

Spectrophotometric Study on Adduct Formation Constants of Nickel(II) Chelates of Di(O-Tolylcarbazone) and Di(O-Tolylthiocarbazone) with Nitrogen Bases Using Job's Method of Continuous Variation Method

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ABSTRACT

Job's method of continuous variation technique was employed to determine the adduct formation constant of nickel(II) chelates of di(o-tolylcarbazone) and its sulphur analogue di(o-tolylthiocarbazone) with different nitrogen bases using UV-visible spectrophotometer at $25 \pm 0.10^\circ\text{C}$ in chloroform. Monodentate nitrogen bases were found to be form adducts in 1:2 ratio of nickel(II) chelate to nitrogen bases, whereas bidentate nitrogen bases form 1:1 adducts. The influence of substituents on the adduct formation constants has been examined with a view to better understanding of the effect of different organic nitrogen bases in the formation of adducts. The adducts formed have been discussed in terms of basicity of nitrogen bases, steric factors caused by substituents and donor atoms in nickel(II) chelates.

Keywords: Stability constant, steric hindrance, adduct formation, di(o-tolylcarbazone), di(o-tolylthiocarbazone).

I. INTRODUCTION

Stability constant values of adducts of metal(II) chelates with nitrogen bases provide knowledge about the various important factors like bond type and strength in complexes, the effect of different substitutions in nitrogen bases and the adducting ability of metal(II) chelates with nitrogen bases. Stability constants of adducts with different nitrogen bases (ligands) have been determined using different instrumental techniques viz., potentiometric, polarographic and spectrophotometric studies¹⁻⁵. Nickel is one of the several metal ions that play important role in biological system^{1,6} and complexes of nickel were also well known for industrial applications⁷⁻¹⁰ and it forms stable complexes with N, O & S donor ligands¹¹. Determination of stability constants of adducts of nickel(II) chelates of di(o-tolylcarbazone) [Ni(OTC)₂] and its sulphur analogue, di(o-tolylthiocarbazone) [Ni(OTTC)₂], with nitrogen bases leads to gain a systematic information about the factors affecting the stability of adducts, type of substituents, effect of solvent and metal chelate acidity¹²⁻¹⁵.

The present investigation is an attempt to study the relative importance of steric hindrance with pyridine, substituted pyridines, aniline, substituted anilines and

other monodentate and bidentate nitrogen bases with Ni(OTC)₂ and Ni(OTTC)₂ spectrophotometrically using Job's method of continuous variation in chloroform medium at $25 \pm 0.10^\circ\text{C}$. Further in this report a comparative study of adduct formation constants of Ni(OTC)₂ and Ni(OTTC)₂ and effect of electron withdrawing and electron donating groups on the adduct formation constants were discussed by comparing with the stability constant values of nickel(II) diphenylcarbazonate [Ni(DPC)₂] and nickel(II) dithizonate [Ni(Dz)₂].

Importance of stability constants

Stability constant is equilibrium constant for the evaluation of a adduct formation in solution. It is the magnitude of the strength of the interaction between the metal(II) chelate and the nitrogen base that form the adduct. For a stable adducts, stability constant values ($\log K_f$) is found to be greater than zero, which illustrate the existence of adduct species in solution. For a particular adduct if all the possible stability constants were determined, then it is possible to calculate the concentration and activity of each of the species present in the selected adduct. Such exact knowledge of the composition of a solution is essential for a correct interpretation of its kinetic properties and its biological behaviour.^{16,17}

II. METHODS AND MATERIAL

A. Apparatus

Bausch and Lomb Spectronic 2000 spectrophotometer was used to determine the composition of the adduct at $25 \pm 0.1^\circ\text{C}$.

B. Reagents

All the reagents were of analytical grade. Di-(o-tolylcarbazon) was prepared by the method described elsewhere¹⁸, involving persulphate oxidation of di(o-tolyl)carbazine. Di(o-tolyl)carbazine was synthesized¹⁹ by heating o-tolylhydrazide and guicol carbazine for 3 hrs at 160°C . The melting point of di(o-tolylcarbazon) was found to be 137°C . Aniline, 2-methylaniline, 3-methylaniline (B.D.H), 2,3-dimethylaniline, 2,4-dimethylaniline, 2,6-dimethylaniline, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, 4-bromoaniline (Merck), pyridine (Fisher), 2,4-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. 4-Methyl aniline (Aldrich), neocuproine, 2,2'-bipyridyl, 1,10-phenanthroline (Merck), 2-nitroaniline, 3-nitroaniline, 4-nitroaniline (B.D.H) and nickel chloride hexahydrate (Merck) were used without purification. Fisher AR grade chloroform was used.

