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Spectrophotometric Studies of Complexes of Nickel(II) with 6-Substituted-1-Hydroxy-1, 2, 3-Benzotriazoles Part-VII

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Job's method of continuous variation as well as molar ratio method have been used in order to establish the stoichiometry of complexes of nickel(II) with 6-substituted-1-hydroxy-1, 2, 3-benzotriazoles (6-Chloro-, 6-bromo and 6-nitro-1-hydroxy-1, 2, 4-benzotriazole). The metal to ligand ratio is found to be 1 : 2. Stability constant of the order of 10^7 to 10^8. Free energy values of the complex formation are also given.

INTRODUCTION

The property of triazoles and their derivatives to form complexes with metal ions have been utilised by many workers for estimation of metal ions[1,2]. Several compounds containing the grouping >NOH have been reported to be useful as organic precipitating agent.[3] 6-Chloro-4-nitro-1-hydroxy-1,2,3-benzotriazole also contain a similar grouping and is therefore used for estimation of silver[4]. Lorionov *et.al*[5] have reported IR studies on triazoles. The IR spectra of benzo-1,2,3-triazoles have been described by O'Sullivan[6]. Rees and Storr[7] have reported NMR spectra of 1-chloro-benzotriazole. Thompson *et al.*[8] have carried out UV studies on triazoles. Benzotriazoles complexes with palladium have been reported by Wilson and Wilson.[9]

Survey of literature reveals that no work, however, seem to have carried out on spectrophotometric studies of complexes of 6-substituted-1-hydroxy-1,2,3-benzotriazoles. The present study deals with determination of molar ratio, stability constant and free energy of nickel(II) complexes with 6-chloro-, 6-bromo-, 6-nitro-1-hydroxy-1, 2, 3-benzotriazoles.

EXPERIMENTAL

Apparatus

Bausch and Lomb spectronic 20 was used to determine the composition of the complex at 25±1°C the mixture of ethanol and water.

Reagents : 6-substituted-1-hydroxy-1, 2, 3-benzotriazoles

6-Chloro-1-hydroxy-1,2,3-benzotriazole and 6-bromo-1-hydroxy-1,2,3-benzotriazole were prepared by method given by Joshi and Deorha[10] and 6-nitro-1-hydroxy-1,2,3-benzotriazole by Macbeth and Price[11]. These were recrystallised before use from hot water and dried in

vacuum. Purity of these compound was established by m. pt., IR and NMR spectra. Solution were made of 10^{-3}M by dissolving reagents in ethanol and water mixture.

Nickel(II) Chloride Solution

A stock solution (10^{-3}M) was prepared by dissolving A. R. Grade nickel (II) chloride in double distilled water and was standardised volumetrically.

To determine the composition of complexes, a large number of studies were carried out by changing the concentration of nickel (II) chloride & 6-substituted-1-hydroxy-1, 2, 3-benzotriazoles and making absorption measurement at different wavelength.

Nickel (II) Chloride Reaction

The reagent solution in ethanol and water mixture react with nickel (II) chloride solution and yield light green coloured extracts. Optical density measurement revealed that these extracts show maximum absorbance at certain wavelength. The wavelength of maximum absorbance λ_{max} lies at 370 to 380 nm. This evidently suggests that only one complex is formed in solution.[12]

Stoichiometry of the Complexes

The absorption of Ni(II) complexes of reagent was measured in solution to determine metal to ligand ratio by Job's method and molar ratio method. The procedure for a typical Job's study was as follows :

Procedure

The following set of mixture was prepared in Job's method of continuous variation to find the composition of the complex formed, after selecting the wavelength of maximum absorption by Vosburgh and Cooper method 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 ml of 1×10^{-3}M nickel (II) chloride solution were mixed with 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0 ml of 1×10^{-3}M 6-substituted-1-hydroxy-1, 2, 3-benzotriazoles in a 10 ml of cell.

For the molar ratio method the procedure for a typical study was as follows :

In this method the volume of nickel(II) chloride was kept constant. The constant volume of nickel (II) chloride was 2 ml. The following set of mixtures were prepared: 1.0, 2.0, 3.0, 4.0, 5.0, 0.6, 7.0, 8.0 ml of 1×10^{-3} M 6-substituted-1-hydroxy-1, 2, 3-benzotriazole added to 2 ml of 1×10^{-3} M of nickel(II) chloride.

