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Spectroscopic Determination Of Co(II) With 2, 4 Dihydroxy-5-Bromo[2'-Methyl] Propiophenone Oxime

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Abstract: Co(II) was determined spectrophotometrically after co-precipitation with 2, 4 Dihydroxy-5-bromo[2'-methyl] propiophenone oxime (DHBMPO) at room temperature at pH 7.0 in chloroform at 440nm. Beer's law was obeyed upto 11.79 ppm of Co(II). Molar absorptivity and Sandell's sensitivity were found to be 2.125 x 10^3 lit mol^{-1} cm^{-1} & 0.02773 µg/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 1.23 x 10^{10}. Gibb's free energy change for complex formation reaction was also calculated and found to be -13.85 k cal/mol. From TGA, the energy of activation was calculated using Broido method and found to be 12.54 K Cal/mol for first step and 14.57 K Cal/mol for second step decomposition. The reagent has been satisfactorily applied for the determination of cobalt in pure Co-metal sample.
Key words: Spectroscopic determination, Propiophenone oxime, DHBMPO.

Introduction

Organic reagents forms chelate with metal ions. Formation of coordination compounds by organic reagents with metal ions has been extensively used in analytical chemistry. Many organic reagents like o-hydroxy oximes[1-7], oximes[8-9], thiosemi carbazones[10-14], chalcone oxime[15], anilides[16], various heterocyclic compounds have been used for gravimetric and spectrophotometric determination of Co(II). Here we have synthesized a novel reagent [DHBMPO] for gravimetric and spectroscopic determination of Co(II).

Experimental

Reagents & solutions

DHBMPO was synthesized using the method of H. Nogami[17] by the condensation of resorcinol with isobutyric acid in presence of anhy. $ZnCl_2$ giving 2, 4 dihydroxy [2'-methyl] propiophenone. It was than brominated with Bromine in acetic acid giving 2, 4 dihydroxy-5-bromo[2'-methyl]propiophenone.
Bromo derivative was then converted to oxime using hydroxyl amine hydrochloride and sodium acetate. The oxime was re-crystallized from ethanol bearing M.P. 162.1° C.

Co(II)-metal solution: A stock solution of cobalt(II) (0.05M) was prepared by dissolving an accurately weighed amount of cobalt chloride hexahydrate in deionized water.
Solutions of other diverse ions were prepared by dissolving their salts (A.R.) in deionized water.

Characterization of reagent

Elemental analysis: Elemental analysis of the reagent was done using Elementar Vario EL III analyzer. The percentages are in agreement with its

molecular formula. The results are represented in Table:1.

UV-Visible spectral studies: The UV-Visible spectrum of reagent in ethanol was recorded on "Perkin-Elmer Lambada-35 UV-Visible spectro photometer". Wavelength of maximum absorption is 226nm.

FT-IR Spectral studies: FTIR spectrum of the reagent was recorded on "Perkin Elmer-Spectrum RX-I" in KBr pellet. The bands which are observed are given in Table:2 .

^{1}H-NMR Spectral studies: The NMR spectrum of the reagent was taken in DMSO. The NMR spectrum was recorded on Brucker Avance-II 400 NMR spectrophotometer using TMS as reference. Assignment of signals to different protons is given in Table:3.

Results and Discussion

Gravimetric determination of Co(II): A 0.05M solution of the reagent in 50% aqueous ethanol was used. $CoCl_2$ solution (0.05M, 10ml) was taken in clean beaker and diluted to about 100ml with distilled water. A small excess of reagent (0.05M, 22ml) was added and desired p^H was adjusted using ammonia & ammonium chloride buffer. Brown precipitate obtained was digested on water bath for 1 hr at 60ºC. The precipitate was filtered through a weighed sintered glass crucible (G4) & washed with warm water followed by 50% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weighed at 110º-115ºC in hot air oven, cooled & weighed. The experiment was repeated at different p^H of solution. The results obtained are given in Table:4.