C. Preparation of nickel(II) chelates of di(o-tolylcarbazon) and di(o-tolylthiocarbazon)

1) Preparation of nickel(II) di(o-tolylcarbazon) complex: In the preparation of nickel(II)di-(o-tolylcarbazon), 1g of AR grade nickel chloride hexahydrate was dissolved in minimum quantity of distilled water and to this 30-40 ml of acetate buffer of pH 6 was added. The resulting solution was heated to around 50°C - 60°C and to this hot solution, a solution of di(o-tolyl carbazon) in alcohol was added dropwise by means of burette with constant stirring. The mixture was diluted with distilled water and the precipitate obtained was digested on low heat for an hour. After digestion formed precipitate was filtered under suction and

washed with water to remove unreacted metal and finally twice with alcohol to remove unreacted ligand residue. The product obtained was dried at room temperature over phosphorus pentoxide under vacuum. The nickel content of the complex was found to be 9.81% by phenanthroline-dithizone method²⁰ (Calculated 9.93%).

2) Preparation of nickel(II) di(o-tolylthiocarbazon) complex:

In order to prepare nickel(II) di(o-tolylthiocarbazon) similar procedure was adopted as in case of preparation of nickel(II) di(o-tolylcarbazon), an alcoholic solution of di(o-tolylthiocarbazon) was mixed with the nickel chloride hexahydrate, formed complex was digested on low heat and filtered using suction, finally washed with water and alcohol. The product was dried over phosphorus pentoxide under vacuum. The nickel content of the complex was found to be 9.11% by phenanthroline-dithizone method²⁰ (Calculated 9.40%).

D. Selection of analytical wavelength

Vosburgh and Cooper method²¹ was employed to select the suitable wavelength for both $\text{Ni}(\text{OTC})_2$ and $\text{Ni}(\text{OTTC})_2$ adducts. In this technique series of solutions were prepared by mixing different volume of stock solution in chloroform medium. Finally, λ_{max} of the adducts was obtained by taking chloroform as a reference, the absorbance of the metal chelates with nitrogen bases was scanned between 400-800nm range by using a UV-visible spectrophotometer. The wavelength of maximum absorption was found to be 630 nm for $\text{Ni}(\text{OTC})_2$ (Figure 1) and 660 nm for $\text{Ni}(\text{OTTC})_2$ (Figure 2).

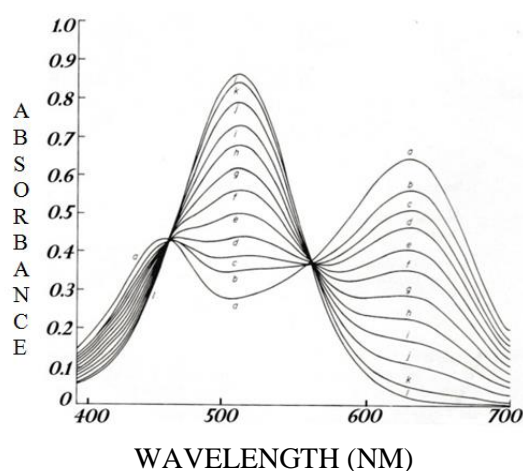


Figure 1. Absorption spectra of $\text{Ni}(\text{OTC})_2$ & 2,2'-bipyridyl mixture in chloroform: $[\text{Ni}(\text{OTC})_2] = 3 \times 10^{-5} \text{ M}$.

[2,2'-bipyridyl] $\times 10^{-5}$ M= (a) 0.00, (b) 0.05, (c) 0.10, (d) 0.20, (e) 0.40, (f) 0.80, (g) 1.20, (h) 2.00, (i) 3.00, (j) 5.00, (k) 9.00.