Stability Constant of the Complexes

It was intersting to determine the stability constant of the complexes Ni(II) with 6-substituted-1-hydroxy-1, 2, 3-benzotriazoles. These were evaluated from a study of the absorptions obtained by molar ratio method (Fig. 3). The degree of dissociation α, is given by the equation :

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

where E_m is the absorbance of the complex when excess of the reagent is present and E_s is the absorbance of the complex at equivalent point. Hence, in the reaction $ML_2 \rightleftharpoons M^{2+} + 2L^-$ the stability constant K of the complex can be calculated from the following equation

$$K = \frac{1 - \alpha}{4\alpha^3 c^2}$$

Here α and C denote the degree of dissociation and the total concentration of the complex in moles per litre assuming no dissociation respectively. Results obtained on the basis of these equations are given in Table 1. The free energy of formation $\Delta G°$ for each complex calculated according to Van't Hoff isotherm $\Delta G° = -RT\ln k$ is also compiled in Table 1.

TABLE 1

SPECTRAL CHARACTERISTICS AND STABILITY CONSTANTS OF Ni(II)-6-SUBSTITUTED-1-HYDROXY-1, 2, 3-BENZOTRIAZOLES

Temperature : 25 ± 1°

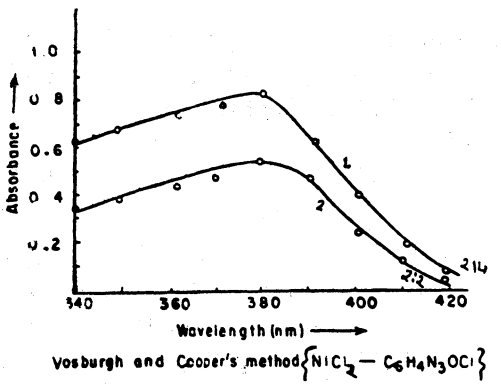
Compound	Colour of the complex	Wavelength of maximum absorption (nm)	Stability constant K ($\times 10^7$)	Free energy $\Delta G°$ (Kcal/mole)
6-Chloro-1-hydroxy-1, 2, 3-benzotriazole	light green	380	3.32	−10.18
6-Bromo-1-hydroxy-1, 2, 3-benzotriazole	light green	380	3.30	−10.17
6-Nitro-1-hydroxy-1, 2, 3-benzotriazole	light green	370	5.80	−10.51

RESULTS AND DISCUSSION

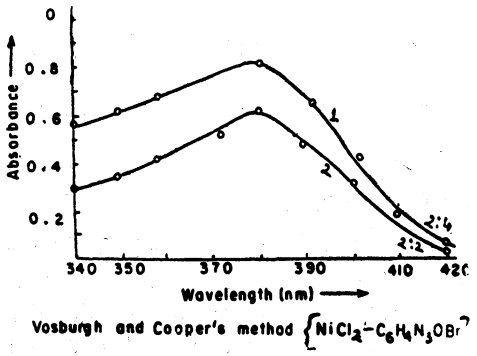
All the ligands *viz.* 6-chloro-, 6-bromo-, 6-nitro-1-hydroxy-1, 2, 3-benzotriazole give green coloured complex with Ni(II) ion in water and ethanol mixture, which are stable and seemed to have a very definite stoichiometry. Water and ethanol mixture is used as solvent because (i) the reagent is more freely soluble in it than another solvents (ii) the extraction of coloured complexes is readily obtained (iii) the reagents solution has no absorption at the wavelength of interest.

In the method proposed by Job's[12] and modified by Vosburgh and Cooper[13], the solution of the cation and ligand with identical concentration are mixed in varying amount but their sum (total volume) is kept constant. The absorption of each solution is measured at suitable wavelength. The absorbance is then plotted against the molar fraction of one of the reactant *i.e.* $\frac{M}{M+L}$ where M is volume of cation solution and L is of the ligand.

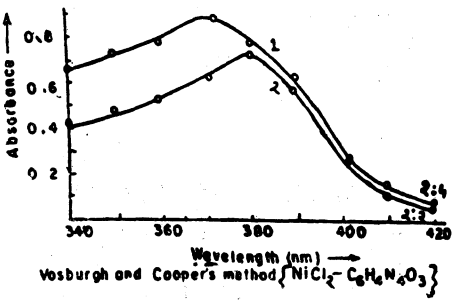
Optical density measurements give wavelength of maximum absorbance for Ni(II) ion complexes with ligands which was found to be between 370–380 nm as it is evident by graph plotted between different wavelength and optical density (Fig. 1). The observation of Job's curve



(a)



(b)



(c)

Fig. 1

(Fig. 2) where the curve shows maximum at a volume ratio (M/L) shows that in each of the complexes the metal to ligand ratio is 1 : 2 as two molecules of ligand for one atom of metal.

