International Journal Of
Recent Scientific Research
ISSN: 0976-3031
Volume: 7(3) March -2016

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THE OFFICIAL PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH (IJRSR)
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International Journal of Recent Scientific Research
Vol. 7, Issue, 3, pp. 9734-9737, March, 2016

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ISSN: 0976-3031

RESEARCH ARTICLE

SPECTROPHOTOMETRIC STUDY OF STABILITY CONSTANTS OF ADDUCTS OF NICKEL (II)-DIPHENYLTHIOCARBAZONATE WITH NITROGEN BASES BY JOB'S METHOD OF CONTINOUS VARIATION

Shivaraj[1]., Suresh T[1]* and Hiremath Suresha Babu[2]

[1]Department of Chemistry, Vijayanagar Sri Krishnadevaraya University, Ballari-583105, Karnataka
[2]Department of Engineering Chemistry, Rao Bahadhur Y Mahabaleshwarappa Engineering College, Ballari-583104, Karnataka

ARTICLE INFO

Article History:
Received 06th December, 2015
Received in revised form 14th January, 2016
Accepted 23rd February, 2016
Published online 28th March, 2016

Keywords:

Adduct, spectrophotometer, nickel (II)diphenylthiocarbazonate, adduct formation, steric factors.

ABSTRACT

The stability constants of adducts of nickel (II)diphenylthiocarbazonate($NiDz_2$) with different nitrogen bases was determined by using Job's continuous variation method spectrophotometrically in chloroform solution. In case of bidentate bases the Job's curves displayed a maximum at a mole fraction X_{NiDz2} = 0.5 indicating the formation of adducts with 1:1 $NiDz_2$ to bidentate bases and mole fraction X_{NiDz2} = 0.66 indicating the formation of adducts with 1:2 $NiDz_2$ to monodentate bases. The planar complex nickel (II)diphenylthiocarbazonate; diamagnetic, with dsp^2 hybridization, which forms adducts with two molecules of various monodentate nitrogen bases and one molecule with bidentate nitrogen bases. The main factor controlling the stability of the adducts have been investigated and relationship between the base strength and coordination tendency towards nickel (II)diphenylthiocarbazonate is discussed in terms of steric factors.

INTRODUCTION

Nickel is one of the several metal ions that play an important role in biological system. It has a vital role in enzyme systems (Dixon *et al*, 1975, Stephen Ragsdale, 2009), in plant culture (Anke *et al*, 1984) and in a chemical looping combustion (Juan Adanez *et al*, 2006).

Metal ions play an vital role in biological systems and any malfunctioning of these ions can initiate a number of physiological abnormalities (Jadumani Singh and Manihar Singh, 2011) Transition metals are responsible for proper functioning of different enzymes. Coordination chemistry of nickel complexes as models for the active sites in nickel-containing enzymes. This is largely due to the discovery of nickel at the centers of many important enzymes (Ragsdale, 2007).

Nickel diphenylthiocarbazonate, (dithiozonate), $NiDz_2$, is diamagnetic in contrast to the nickel chelates of diphenylcarbazone, di-m-tolylcarbazone and di-p-tolylcarbazone, which are paramagnetic (Math and Suresh, 1985). The spectrum of $NiDz_2$ is remarkably different from the spectra of most other metal-diphenylcarbazonates, which closely resemble those of the nickel-dithizonate adducts of pyridine or other nitrogen bases (Math and Henry Freiser, 1969a). In recent years, many adduct complexes of the type Ni-N_2O_2 chelates have been prepared, very little is known, however, on the reaction of the adduct formation in non aqueous media (Suresh *et al*, 2004, 2006).

The present work deals with the determination of stability constants for adduct formation of $NiDz_2$ with 1, 10-phenanthroline, pyridine and other nitrogen bases in chloroform spectrophotometrically by using Job's continuous variation method. Stable complexes of bidentate ligands viz., 1,10-phenanthroline, 2,2'-bipyridyl, ethylenediamine, 2,9-neocuproine and monodentate ligands viz., 3,4-lutidine and 4-aminopyridine are found to form with $NiDz_2$. In this report, we gave some results of study of relative importance of steric hindrance of substituted pyridines and other bidentate nitrogen bases with $NiDz_2$.

Corresponding author:* **Suresh T
Department of Chemistry, Vijayanagar Sri Krishnadevaraya University, Ballari-583105, Karnataka

MATERIALS AND METHODS

Apparatus Bausch and Lomb Spectronic 2000 spectrophotomer was used to determine the composition of the complex at 25±0.1^{0}C.

