Int. J. Chem. Sci.: 8(2), 2010, 1226-1230

SPECTROPHOTOMETRIC DETERMINATION OF Ni (II) WITH 1,6 -DIMERCAPTO-1,6-DIAMINO-2,4,5-TRIAZA-3-PHENYL-3-HEXENE (N-BENZOYLTHIOUREA THIOSEMICARBAZONE)

MRINAL CHANDRA[*] and S. K.MISHRA[a]

Department of Chemistry, Jai Prakash University, CHAPRA - 841301 (Bihar) INDIA
[a]P.G. Department of Chemistry, Jai Prakash University, CHAPRA - 841301 (Bihar) INDIA

ABSTRACT

1,6-Dimercapto-1,6 -diamino-2,4,5-triaza-3-phenyl-3-hexene (MAAPHE) was synthesised and used as a spectrophotometric reagent for nickel. Ni (II) forms pale yellow coloured complex between pH range 7.0 to 11.0 and shows maxm absorption at 385 nm. Molar absorptivity for Ni- MAAPHE is 2.850 x 10^3 L/mol/cm. Ni-MAAPHE has 1 : 2 (M : L) stoichiometry. Beer's law is obeyed up to 16.49 ppm for Ni (II). The reagent has been found to give satisfactory results for the analysis of nickel in German-silver alloy. Formation of the complex has been supported from the IR spectral data.

Key words: Spectrophotometry, Ni (II), MAAPHE, German - silver alloy.

INTRODUCTION

Nickel is one of the important alloying elements for steel and cast iron. It is biologically important being an essential trace element in human diet. It has been reported that normal human plasma contains 0.012 - 0.085 ppm of Ni (II).

Many organic compounds like oximes[1], semicarbazones[2], thiosemicarbazones[3,4] have been used for spectrophotometric determination of Ni (II) in German- silver alloy. Several thiosemicarbazone have been employed as chromogenic agents for the spectrophotormetric determination of nickel. Some of them are less sensitive; some are less selective while others involve extraction into carcinogenic organic solvents[5].

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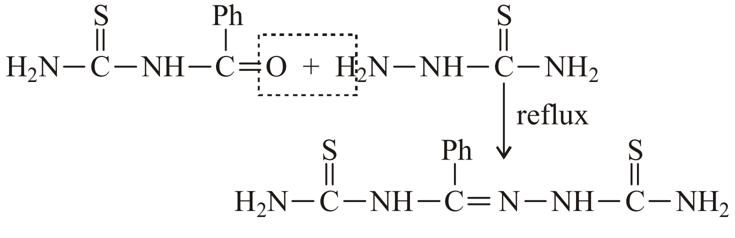
[*] Author for correspondence

EXPERIMENTAL

Spectrophotometric measurements were made on a Shimadzu UV-160 recording spectrophotometer. All pH measuments were done on Systronics digital pH meter and buffer solutions of required pH were obtained using disodium hydrogen phosphate-potassium dihydrogen phosphate, borax-hydrochloric acid and ammonia-ammonium chloride of suitable concentrations. The IR spectra were recorded on Perkin-Elmer Spectrophotometer in KBr pellets.

Synthesis of 1,6-dimercapto-1,6-diamino-2,4,5-triza-3-phenyl-3-hexene (MAAPHE)

The reagent 1,6- dimercapto - 1,6 - diamino -2,4,5- triaza -3- phenyl -3 - hexene was prepared by refluxing equimolar concentrations of thiosemicarbazide and N-benzoyl thiourea in ethanolic medium for 3 to 4 hours. The resulting products were cooled and filtered. Silky crystals were obtained. The crystals were washed successively with DMF, cold ethanol and dried in vaccuo and analysed (m.p. = 232 ± 2°C) as $C_9H_{11}N_5S_2$.[6]



$$H_2N-\overset{\overset{S}{\|}}{C}-NH-\overset{\overset{Ph}{|}}{C}=O + H_2N-NH-\overset{\overset{S}{\|}}{C}-NH_2 \xrightarrow{\text{reflux}} H_2N-\overset{\overset{S}{\|}}{C}-NH-\overset{\overset{Ph}{|}}{C}=N-NH-\overset{\overset{S}{\|}}{C}-NH_2$$

(MAAPHE)

Preparation of solutions

All the chemicals used in the work were of Analytical grade. Stock solution of ligand (MAAPHE) (0.02 M) was prepared by dissolving thiosemicarbazone in ethanol. Stock solution of Ni (II) (0.05 M) was prepared by dissolving $NiSO_4$ in double distilled water with little free acid and stand titrimetrically[7].