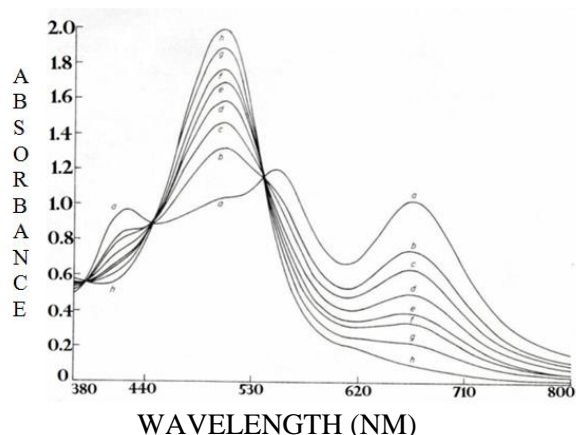


Figure 2. Absorption spectra of Ni(OTTC)₂ & 1,10-phenanthroline mixture in chloroform:

[Ni(OTC)₂]= 3×10^{-5} M. [1,10-phenanthroline] $\times 10^{-5}$ M= (a) 0.00, (b) 1.67, (c) 3.35, (d) 5.02, (e) 6.70, (f) 8.37, (g) 13.40, (h) 26.80.

E. Determination of Adduct Formation Constants

Stability constant values of adducts (K_f) of nickel(II)di(o-tolyl)carbazonate [Ni(OTC)₂] and nickel(II)di(o-tolyl)thiocarbazonate [Ni(OTTC)₂] with nitrogen bases have been determined by Job's method of continuous variation method, which is one of the reliable method for determination of adduct formation constants. Job's method consists of equimolar solutions of nickel(II) chelate and nitrogen base (ligand) varying proportion in such a manner that total concentration of nickel(II) chelate and ligand must remain constant in resulting mixture. After selecting λ_{max} (analytical wavelength) by Vosburgh and Cooper method²¹, 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10 ml of 5.9×10^{-4} M metal chelate were taken in 25 ml standard volumetric flask and mixed with 10, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0, 0 ml 5.9×10^{-4} M nitrogen base, keeping number of moles of nickel(II) chelate and nitrogen base constant but varying mole fractions of nickel(II) chelate or ligand (whereas in case of most of the monodentate bases 5.9×10^{-1} M metal chelate and 5.9×10^{-1} M nitrogen bases were used). The absorption for all prepared series of solutions was recorded at a constant wavelength (λ_{max} , 630nm for Ni(OTC)₂). Absorption values obtained from the above measurement was plotted with a mole fraction of nickel(II) chelate at the constant temperature ($25 \pm 0.1^\circ\text{C}$) and curves were constructed. Stability

constants of the adducts were calculated by using formulae 1. Typical plots of Ni(OTC)₂ with nitrogen bases is shown in Figure 3. Similar method is adopted to determine the stability constants of Ni(OTTC)₂ adducts at λ_{max} 660nm and typical plot of Ni(OTTC)₂ with nitrogen bases is shown in Figure 4.

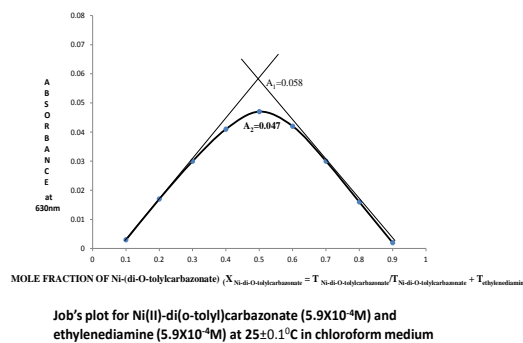


Figure 3(A)

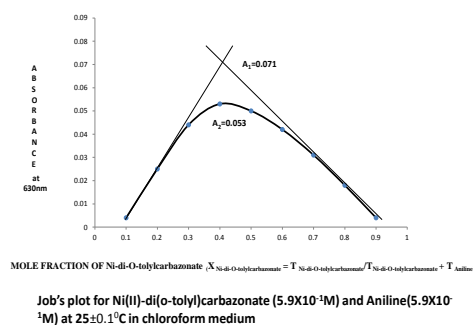


Figure 3(B)

Figure 3. Job's curves of equimolar solutions of Ni(OTC)₂ – nitrogen bases at $25 \pm 0.1^\circ\text{C}$ in chloroform

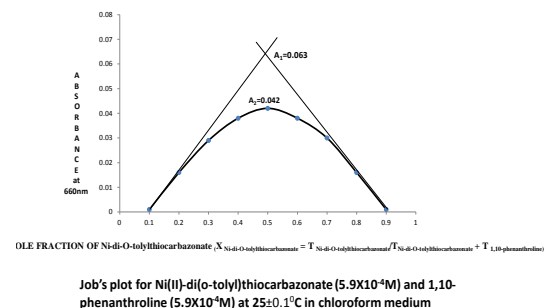


Figure 4(A)

