelate shows shoulder band at 410 nm and this wave length was selected for further spectrophotometric work. pH study of chelate from pH=7.0 - 10.0 was done using Ammonium hydroxide-ammonium chloride buffer and maximum absorbance was observed at pH=9.0. Hence this pH was selected for further spectrophotometer work.

Verification of Beer's law and optimum concentration range: To 4.0mL (0.002M) solution of DHBMP reagent varying amount of the cobalt ion solution (0.001M) was added and pH was maintained

9.0 using ammonium hydroxide and ammonium chloride. Then dilute it to 25mL with (50% v/v) aqueous ethanol. Absorbance of this solution was measured at 410 nm against ligand blank. Absorbances were plotted against the concentration of Co(II). A straight line passing through the origin, indicating the obeyance of the Beer law was obtained up to 9.43 ppm of Co(II). The Molar absorptivity and Sandell's sensitivity [15] were found to be $2.487 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and $0.0237 \mu\text{g}/\text{cm}^2$ respectively.

Stoichiometry of complex: Job's method [16] and Mole ratio method [17] were used to determine the stoichiometry of the Co (II)-DHBMP complex. From both the method it was found to be 1:2[M: L]. This is in agreement with the stoichiometry found from thermogravimetric method.

$$K = \frac{1-\alpha}{4 \alpha^3 C^2}, \text{ where } \alpha = \frac{E_m - E_s}{E_m}$$

Where, α = degree of dissociation, E_m = maximum absorbance found from graph, E_s = absorbance at the stoichiometric molar- ratio of the metal to reagent in complex, C = concentration of complex.

The average stability constant from two methods was found to be 2.73×10^{10} and Gibb's free energy change for complex formation reaction was calculated using the formula $\Delta G^\circ = -RT \ln K_s$ and found to be $-14.324 \text{ k cal. mol}^{-1}$ at 27°C .

Effect of diverse ion: Interference due to associated ions was examined in the determination of 9.43 ppm of Co (II) at pH- 9.0 using the reagent DHBMP. The tolerance limit was taken as the amount of foreign ion required to cause $\pm 2\%$ error in the absorbance. Many anions like F^- , Cl^- , Br^- , NO_3^- and SO_4^{2-} do not interfere in the determination of cobalt at pH-9.0, 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.

Antibacterial activity of reagent and chelate: Thiosemicarbazones being chelating agent's shows good antibacterial activity [19-21] 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" [22, 23]. The results are given in table 5.

Table 5.

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
Sample	E.Colli / gram -ve / microgram/ml	S.Aures / gram +ve / microgram/ml
Dhbmpt	250	125
Co(II) - DHBMP	100	125

DHBMP reagent shows poor activity against E.coli (Gram-ve) bacteria while shows good activity for S. Aureus (Gram+ve) bacteria which is more than "Ampicillin Drug".

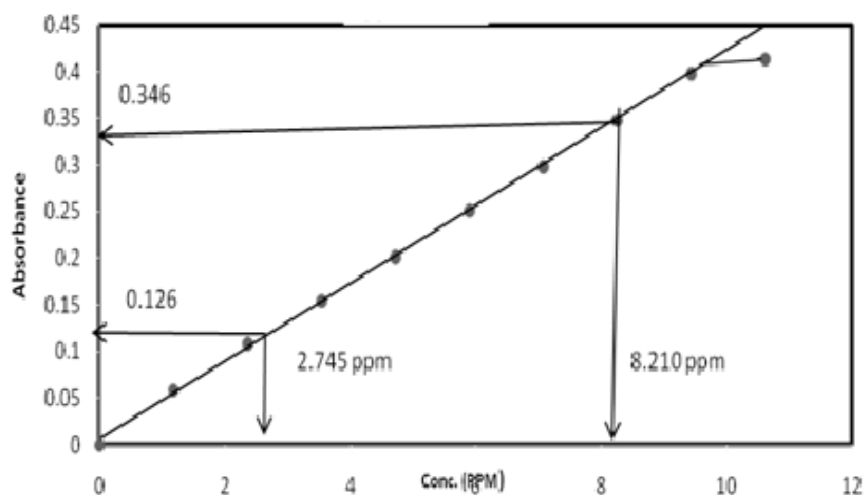
Co(II) -DHBMPT chelate shows good activity against E.coli (Gram -ve) bacteria which is same as “Ampicilline Drug” and also exhibit very good activity against S. aureus (Gram +ve) bacteria which is more than “Ampicilline Drug”.

APPLICATIONS

Determination of Percentage Purity of Cobalt From Cobalt Metal Sample: Pre analyzed sample of cobalt metal, was weighed exactly (0.2760 g) 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 doubly distilled water in a volumetric flask. From this stock solution, 25.0 ml solution was taken and again diluted with doubly distilled water to 100 ml (1ml = 69 μ g). Above stock solution is also analyzed by conventional titrimetric method [13] and percentage of cobalt was determined (average of three determinations) it was found to be 99.63% cobalt (II). Complexation behavior of Co(II) present in 1.0ml and 3.0mL of diluted solution was studied with excess of reagent (4.0ml, 0.01M) at pH 9.0 by diluting final volume 25ml with 50% aqueous ethanol and the absorbance of the above solutions were measured at 410nm using ligand blank. Absorbance values obtained were plotted in Beer's law plot.

Reported percentage of cobalt in cobalt metal sample = 99.63%

Absorbance	ppm of Co(II) taken	ppm of Co(II) found	percentage of Co(II) obtained	%Error
0.126	2.76	2.745	99.09	-0.54%
0.346	8.28	8.210	98.79	-0.84%



Beer's law plot of Co(II)-DHBMPT

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