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A Study of Adduct Formation of Heterocyclic Nitrogen Bases with Nickel(II) Chelate of Di(2-Bromo,4-Methylphenyl) Carbazone

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Adduct formation constants of various heterocyclic nitrogen bases with Ni(II) chelate of di(2-bromo,4-methylphenyl) carbazone have been determined in a monophase chloroform by spectrophotometric study. The monodentate and bidentate bases form penta and hexacoordinated adducts respectively with 1 : 1 stoichiometry for metal-chelate-base. The behaviour of some saturated heterocyclic bases like pyrrolidine, piperidine, hexamethyleneimine and morpholine has also been studied. The results are discussed in terms of steric hindrance, basicity and ring structure of the heterocyclic bases used.

INTRODUCTION

Much work has been done on the evaluation of factors such as ligand basicity, solvent, steric effects and metal-chelate acidity in the study of adduct formation from metal chelates.[1–5] In this report we give some results of our study of the adducts of Ni(II)-di-(2-bromo,4-methylphenyl) carbazonate [Ni(2B4MPC)$_2$] with various saturated and unsaturated heterocyclic bases. The chelate [Ni(2B4MPC)$_2$] was found to be paramagnetic in nature with the distorted square-planar structure. The saturated heterocyclic nitrogen bases having almost equal basicity and increased ring size were also considered in the study of adduct formation with Ni(II) chelate. Morpholine which has a nitrogen as well as an oxygen in its saturated 6-membered ring system was included in this study for the purpose of comparison.

EXPERIMENTAL

The reagent di(2-bromo,4-methylphenyl) carbazone, D2B4MPC, was prepared by the persulphate oxidation of the corresponding carbazide.[6] The product was purified by passing its ethereal solution through the silica gel column using dry ether as an eluent to obtain pure sample (m.p. 135–137°C). Pyridine (Fischer), picolines (Eastman), lutidines, collidine, ethylenediamine (B.D.H.) were dried over KOH and distilled to get pure samples. Pyrrolidine, piperidine, morpholine (B.D.H.) and hexamethyleneimine were once again purified.[3] Chloroform

(B.D.H.) was purified by the method suggested by Vogel.[7] 2,2′-Bipyridyl (Eastman) 1,10-phenanthroline (G. Fredrick Smith & Co.), 2,9-neocuproine (B.D.H.) and 4-cyanopyridine (Fluka A.G.) were used directly.

The absorbances were measured by using Hitachi 150–20 UV-VIS spectrophotometer.

Preparation of Ni $(2B4MPC)_2$ complex

Approximately 1 g of nickel(II) chloride (Fischer AnalaR) was dissolved in an acetate buffer (pH = 6.2) and mixed with an alcoholic solution of 0.01 M D2B4MPC at room temperature. The mixture was stirred and the precipitate formed was washed several times with water. The complex was dried at room temperature over phosphorous pentoxide under vacuum. It was then purified by Soxhlet method[8] using dry ether to get pure complex (m.p. 219–221°C). The nickel content of the complex was found to be 6.40% by standard EDTA titration method[9] (theory requires 6.46%).

Measurement of absorbances

Known volumes of chloroform solutions of the given nickel complex were pipetted into 10 mL standard flasks containing various amounts of the nitrogen base (dissolved in chloroform) and the mixtures were diluted to the mark with the solvent. The absorption spectra of the solutions were taken within the range 400–700 nm with an optical path length of 10 mm and chloroform as a reference.