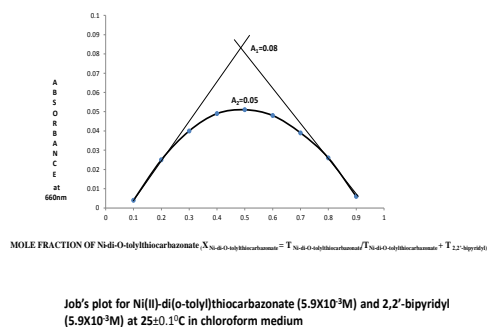


Figure 4(B)

Figure 4. Job's curves of equimolar solutions of Ni(OTTC)₂ – nitrogen bases at 25±0.1⁰C in chloroform

F. Calculations

By constructing a graph of absorbance vs mole fraction of a nickel(II) chelate, the ratio of nickel(II) chelate to the nitrogen base was determined. Adduct formation constants of the adducts of Ni(OTC)₂ and Ni(OTTC)₂ with different nitrogen bases were determined by Job's method of continuous variation by using the following equation,^{6, 22}

$$K_f = \frac{[A_2/A_1]}{[1 - \frac{A_2}{A_1}] \times [C_L - C_M \times \frac{A_2}{A_1}]} \text{----- (1)}$$

Where, K_f: adduct formation constant

A₁: absorbance at break point

A₂: actual absorbance

C_M: concentration of Ni(OTC)₂/Ni(OTTC)₂

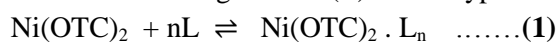
C_L: concentration of nitrogen base

III. RESULTS AND DISCUSSION

In continuation of our earlier work²³ on adduct formation of nickel(II) diphenylcarbazonate, in the present work, we have investigated the interaction of

nickel(II) chelate of di(o-tolylcarbazonate) and di(o-tolylthiocarbazonate) with mono and bidentate nitrogen bases to gain quantitative information about the nature and stability of the adducts formed. The study of literature concedes that some of the researchers have undertaken to study the stability constant values of metals with distinct organic bases^{2,5,24}.

Ni(OTC)₂ and Ni(OTC)₂²⁵ reported elsewhere are diamagnetic and have attributed to the square-planar structure with dsp² hybridization. It gives blue colour in non-coordinating solvents like chloroform & carbon tetrachloride. While in the solution of donor nitrogen bases like anilines, substituted anilines, pyridines and substituted pyridines forms pink colour, this may be probably due to the formation of the adducts of nickel(II) chelate with nitrogen bases(L) of the type:



The adduct formation constants of the Ni(OTC)₂ and Ni(OTTC)₂ with nitrogen bases at 25±0.1⁰C are listed in Table 1.

The stabilities of nickel(II)di-(o-tolyl)carbazonate adducts were found to increase in the following order of bases:

2-chloro aniline < 2,6-dimethyl aniline < 2-methyl aniline < 4-bromo aniline < 3-chloro aniline < 2,3-dimethyl aniline < 4-chloro aniline < 2,4-dimethyl aniline < 3,4-dimethyl aniline < aniline < 3-methyl aniline < 4-methyl aniline, 2,6-lutidine < quinoline < 2-picoline < morpholine < 2,4-,lutidine < 2,4,6-collidine < piperidine < ethylenediamine < 2,2'-bipyridyl < 2,9-neocuproin < 1,10-phenanthroline.

Table 1. Adduct formation from nickel(II) chelates with nitrogen bases.