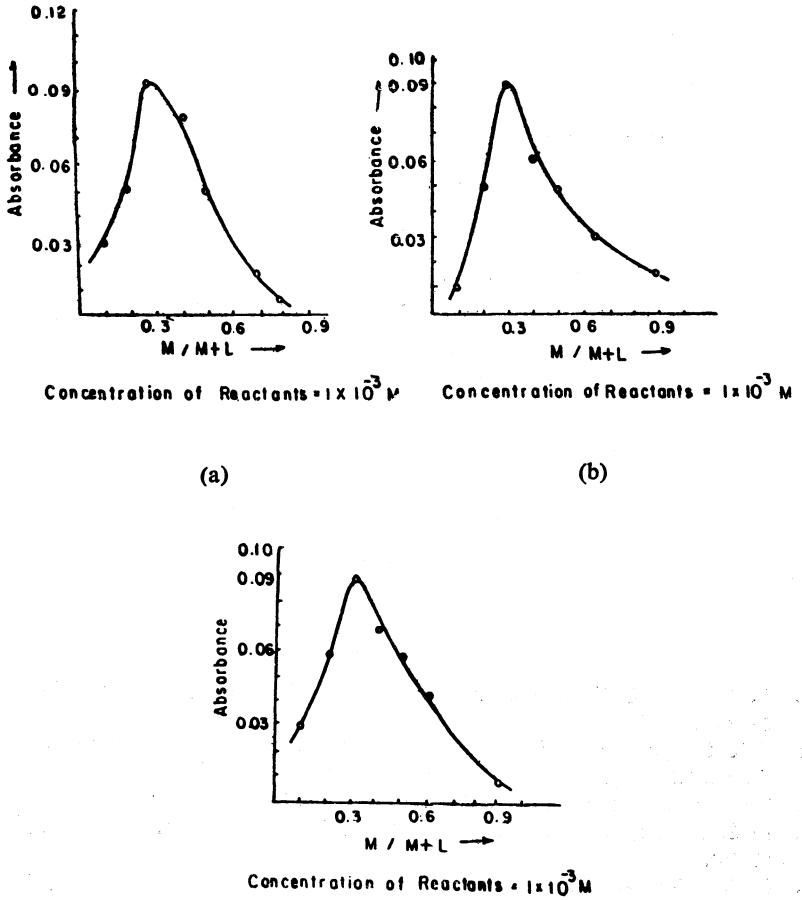


Fig. 2. Job's Method

Studies of molar ratio method (Fig. 3) show no sharp break in the plot. The continuous curves become parallel to molar ratio axes when an excess of ligand 6-substituted-1-hydroxy-1,2,3-benzotriazole is added. The results obtained by extrapolation of these plots are little uncertain although in a few instances molar ratio close to 1 : 2 ligand : Ni(II) is observed.

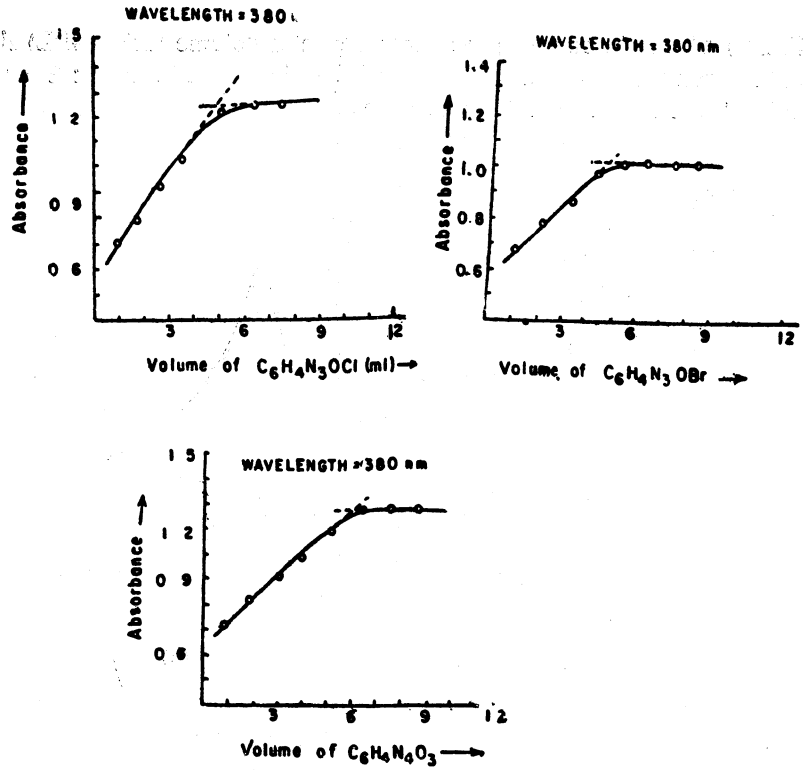


Fig. 3. Mole Ratio Method

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