Table 1: Elemental analysis of Reagent

Reagent	Percentage found (Calculated)		
	Carbon	Hydrogen	Nitrogen
DHBMPO	43.55% (43.79%)	4.367% (4.379%)	5.020% (5.109%)

Table 2: IR Spectra

Reagent	$\nu^{(O-H)}$ Phenolic	$\nu^{(O-H)}$ Oximino	$\nu^{(C-H)}$ aliphatic	$\nu^{(C=C)}$ aromatic	$\nu^{(C=N)}$	$\nu^{(N-O)}$
DHBMPO	3484 cm^{-1}	3389 cm^{-1}	2965 cm^{-1}	1599 cm^{-1}	1633cm^{-1}	927 cm^{-1}

Table 3: NMR Spectra

Reagent	Alkyl group	Methine Proton	Phenolic (-OH)	Oximino (-OH)	Aromatic proton
DHBMPO	1.3680-1.3855 ppm (singlet)	3.3836-3.4531 ppm (multiplet)	12.9897 ppm	11.2118 ppm	7.5682 ppm

Table 4: Gravimetric determination of Co(II)-DHBMPO

p^H	Co(II) complex in gm	Co(II) found in mg	Error	
			in mg	%
5.0	0.2994	29.1678	-0.2987	-1.01
5.0	0.2997	29.1970	-0.2695	-0.91
5.5	0.3002	29.2457	-0.2208	-0.74
5.5	0.3006	29.2847	-0.1818	-0.62
6.0	0.3007	29.2941	-0.1724	-0.58
6.0	0.3010	29.3237	-0.1428	-0.48
6.5	0.3011	29.3334	-0.1331	-0.45
6.5	0.3008	29.3042	-0.1623	-0.55
7.0	0.3020	29.4210	-0.0455	-0.15
7.0	0.3019	29.4113	-0.0552	-0.18
7.5	0.3037	29.5867	+0.1202	+0.41
7.5	0.3035	29.5672	+0.1007	+0.34
8.0	0.3013	29.3529	-0.1136	-0.38
8.0	0.3012	29.3432	-0.1233	-0.42

Conversion factor: 1gm complex= 97.4207mg Co(II)

Effect of diverse ion: To study the effect of foreign ions on gravimetric determination of Co(II), 8-10mg of various cations were added to a solution containing 29.4665 mg Co(II) at p^H 7.0 and gravimetric estimation were done. It was observed that Sr(II), Ca(II), Mg(II), Zn(II), Ba(II), Pd(II), Cd(II), do not interfere at this p^H but Mn(II), Ni(II) interfered seriously. Many common anions like nitrate, nitrite, sulphate, chloride, bromide and iodide were not found to interfere.

Spectrophotometric study of Co(II)-DHBMPO: In absorption spectra of Co(II) complex in chloroform a shoulder band is obtained at 440nm and hence all spectrophotometric measurements were done at this wavelength. Different aliquots of Co(II) solution were taken and buffer solution was added to maintain the p^H 7.0. The excess reagent was added to get complete precipitation of complex. It was extracted in three 5.0ml portion of chloroform and final volume of this solution was adjusted to 25ml with chloroform. The absorbance was measured at 440nm and plotted against the concentration of Co(II). It was found that Beer's law was obeyed upto 11.79 ppm of Co(II). Molar absorptivity and Sandell's sensitivity were calculated form graph and it was found to be 2.125 x 10^3 lit mol^{-1} cm^{-1} & 0.02773 µg/cm^2 respectively. Job's method of continuous variation[18] and Yoe and Jones mole ratio method[19] were used to determine the stoichiometry of the complex. It was found to be 1:2[M:L]. This is in agreement with stoichiometry determined from gravimetric analysis. The stability constant was calculated using the formula,

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

where, α= 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 the above two methods was found to be 1.23 x 10^{10} and ΔG° for complex formation reaction at 27°C was found to be -13.85 K Cal/mol.

Thermogravimetric analysis: From TG analysis of the Co(II) chelate, it was found that there is no weight loss upto 125°C indicating that the chelate can be dried safely without decomposition at 110°C. Loss in weight from 125-760°C is due to removal of organic ligand molecules. Observed loss and weight of metal residue agrees well with the formula of the chelate in which M:L ratio is 1:2. Activation energy Ea was calculated using Broido method[20] and found to be 12.54 K Cal/mol for first step and 14.57 K Cal/mol for second step decomposition.