Reagents Commercial sample of dithizone (Robert Johnson) was purified by the method suggested by Cowling and Miller (Cowling and Lisa J Miller, 1941). Pyridine (Fisher), 2,4-lutidine (dimethyl analogue of pyridine), 3,4-lutidine (dimethyl analogue of pyridine), morpholine, piperidine (Merck), 2-picoline (methyl analogue of pyridine), 3-picoline (methyl analogue of pyridine), 4-picoline (methyl analogue of pyridine), 2,6-lutidine (dimethyl analogue of pyridine), 2,4,6-collidine (trimethyl analogue of pyridine), ethylenediamine(B.D.H) were dried over potassium hydroxide and distilled. The constant boiling fraction was collected and used. Neocuproin,4-methyl aniline, 2,2'-bipyridyl, 1,10-phenanthroline, 2-aminopyridine, 4-aminopyridine, 2-amino-4-methyl pyridine, 2-aminothiazole (B.D.H) and nickel chloride hexahydrate (Merck) were used without purification.

Preparation of Nickel Dithizonate

About 1g of nickel chloride hexahydrate was dissolved in 50ml of acetate buffer of pH 6. The solution was heated to 60^{0}C and to this hot solution alcoholic solution of dithizone was added drop wise. The mixture was diluted with water and the precipitate obtained was digested on low heat for an hour. It was filtered under suction and washed several times with water and finally twice with carbontetrachloride to remove unreacted metal and ligand residues. The product obtained was dried at room temperature over phosphorus pentoxide under vacuum for 12hr. The nickel content of the complex was found to be 9.74% by phenonthroline-dithizone method (Math *et al,* 1969b). (Calculated 9.63%).

Determination of Adduct Formation Constants

Adduct formation constants, K_f of nickel(II)dithizonate[$NiDz_2$] with nitrogen bases have been determined by Job's method of continuous variation to find the composition of complex formed, after selecting the wavelength of maximum absorption by Vosburgh and Cooper method (Vosburgh and Cooper, 1941) 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10ml of 1X10^{-4}M $NiDz_2$ was pipetted in to 25ml volumetric flask were mixed with 10, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0, 0ml 1X10^{-4}M nitrogen base was added keeping both the number of moles of $NiDz_2$ and bidentate nitrogen base, constant but varying either mole fractions of $NiDz_2$ or ligand (where as in case of monodentate bases 1X10^{-2}M $NiDz_2$ and 1X10^{-2}M nitrogen bases are used). λ_{max} was determined using one of the composition at which there is maximum absorption(Fig 1). The absorption for all the compositions was recorded at a constant wavelength (λ_{max}, 530nm) (Meshram *et al,* 2011). The data of absorption and percentage composition of $NiDz_2$ and ligand solution at the constant temperature (25±0.1^{0}C) can be used and curves were constructed. A typical plot is shown in Fig 2.

Calculations

By constructing graph of absorbance versus mole fraction of metal chelate, the ratio of metal chelate to base was determined. And formation constants of the adducts (K_f) of $NiDz_2$ with nitrogen bases were determined by Job's method of continuous variation by using the following equation, (Syed Ahmad Tirmizi *et al,* 2012)

$$K_f = \frac{[A_2/A_1]}{\left[1 - \frac{A_2}{A_1}\right] X \left[C_L - C_M X \ A_2/A_1\right]}$$

Where, K_f : adduct formation constant
A_1: absorbance at break point
A_2: actual absorbance
C_M: concentration of $NiDz_2$
C_L: concentration of base (ligand)

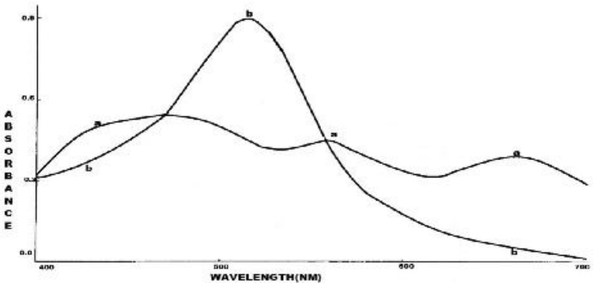


Figure 1 Plot of absorbance versus wavelength at 25±0.1^{0}C in chloroform

RESULTS AND DISCUSSION

One of the objectives in this work was to evaluate quantitatively any steric effects in the formation of adducts between $NiDz_2$ and heterocyclic nitrogen bases in a solvent such as chloroform.

