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NOTE

2,4-Dihydroxy-5-Nitropropiophenone Oxime as an Analytical Reagent: Studies on Cobalt Chelate

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2.4-Dihydroxy-5-nitropropiophenone oxime (DHNPO) has been used as an analytical reagent for gravimetric and spectrophotometric determination of Co(II). Metal-ligand ratio (1 : 2) has been determined using spectrophotometric method. Stability constant of complex has been calculated. The complex was found paramagnetic in nature. TGA studies were done on complex. Energy of activation for decomposition steps has been calculated, using Broido method.

Key Words: 2,4-Dihydroxy-5-nitropropiophenone oxime, Cobalt, Chelate.

The importance of *o*-hydroxy ketoximes[1–4] phenyl hydrazones, thiosemicarbazones, chalcone oximes etc. is increasing day by day. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. In this work, we report the use of 2,4-dihydroxy-5-nitropropiophenone oxime (DHNPO) as a gravimetric reagent for Co(II).

All the spectrophotometric and pH measurements were done on Bausch and Lomb spectrophotometer (Spectronics-20) and ELICO pH-meter (LI-10T) respectively.

Synthesis of DHNPO: 2,4-Dihydroxypropiophenone (respropiophenone) was synthesized by the condensation of resorcinol with propionic acid in presence of anhydrous zinc chloride according to the method of Brewster and Harris[5, 6]. 2,4-Dihydroxy-5-nitropropiophenone was obtained by nitrating respropiophenone with fuming nitric acid in glacial acetic acid at 0–5°C temperature. The ketone was converted to oxime[7] using hydroxylamine hydrochloride and sodium acetate. The oxime was recrystallized from ethanol. The obtained pale yellow crystal has m.p. 193°C.

The NMR spectra of reagent were taken in $CDCl_3$ using TMS (tetramethyl silane) as reference. The shift values obtained can be assigned to different types of protons. The ethyl group present in the reagent is splitting into quartet and triplet. The chemical shift value for —CH_2 quartet ($\delta = 2.70–2.90$ ppm) and for —CH_3 ($\delta = 1.18–1.25$ ppm) is observed. Quartet is appearing at slightly downfield due to adjacent highly electronegative carbonyl group. Two phenolic protons give signal at $\delta = 13.19$ ppm which appear at extremely downfield region due to adjacent highly electronegative oxygen atom as well as acidic character of phenolic proton. The oximino —OH group gives signal at $\delta = 8.19$ ppm. Aromatic protons appear at $\delta = 6.53$ and 6.57 ppm.

Gravimetric determination of Co(II): A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Cobalt chloride solution (0.05 M, 10 mL) was taken in clean beaker and diluted to about 100 mL with distilled water and desired pH was adjusted using ammonia and ammonium chloride buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 22 mL). A brown precipitate obtained was digested on water bath for 1 h at 60°C. The precipitate was filtered through a weighed sintered glass crucible (G-4) and 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 weight at 110–115°C in hot air oven, cooled and weighed. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH = 8.0 to evaluate its applicability. In any case the error did not exceed ± 1.0%.

Interference: To study the effect of foreign ions on gravimetric determination of Co(II), 8–10 mg of various cations were added to a known amount of Co(II) solution at pH 8.0 and gravimetric estimations 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 pH, while Mn(II), Cu(II) and Ni(II) interfered seriously. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were also not found to interfere.

Spectrophotometric study of Co(II)-DHNPO complex: It was found that Co(II) complex with DHNPO absorbs maximum at 570 nm 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 pH 8.0. The excess of reagent was added to get precipitate of complex. It was extracted with three 5.0 mL portions of chloroform and the combined extracts were diluted to 25 mL. The absorbance was measured at 570 nm. The absorbances were plotted against the concentration of Co(II). It was found that Beer's law was obyed up to 8.25 ppm of Co(II). Molar absorptivity and Sandell's sensitivity was calculated from graph and was found to be 7.71×10^2 L mol^{-1} cm^{-1} and 0.076 μg of Co(II)/cm^2 respectively.

Job's method[8] and mole ratio method[9] were used to determine the stoichiometry of the complex, it was found to be 1 : 2 (M : L). This is in agreement with the stoichiometry from gravimetry. The stability constants were calculated using the formula, α is degree of dissociation.

$$K_s = \frac{1-\alpha}{4\alpha^3 C^2}$$

where

$$\alpha = \frac{E_m - E_s}{E_m}$$

E_m = maximum absorbance obtained from the graph,

E_s = absorbance at the stoichiometric molar ratio of the metal to reagent in complex.

The average stability constant obtained from two methods is 2.74×10^9. and $\Delta G°$ for complex formation at 27°C is –12.95 kcal/mol.

Thermogravimetric anaysis: TGA of the cobalt chelate was done on Universal V_1-12E-TA thermal analysis system. It was found that there is no loss in weight up to 125°C indicating that the chelate can be safely dried without decomposition at 110°C. Loss in weight above 125°C is due to decomposition of chelate and loss of ligand molecules. Weight of final residue corresponds to CoO in accordance with the formula $(C_9H_9O_5N_2)_2Co$. The observed loss and weight of residue agreed well with the loss and weight expected as per formula of chelate in which M : L ratio is 1 : 2 in the complex.

Broido's method[10] was applied to TGA thermograms of Co(II)-DHNPO complex obtained at 10°C/min. Activation energy E_a was calculated using this method for thermal decomposition of chelate and the value of E_a was found to be –22.22 kcal/mol.

Magnetic susceptibility measurement: The magnetic measurements of complex at room temperature were carried out on Gouy balance as per method suggested by Prasad and co-workers[11]. The magnetic moment of solid Co(II)-DHNPO complex was determined, which indicates the paramagnetic character. Values of magnetic moments at 4 and 6 ampere are 1.86 and 1.88 BM respectively. Effective magnetic moment values of Co(II)-DHNPO complex indicate the presence of one unpaired electron.

IR spectra: The IR spectrum (KBr) of the ligand shows two bands in —OH stretching region. One band at 3399 cm^{-1} which disappears in the spectra of chelate is due to phenolic —OH group. Deprotonation of —OH group takes place and metal coordinates with the oxygen by covalent bond. The coordination of metal through nitrogen of oximino group may be seen by lowering of $\nu(C{=}N)$ frequency from 1591 cm^{-1} in ligand to 1540 cm^{-1} in the chelate. This is also supported by slight downward shift of $\nu(NO)$ at 993 cm^{-1} in the ligand to 930 cm^{-1} in the chelate.

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