IR Spectra: Interpretation of IR-spectra of the chelate shows weak band around 3478 cm^{-1} in comparison of ligand molecule. The weak band due to ν^{-OH} of oximino group is found at 3391 cm^{-1} in ligand, is observed at nearly the same position in the complex. $\nu^{C=N}$ stretching band observed at 1633 cm^{-1} in ligand is shifted to 1618 cm^{-1} in chelate, this indicates nitrogen is coordinately bonded with metal ion and covalently bonded with oxygen atom. It is

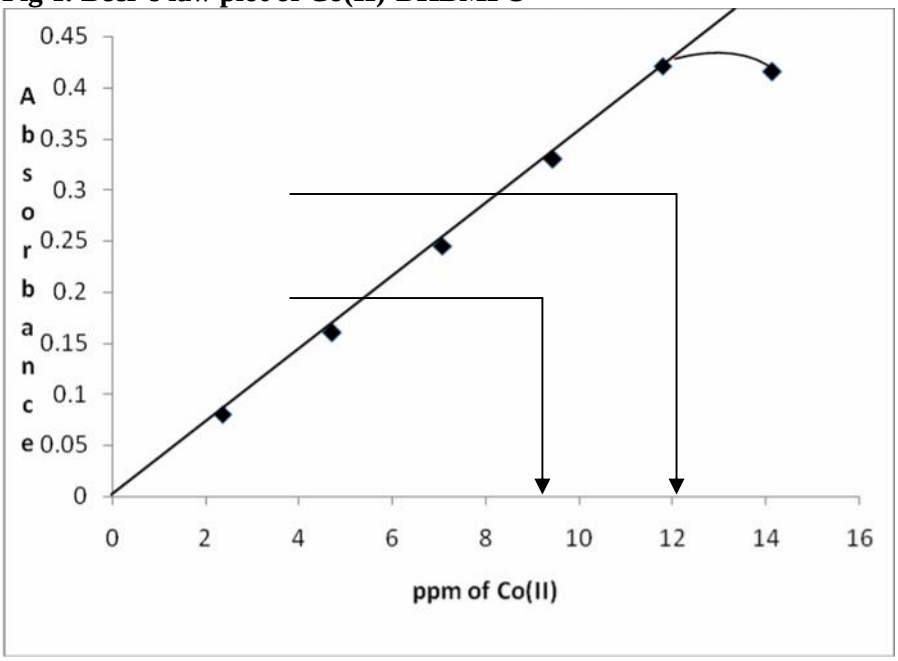
also supported by the downward shift of ν^{N-O} group i.e. from 927 to 876 cm^{-1}.

Spectrophotometric determination of Co(II): A pure sample of Co(II) weighing 0.276gm was dissolved in nitric acid and excess HNO_3 was evolved by boiling with HCl, and diluted to 1000ml with double distilled water. 25ml of stock solution was further diluted to 50ml. Above stock solution was also analyzed by conventional titrimetric method and percentage of cobalt was determined and found to be 99.50% cobalt(II). A 1.0ml and 1.5ml of this diluted cobalt metal sample was taken in two different beakers containing 4.0ml (0.01M) of reagent solution each. Small amount of double distilled water was added and pH of the solution was adjusted to 7.0 with ammonia and ammonium chloride buffer. Complex was extracted in $CHCl_3$ and final volume was made 25ml. The absorbance was measured and ppm of Co(II) was calculated by using Beer's law plot. Results obtained are given in Table:5 and Fig. I.

Table 5: Percentage Co(II) reported in Co metal sample=99.50%

Co(II) taken in ml	Absorbance	ppm found	ppm taken	% Co(II) observed	% Error
1.0	0.196	5.50	5.52	99.14	-0.36
1.5	0.290	8.24	8.28	99.02	-0.48