Nickel(II) di-(o-tolylcarbazonate) adducts					Nickel(II) di-(o-tolylthiocarbazonate) adducts		
Nitrogen Bases	pKa	n*	λ_{\max} (NM)	logK _f	n*	λ_{\max} (NM)	logK _f
Aniline	4.63 ^[a]	2	630	1.22	2	660	NA**
2-Me aniline	4.44 ^[a]	2	630	NA**	2	660	NA**
3-Me aniline	4.73 ^[a]	2	630	1.25	2	660	NA**
4-Me aniline	5.08 ^[a]	2	630	1.30	2	660	NA**
2,3-di Me aniline	4.64 ^[d]	2	630	0.84	2	660	NA**
2,4-di Me aniline	5.00 ^[a]	2	630	0.91	2	660	NA**
2,6-di Me aniline	4.10 ^[a]	2	630	NA**	2	660	NA**
3,4-di Me aniline	5.22 ^[c]	2	630	1.07	2	660	NA**
2-chloroaniline	2.65 ^[a]	2	630	NA**	2	660	NA**
3-chloroaniline	3.46 ^[a]	2	630	0.83	2	660	NA**
4-chloroaniline	4.15 ^[a]	2	630	0.89	2	660	NA**
4-bromoaniline	3.86 ^[a]	2	630	0.76	2	660	NA**
Piperidine	11.12 ^[a]	2	630	3.83	2	660	NA**
Morpholine	8.35 ^[b]	2	630	2.66	2	660	NA**
Quinoline	4.90 ^[a]	2	630	1.80	2	660	NA**
Pyridine	5.20 ^[b]	2	630	NA**	2	660	NA**
2-picoline	5.90 ^[b]	2	630	2.18	2	660	NA**
4-picoline	6.08 ^[b]	2	630	NA**	2	660	NA**
2,4-lutidine	6.99 ^[b]	2	630	2.74	2	660	NA**
2,6-lutidine	4.95 ^[d]	2	630	1.30	2	660	NA**
2,4,6-collidine	7.43 ^[a]	2	630	3.68	2	660	NA**
2,2'-bipyridyl	4.40 ^[b]	1	630	5.01	1	660	3.20
1,10-phenanthroline	4.95 ^[b]	1	630	5.26	1	660	4.31
2,9-neocuproin	5.85 ^[b]	1	630	5.06	1	660	NA**
Ethylenediamine	6.84 ^[b]	1	630	4.90	1	660	2.19

n* = number of molecules of base per chelate molecule.

NA** = No adduct formation under experimental condition.

^[a] T. Suresh, S. S. Hippargi, V. H. Kulkarni. **1994**. *National Academy of Science Letters. (India)*. 17(7), 141-144.

^[b] A. H. M. Siddalingaiah, A. F. Doddamani, G. Sunil Naik. **2001**. *Spectrochimica Acta, Part A*. 57, 2721-2727.

^[c] A. H. M. Siddalingaiah, B. Rajesh Bhat. **1995**. *Asian Journal of Chemistry*. 7(4), 761-766.

^[d] C. Golubic, G. Goldbach. **1951**. *Journal of American Chemical Society*. 73(8), 3966-67.

From Table 1 it is clear that stability constant values obtained for adducts formed from Ni(OTC)₂ with different monodentate and bidentate nitrogen bases exhibits expected increase with increase in pKa values.

The decrease in the stability constants of 2-methylaniline and 2-chloroaniline with Ni(OTC)₂ adducts compared to aniline is due to the lower pKa values of these bases and steric hindrance due to the methyl, chloro groups in the ortho position. A comparable outcome was also observed in case of 2,4-dimethylaniline and 2,6-dimethylaniline, 2,4-dimethylaniline which has higher pka value than aniline, even though due to the steric hindrance caused by a methyl group in o-position its logK_f value is low. So for this reason, these bases did not form stable adducts as expected by observing their pKa values.

The stability constant of 4-chloroaniline was found to be greater than 4-bromoaniline. Since in case of 4-substituted aniline and pyridine stability constant firmly based on the electron withdrawing or donating character of the substituent²⁶, as a resulting stability constant of 4-chloro adduct compare to the 4-bromo adduct indicates the elevated donor power of nitrogen atom as a result of substituent impact.

The stability constants of methylanilines were found to be higher than chloro and bromo anilines. It is because of the reason that, stability constant of metal(II) chelates strongly depends on the electron withdrawing or donating characteristics of the substituents in a series of substituted anilines and pyridines. Therefore, higher stabilities of 3-methylaniline and 4-methylaniline adducts relative to that of 3-chloro and 4-chloroaniline

adducts reflects the increased donor power of the nitrogen atom due to substituent effect.

The decreased stability constant values of the adduct of Ni(OTC)₂ with morpholine may be due to the weakened basicity of the nitrogen atom in the morpholine ring. The stability constant values for the piperidine are considerably low even though pK_a values of this base is very high, this may be due to the saturation of the ring.

It is interesting to note that pink coloured adducts of Ni(OTC)₂ with nitrogen bases such as pyridine, 4-picoline are volatile and instantly decomposes, while those of with 2-picoline, 2,6-lutidine, 2,4-lutidine and 2,4,6-collidine which have steric hindering groups are stable for at least one hour. This is may be due to the fact that, strong bases such as pyridine, 3-picoline and 4-picoline establish strong bonds with Ni(OTC)₂ and may thus dislocate the chelating reagent or decomposes the chelate. On the contrary methyl group containing sterically hindered monodentate bases such as 2-picoline, 2,6-lutidine, 2,4-lutidine and 2,4,6-collidine form weakened bonds and thus will not be able to dislocate the chelating agent, and hence these bases are capable of establishing stable adducts with the Ni(OTC)₂. Further stability constant values of adducts of Ni(OTC)₂ with 2-picoline, 2,4-lutidine, 2,6-lutidine and 2,4,6-collidine was found to be increased linearly with increase in pK_a values of the bases.