Preparation of Ni (II)-MAAPHE complex

A series of buffer solutions with pH values ranging from 7.0 to 11.0 were prepared using Na_2HPO_4-KH_2PO_4, borax- HCl and NH_3-NH_4Cl. 1.0 mL of 0.05 (M) Ni (II) solution and 5.0 mL of 0.02 (M) ethanolic solution of MAAPHE were taken in 50 mL beaker. The pH of the solution was adjusted within the range where maximum colour was developed. This solution was diluted to 25 mL with ethanol so as to keep 50% concentration of alcohol in final solution. The spectra of the above solution were recorded from 350 nm to 800 nm.

The absorbance constantly increases towards shorter wavelength. A shoulder was obtained at 385 nm and hence, all measurments were done at this wavelength

In case of Ni (II), maximum complex formation occurs at pH 9.0 and hence, in all further studies, this pH value was used. Beer's law was obeyed for Ni (II) at 385 nm. Jobs method of continuous variation and molar ratio method indicated 1 : 2 (M : L) ratio for Ni (II) complex and the stability of the complex calculated from Jobs method was found to be 2.121 x 10^4.

RESULTS AND DISCUSSION

Interference

Interference due to associated ions was examined during the determination of 16.50 ppm of Ni (II) at pH 9.0 using the reagent MAAPHE. Many anions like chloride, bromide, iolide, nitrate, sulphate, acetate, carbonate, citrate, EDTA disodium salt and phosphate do not interfere in the determination of nickel at pH 9.0, even when these are present in 50 fold excess. Thiourea (22) and oxalate (5) can be tolerated. A 24- fold excess of Zn (II), Sn (II), Ca (II), Mg (II), Cd (II) and K (I) do not interefere. There is no interference from Fe (II) and Mo (VI) also at this pH.

Table 1: Spectral data for Ni (II)- MAAPHE complex

Characteristics	Ni (II) – MAAPHE
λmax (nm)	385
Optimum pH	7.0-11.0
Colour	Plae yellow
Beer's law obeyed (ppm)	16.49
Stoichiometry (M : L)	1 : 2
Molar absorptivity x 10^4	0.2850
Stability constant (Ks)	2.121 x 10^4
Sandell's sensitivity (mg/cm^2)	0.0287

Stoichiometry of complex

Metal to ligand ratio in complex was determined spectrophotometrically using Job's method of continuous variation and mole ratio method. It was found to be 1 : 2. The data of these were utilized to calculate stability constant of complex.

Determination of nickel in german-silver alloy

The standard sample of German-silver alloy (0.3745 g) was dissolved in HNO_3 (1 : 1) by heating slowly. The excess nitric acid was removed by evaporation. The solution was diluted with distilled water to 250 mL volumetric flask. 10 mL of this solution was taken to determine Ni (II) spectrophotometrically using MAAPHE at 385 nm following the same procedure. The experiment was repeated three times.

Table 2: Determination of nickel in German-silver alloy

Sample	Metal determined	Amount of nickel (%) (Expected) found
Germal-silver alloy	Nickel	(25.04) 24.49

*Average of three determinations

IR Spectra of ligand and complexes

The complexe waw obtained in solid state by refluxing stoichiometric amount of ligand and metal solution for 3 to 4 hours and then removing the solvent. The spectra were recorded in KBr pellets. The IR spectra of MAAPHE show a group of strong and broad bands in the range 3400-3100 cm^{-1}; combined mode of $\nu_{N\text{-}H}$, $\nu_{S\text{-}H}$ and ν_{NH} suggesting ligands to exists in thione/thiol forms in solid state. These bands are not affected in the spectrum of the complex indicating the non-partcipation of amino group. The bands at 1680 cm^{-1} and 950 cm^{-1} are assigned to ν (C=N) and ν (N-N) resptectively[8,9]. In case of Ni (II) - MAAPHE complex, ν (C=S) bands shows slightly downward shift at 780 cm^{-1}, while ν (C=N) shows decreased sharpness and intensity around 1680-1690 cm^{-1}, which indicates the participation of azomethine nitrogen[10]. In the far IR region, new additional bands in the region 450-455 cm^{-1} and 400-420 cm^{-1} were assingned to ν (M-N) and ν (M-S), respectively.

ACKNOWLEDGEMENT

The author are thankful to HOD, P.G. Department of Chemistry, Jai Prakash University, Chapra and Senior Colleagues, who supported a lot in this work.

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Accepted : 02.03.2010