$NiDz_2$ described elsewhere (Fachun Chou and Henry Freiser, 1968) is diamagnetic and has been attributed square planer structure with dsp^2 hybridization. It gives brown solution in solvents like $CHCl_3$ and CCl_4 etc, while the solutions in pyridine and substituted pyridine are pink in colour. This may probably due to the formation of the $NiDz_2$ and pyridine (base) adduct of the following type:

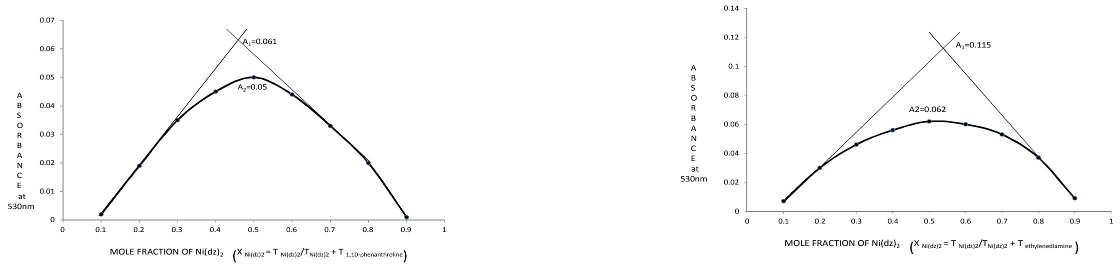
$NiDz_2$ + n Base -------------> $NiDz_2$. n Base ……………(1)

The spectrum for $NiDz_2$ has four characteristic absorption bands (λ_{max}= 340, 475, 565 and 675 nm, ε_{mol}= 20.0, 27.0, 23.6 and 19.9X10^3 mol^{-1} cm^{-1}, respectively). The spectrum of $NiDz_2$ undergoes profound change upon the addition of nitrogen bases, collapsing to a single absorption band in the visible range between 520-530 nm with a ε_{mol} = 48~50X10^3 mol^{-1}cm^{-1}. In contrast to most of other metal-dithizonate, e.g., those of Zn, Co, Cu which each have a single absorption band around 530nm.

The adduct formation constants of the $NiDz_2$ with nitrogen bases at 25±0.1^{0}C are listed in Table 1. Column III gives the values of pKa of N-bases that were selected for this investigation, Column IV gives the values of formation constants in $CHCl_3$.

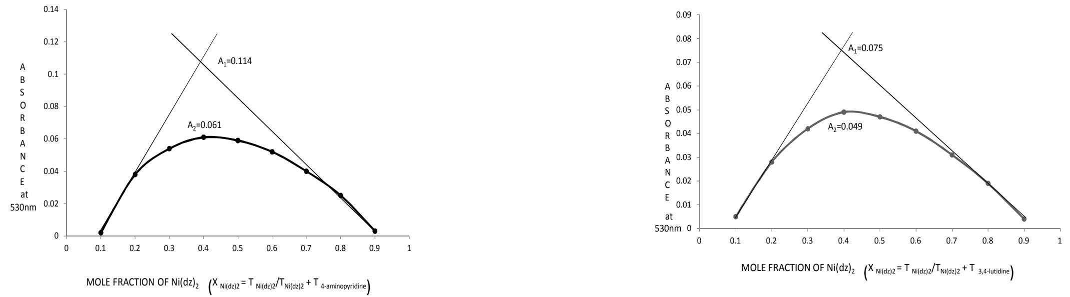
In case of 2-picoline, 2,6-lutidine, 2,4-lutidine, 2,4,6-collidine, did not form adducts which is indicative of steric hindrance due to methyl group in ortho position.

Figure 2 Job's curves of equimolar solutions of $NiDz_2$ – nitrogen bases at 25±0.1^{0}C in chloroform



(a) Job's plot for $Ni(dz)_2$ (5.9X10^{-4}M) and 1,10-phenanthroline (5.9X10^{-4}M) at 25±0.1^{0}C in chloroform medium

(b) Job's plot for $Ni(dz)_2$ (5.9X10^{-4}M) and ethylenediamine (5.9X10^{-4}M) at 25±0.1^{0}C in chloroform medium



(c) Job's plot for $Ni(dz)_2$ (5.9X10^{-3}M) and 4-aminopyridine (5.9X10^{-3}M) at 25±0.1^{0}C in chloroform medium

(d) Job's plot for $Ni(dz)_2$ (5.9X10^{-2}M) and 3,4-lutidine (5.9X10^{-2}M) at 25±0.1^{0}C in chloroform medium