However stability constant value of Ni(OTC)₂ with 2,4,6-collidine is smaller with consideration to its high pK_a value, this can be attributed to the steric hindrance caused by the three methyl groups present at 2,4 and 6 positions.

Whereas in case of bidentate nitrogen bases like 2,2'-bipyridyl, 1,10-phenanthroline and ethylenediamine forms almost equally stable adducts, since these are not adversely affected by steric hindrance this may be due to the rearrangement of the chelate ring in order to form *cis*-position for bidentate adducting bases²⁷. This high stability of the chelates can also be attributed to resonance from benzene rings, where there could be delocalization of electrons between the ligand-metal π -bonding their by providing extra stability for the chelates. Formation of chelate rings from these bidentate nitrogen bases prevents elongation or compression of bonds,

which consequently stabilizes the complex ion. But whereas in case of 2,9-neocuproine, a bidentate ligand which forms a less stable adduct, which is attributed to the steric hindrance caused by the methyl groups which are present at 2- and 9-positions forms weaker adducts by blocking nitrogen atom in the base.

It is astonishing to spot that the absorption spectrum of Ni(OTC)₂ does not change upon addition of 2-nitroaniline, 3-nitroaniline & 4-nitroaniline. This may be due to the reason that these nitrogen bases are very weak and hence do not form adducts with the Ni(OTC)₂ under experimental conditions.

It is however, provoking to note that, adduct formation constants values of Ni(OTC)₂ with aniline, substituted anilines, substituted pyridines and other monodentate and bidentate nitrogen bases were found to be lower than that of stability constant values of Ni(DPC)₂. This can be accredited to the **existence** of methyl group in Ni(OTC)₂, methyl group being an electron donating group, it decreases the acidity of the nickel metal by decreasing the interaction and thereby decreases the strength of the bond formed between the metal chelate and ligand.

Further results of our studies on adduct formation constants of nickel(II)(o-tolylthiocarbazonate) with nitrogen bases are given in Table 1. From Table. 1, it was found that Ni(OTTC)₂ capable of forming stable adducts only with bidentate ligands, whereas it does not form adducts with the monodentate nitrogen bases. This may be due to the existence of methyl group in ortho-position in benzene ring of the ligand. This result in the crowding around the central nickel atom, which will interfere with the adduct base-metal ion interaction. This is clearly seen when Ni(OTTC)₂ fails to exhibit any kind of relation towards bases having sterically hindering substituents like 2-picoline.

Whereas in case of bidentate ligands possibility of formation of adducts arises as a result of the re-orientation of di-(o-tolylthiocarbazonate) molecules which were in the plane, so as to provide a *cis*-position for bidentate ligands. Further log K_f values of Ni(OTTC)₂ are lower than the corresponding Ni(Dz)₂ adducts, this is probably because of the steric influence of the methyl group in o-position of the reagent. Further Ni(OTTC)₂

does not form an adduct with neocuproine, predicting the adverse steric effects of the methyl group in ortho-position to donor N-atom which introduce steric strain.

From our present study it is also found that adduct formation constants of Ni(OTC)₂ are significantly higher than its sulphur analogue Ni(OTTC)₂, in general, it is found that the adducts of nickel(II) chelates with S and N as donor atoms are considerably less stable than the adducts of chelate with O and N as donor atoms.

IV. CONCLUSION

In our study during the reaction between various monodentate and bidentate nitrogen bases with nickel(II)di(o-tolyl)carbazonate and nickel(II)di(o-tolyl)thiocarbazonate, formation constants of adducts with nitrogen bases have been determined by using Job's continuous variation method spectrophotometrically. Further variation in the stability constant values of these chelates are discussed in terms of the effect of substituents, steric hindrance caused by different electron withdrawing and electron donating groups in substituent & basicity of nitrogen bases. Further, variations in stability constant values of Ni(OTC)₂ and Ni(OTTC)₂ are compared with that of Ni(DPC)₂ and Ni(Dz)₂.

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