Fig-I: Beer's law plot of Co(II)-DHBMPO



References

1. Desai K.K. & Naik H.B.,2-Hydroxy-4-ethoxypropiophenone Oxime as a Gravimetric Reagent for Cu(II), Ni(II) & Pd(II), Indian J. Chem., 1986, 25A, 297.
2. Patel N.B. & Desai K.K., 2,4-Dihydroxy-5-Nitropropiophenone Oxime as an Analytical Reagent: Studies on Ni(II) and Pd(II) Chelates, Asian J. Chem., 2003, 15,751.
3. Patel N.B. & Desai K.K., 2,4-Dihydroxy-5-nitropropiophenone Oxime as a Gravimetric Reagent for Cu(II), Asian J. Chem., 2004, 16(2), 1076.
4. Naidu R. Sheshadri & Naidu R. Raghava, 2-Hydroxy-1-naphthaldoxime as an analytical reagent for titanium(IV), Talanta, 1978, 25, 354.
5. Shingadia S.K. & Desai K.K., 2-Hydroxy-5-methylbenzophenone oxime (HMBO) as an Analytical Reagent for Gravimetric Determination of Cu(II), E.J. Chem., 2007, 4(1), 97.

6. Shingadia S.K. & Desai K.K., 2-hydroxy-5-methylbenzophenone oxime (hmbo) as an analytical reagent for Molybdenum (vi), Oriental J. Chem., 2006, 22(3), 703.
7. Patel V. M. & Patel N. B., 2,4-Dihydroxy-5-Bromo-α-Phenylacetophenone Oxime as an Analytical Reagent: Studies on Ni(II) Chelate, Acta Ciencia Indica, 2008, Vol. XXXIV C, No. 3, 427.
8. Ninan S., Varadarajan A., Jadhav, S.B., Kulkarni, A.J. & Malve S.P., Camphor-3-thioxo-2-oxime as an analytical reagent for extractive spectrophotometric determination and separation of lead, Spectrochimica Acta, Part A, 1999, 55, 825.
9. Wiersma Lawrance K. & Cott Peter F., Glyoximes as reagents for the gravimetric determination of bismuth, Analytica Chimica Acta, 1968, 40, 291.
10. Desai M.J. & Desai K.K., 2,4-Dihydroxy-5-Bromoacetophenone Thiosemicarbazone as an Analytical Reagent: Studies on Cu(II) and Fe(III) Chelates, Asian J. Chem., 1999, 11(4), 1313-1316.
11. Reddy K. Hussain, Prasad N.B.L. & Reddy T. Shreenivasalu, Analytical properties of 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone: simultaneous spectrophotometric determination of copper(II) and nickel(II) in edible oils and seeds, Talanta, 2003, 59, 425.
12. Pavon J.M. Can. & Pino F., The use of furfural thiosemicarbazone for the gravimetric determination of palladium, Talanta, 1973, 20, 339.
13. Satheesh K.P., Ravichandran. S, Rao V.Suryanarayana, Devanna N. and Chandrasekhar K.B., Spectrophotometric Determination of Trace amounts of Molybdenum(VI) Using 4-Hydroxybenz aldehydethiosemicarbazone, International Journal of ChemTech Research, 2011, 3, 4, 1740-1746.
14. Lokhande R. S., Janwadkar S. P., Pitale Shirish, Kulkarni Santosh, Patil Sanjay, Solvent extraction and Spectrophotometeric determination of Mo(VI) by using Acetophenone 2',5'-dihydroxy,semicarbazone as an Analytical reagent, International Journal of ChemTech Research, 2011, 3, 4, 1765-1768.
15. Desai A.M. & Desai K.K., 2',4'-dihydroxy-5'-bromo-chalcone oxime as a gravimetric reagent for Cu(II), Oriental J. Chem., 2006, 22(2), 461-463
16. Chaudhari N.K. & Das J., Cyclopentanone-2-carboxyanilide as a reagent for the gravimetric, titrimetric and spectrophotometric determination of beryllium, Analytica Chimica Acta, 1971, 57, 193.
17. Nogami H., J. Pharm. Soc., Japan,1945, 61, 46.
18. J. E. House, Inorganic chemistry, 2008, 673.
19. Yoe J. H. & Jones A. L.; Ind. Engg. Chem. Anal. Ed. 1944, 16, 111.
20. Broido A., A simple, sensitive graphical method of treating thermogravimetric analysis data, J. Polym. Sci., Part A-2, 1969, 7, 1761.

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