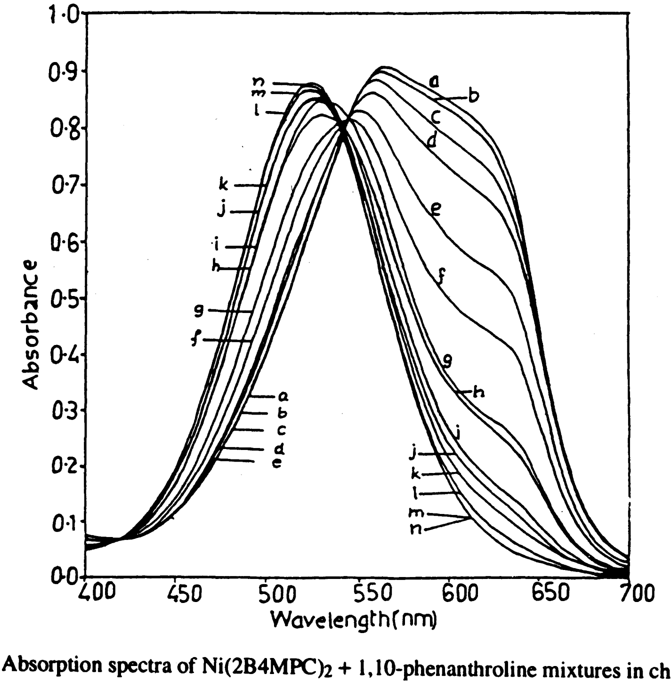

Fig. 1. Absorption spectra of $Ni(2B4MPC)_2$ + 1,10-phenanthroline mixtures in chloroform. [$Ni(2B4MPC)_2$]: 2.1 × 10^{-5} M. [1,10-phenanthroline], 10^{-6} M: (a) 0.0 (b) 0.30 (c) 1.45 (d) 2.90 (e) 5.80 (f) 8.70 (g) 11.61 (h) 14.51 (i) 17.42 (j) 20.32 (k) 23.22 (l) 29.03 (m) 58.06 (n)

The difference between the chelate and adduct was found to be maximum at 630 nm. Therefore the absorbance values at 630 nm were considered for analysis. A typical spectra of $Ni(2B4MPC)_2$-1,10-phenanthroline adduct system is shown in Fig. 1.

RESULTS AND DISCUSSION

An intense blue-coloured chloroform solution of $[Ni(2B4MPC)_2]$ gave an absorption band in the visible region at around 570 nm with $\varepsilon_{570} = 4.0 \times 10^4$ L mol^{-1} cm^{-1} and a shoulder at around 630 nm with $\varepsilon_{630} = 3.5 \times 10^4$ L mol^{-1} cm^{-1}. This resembles closely with the Co(II) complex of D2B4MPC whereas that of Zn(II) and Cd(II) complexes gave only a single absorption band at around 550 nm. The spectrum of $[Ni(2B4MPC)_2]$ undergoes a profound change on addition of chloroform solutions of heterocyclic bases. The pink-coloured adduct was formed with a single absorption band at around 530 nm. There are two isosbestic points for $[Ni(2B4MPC)_2]$ adduct system at around 540 nm and 420 nm.

The change in the spectra of nickel(II) complex on addition of heterocyclic bases can be used to determine the equilibrium constants of the adducts formed.[1] Therefore the absorption values at 630 nm were plotted as a function of −log [B] to obtain sigmoidal curves. The values of A_{ad} were obtained from the extrapolation of these curves which are used in the calculation of log β_n^{ad} values using equation (1).

$$\log \beta_n^{ad} = -n \log[B] + \log\left[\frac{A_{ch} - A}{A - A_{ad}}\right] \qquad (1)$$

where n is the number of base, B, molecules attached to the chelate; A_{ch} and A_{ad} are, respectively, the absorbances due to chelates and adducts and A is the absorbance due to chelate-adduct equilibrium mixture. The stoichiometry of the adducts formed due to the reaction of Ni(II) chelate with bidentate bases was

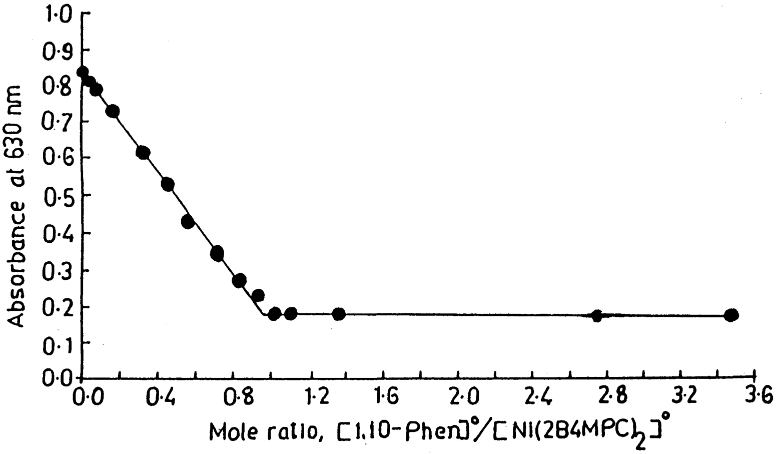

Fig. 2. Mole-ratio plot showing adduct formation between $Ni(2B4MPC)_2$ and 1,10-phenanthroline

established by mole-ratio method. Hexa-coordinated adducts were formed with bidentate bases with 1 : 1 stoichiometry for metal-chelate-base. This is in contrast to the results obtained in the case of Ni(II)-di-*o*-tolyl carbazonate, noticed by Math *et al.*[1] Mole-ratio plot for $Ni(2B4MPC)_2$-1,10-phenanthroline adduct system is shown in Fig. 2. The experimental results are given in Table 1.