Absorbance measurements gave wavelength of maximum absorbance for $NiDz_2$ complex with nitrogen bases which was found to be between 520-530nm as it is evident by graph plotted between different wavelength and absorbance (Fig 1). The observation of Job's curve (Fig 2), where the curve shows maximum at a volume ratio ($NiDz_2$ / monodentate N-base) shows that in each of the complexes the $NiDz_2$ to monodentate N-bases is 1:2 as two molecules of base for one molecule of $NiDz_2$. In case of bidentate bases the Job's curve shows maximum at a volume ratio ($NiDz_2$ / bidentate N-base) shows that in each of the complexes the $NiDz_2$ to bidentate N-bases is 1:1. As one molecule of base for one molecule of $NiDz_2$,which is in accordance with the hexacoordination of the nickel complex. Such type of hexacoordination adducts have been observed for nickel(II)-2-methyl-5-nitrophenylthiocarbazonate with N-bases (Math *et al*, 1986).

The stabilities of Ni(II) adducts were found to increase in the following order of bases: pyridine < 2-aminothiazole < 2-aminopyridine < 3-picoline < piperidine < 4-picoline < morpholine < 2-amino-4-methylpyridine < 3,4-lutidine < 4-aminopyridine < 2,9-neocuproin < ethylenediamine < 2,2'-bipyridyl < 1,10-phenanthroline.

Table 1 Adduct formation constants of nickel (II)dithizonates

Sl.No.	Name of the Base	pKa	$\log K_f$
1	Pyridine	5.25$^{\#}$	1.08
2	2-Picoline	5.97$^{\#}$	N.A*
3	3-Picoline	5.68$^{\$}$	1.32
4	4-Picoline	6.02$^{\#}$	1.45
5	3,4-Lutidine	6.15$^{\#}$	2.08
6	2,4,6-Collidine	7.43$^{\#}$	N.A*
7	Marpholine	8.33$^{\#}$	1.50
8	Piperidine	11.12$^{\#}$	1.40
9	2-Aminopyridine	6.82$^{\#}$	1.28
10	4-Aminopyridine	9.25$^{\#}$	2.74
11	2-Amino-4-methylpyridine	-	1.70
12	2-Aminothiozole	-	1.26
13	1,10-Phenonthroline	4.95$^{\$}$	5.96
14	2,2'-Bipyridyl	4.40$^{\$}$	4.63
15	2,9-Neocuproine	5.85$^{\#}$	3.76
16	Ethylenediamine	6.84$^{\$}$	3.86

*N.A – No adduct formation.

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The stability constants of $NiDz_2$ adduct with monodentate bases such as pyridine, 3-picoline, 4-picoline, 3,4-lutidine there is a decrease in the stability of adducts indicative of steric hindrance due to methyl groups. The formation constant values for marpholine and piperidine are not so high as compared to other nitrogen bases. It may be attributed to the saturity of ring.

The stability constant of 2-aminopyridine was found to be lower than that of 4-aminopyridine. Corquis (Georges Corquis and Deronzier, 1979) have shown that the stability constant strongly depends on electron withdrawing or electron donating characteristics of substituted pyridines. Therefore, the higher stability of 4-aminopyridine adduct relative to that of 2-aminopyridine adduct reflects the increased donor power of the nitrogen atom due to substituent effect.

It is surprising to find that the absorption spectrum of $NiDz_2$ does not change upon addition of 2-chloropyridine, aniline, 2-methyl aniline, 3-methyl aniline, 4-methyl aniline and quinoline. This may be due to the fact that these nitrogen bases are very weak bases and hence do not form adducts with the $NiDz_2$ under these experimental conditions.

Ligands such as bipyridyl, 1, 10-phenanthroline and ethylenediamine, 2, 9-neocuproine are bidentate as indicated by the substantial increase in K_f so that in these complexes, nickel would appear to be 6-coordination.

CONCLUSION

The reaction of pyridine, dipyridyl, phenanthroline and ethylenediamine with $NiDz_2$ under investigation serves not only to give analytically more useful complexes-i.e., more stable, more soluble, and more highly coloured but – changes in their properties help to improve our understanding about the structure of the low spin nickel(II)dithizonate studied here. The behavior of these complexes is indicative of the square planar configuration of nickel. The multiple absorption bands observed in the spectra of the simple nickel chelate might be reasonably attributed to charge-transfer transitions.

Acknowledgement

One of the author (Shivaraj) wishes to express his sincere thanks to Vijayanagara Sri Krishnadevaraya University, Ballari (Karnataka), for providing financial assistance to carry out this research work.

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ISSN 0976-3031

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