TABLE-1
ADDUCT FORMATION CONSTANTS OF NITROGEN BASES WITH Ni(II) CHELATE OF (2-BROMO,4-METHYLPHENYL) CARBAZONE

Base	pKa	Slope (n*)	$\log \beta_n^{ad}$
Pyridine	5.20	1	1.70
2-Picoline	5.90	1	1.10
3-Picoline	5.68	1	1.80
4-Picoline	6.08	1	2.10
2,4-Lutidine	6.72	1	1.40
3,4-Lutidine	6.52	1	2.24
2,4,6-Collidine	7.48	1	1.60
4-Cyanopyridine	—	1	1.52
Pyrrolidine	11.27	1	2.22
Piperidine	11.00	1	2.08
Hexamethyleneimine	11.07	1	1.64
Morpholine	8.35	1	1.32
2,2′-Bipyridyl	4.40	1†	5.42
1,10-Phenanthroline	4.95	1†	5.14
2,9-Necocuproine	5.85	1†	4.96
Ethylenediamine	6.84	1†	5.30

*n = number of base molecules per chelate
†the value obtained from mole-ratio method
Slope = 1 means 1 : 1 ratio of nickel-chelate to base.

In the case of adduct formation of Ni(II) chelate with monodentate bases, it has been found that the adducts contain one mole of base as shown by the slope of 1 for the plots of $\log\left(\frac{A_{ch} - A}{A - A_{ad}}\right)$ vs. $-\log [B]$. This accounts for the formation of penta-coordinated adducts with 1 : 1 stoichiometry for metal-chelate-base. The stabilities of Ni(II) adducts were found to increase in the following order of bases: 2-picoline < 2,4-lutidine < 2,4,6-collidine < pyridine < 4-cyanopyridine < 3-picoline < 4-picoline < 3,4-lutidine. The lower stabilities of 2-picoline, 2,4-lutidine and 2,4-6-collidine compared to pyridine may be attributed due to steric hindrance offered by the methyl groups present at 2- and 6- position, even though their pKa values are much higher than pyridine itself. A similar trend was observed in the case of Ni(II)-5-nitro-8-quinolinate adducts.[5] The stability constant of 4-picoline was found to be higher than that of 4-cyanopyridine. Cauquis *et al.*[10] have shown that the stability constant strongly depends on the electron withdrawing or donating characteristics of substituents in a series of 4-substituted pyridines. Therefore the higher stability of 4-methyl pyridine adduct relative to that of 4-cynopyridine adduct reflects the increased donor power of the nitrogen atom due to substitutent effect.

Penta-coordinated adducts were obtained with saturated heterocyclic bases with 1:1 stoichiometry. The adduct formation constants of Ni(II) chelate decreases when the ring size of the nitrogen base increases from the 5-membered pyrrolidine to 7-membered hexamethyleneimine ring, although their pKa values are almost same. Therefore steric effects are found to be much important in the formation of adducts. The smaller formation constant of the adduct of Ni(II) chelate with morpholine may be attributed due to decreased basicity of the nitrogen atom in the morpholine ring. Strong bases however will form 1:1 adducts and formation of 1:2 adducts is not possible due to steric hindrance produced by the substituents on the two chelate rings which are no longer planar.[11] Also the chelate rings will be disrupted due to the increased basicity of donor nitrogen atom. There is a strong interaction between the nickel atom in [Ni(2B4MPC)$_2$] and pyrrolidine piperidine, etc., and due to this the available positive charge on the nickel atom decreases, and thereby the tendency for the axial addition of a sixth ligand to the nickel atome reduces. This type of electrostatic effect is enhanced by a steric effect, such that the approximately coplanar chelate rings are distorted by the addition of the first axial ligand so as to sterically hinder the *trans* addition of another axial ligand.[2] Hence, when strong bases are used to form adducts with planar metal chelates, 1:1 adducts will be formed almost exclusively.

From the study of adduct formation of Ni(II) chelate with saturated heterocyclic bases, it is clear that the structural and electrostatic rearrangements in the donor as well as in the acceptor molecules must be considered in the interpretation of adduct formation.[3] Fernando[12] has shown that there is a considerable distortion in the Ni(II) chelates when adducts are formed with strong nitrogen bases. The donor molecules themselves must undergo structural changes.[13] For example piperidine, in chair configuration, has the hydrogen on nitrogen atom in the equatorial position. When adduct formation occurs, the hydrogen atom probably shifts to the axial position to allow the nickel atom to bond to the nitrogen and occupy the equatorial position.

From the formation of almost equally stable adducts in the case of bidentate bases such as phenanthroline, bipyridyl etc., it appears that the adduct formation is not adversely influenced by the steric effects. This might be due to the rearrangement of chelate rings in order to provide a *cis*-position for the bidentate adducting bases.[14] 2,9-Neocuproine forms less stable adduct due to the steric hindrance offered by methyl groups present on 2- and 9- positions of the ring.

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