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A study of adduct formation of heterocyclic nitrogen bases with nickel(II) chelate of di(6-chloro-2-methylphenyl)carbazone

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Abstract

The study of the adduct formation of Ni(II) di(6-chloro,2-methylphenyl)carbazonate has been undertaken by synthesising and characterizing it by magnetic susceptibility, UV-VIS, IR and ^{1}H-NMR spectral measurements. The distorted square planar Ni(II) chelate forms adducts with heterocyclic nitrogen bases; spectrophotometric method has been employed for the study of the adduct formation in a monophase chloroform. Both bidentate and unsaturated monodentate heteronuclear nitrogen bases form hexacoordinated adducts with 1:1 and 1:2 stoichiometry, respectively (metalchelate:base). However, the saturated nitrogen bases form pentacoordinated adducts with 1:1 stoichiometry. The results are discussed in terms of basicity and steric factors of the bases. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Adduct formation; Heterocyclic nitrogen bases; Basicity and steric factors

1. Introduction

Diphenylcarbazone (DPC) is an analytical reagent which can form metal complexes of high molar absorptivity by coordinating through the nitrogen and oxygen atoms. It has been used in the determination of Mn [1], Cu [2] and fatty acids [3] in blood serum, as an antibacterial reagent against mycobacterium and tuberculosis [4]. Survey of literature reveals that there are only a few reports on some of the nuclear substituted derivatives of diphenylcarbazones and their metal complexes while there seem to be no reports on di(6-chloro-2-methylphenyl)carbazone (abbreviated as D6Cl2MPC). The study of adduct formation is of an analytical importance wherein, the trace amounts of Ni could be determined more precisely, particularly by the synergetic effect [5]. The extraction of trace amounts of Cd and Zn using dpc through adduct formation with 1,10-phenthroline have been reported [6]. The nickel chelates of dpc and its substituted analogues enlarges produce intense absorption in the optical

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spectra which are characteristic of the (metal-perturbed) ligand itself. Structural changes occurred in the Ni(II) chelates on adduct formation which, therefore, gives rise to profound spectral changes. The hypsochromic and bathochromic shifts are observed in the visible region of the spectra of Ni(II) chelates of dithizone [7] and methyl substituted dpcs [8]. These changes were employed for the determination of adduct formation constants. Such spectral changes also help in confirming the structure of the pyridine adducts of the nickel chelates. Even though lot of work has been done to study the effect of factors such as ligand basicity, steric effects etc. on the adduct formation of Ni(II) chelates with substituted dithizones [7] and quinolines, the study of adduct formation of Ni(II) chelates of many of the substituted dpc derivatives with nitrogen bases seems to have not been made. In continuation of our earlier work [9–11], we report here our studies on the synthesis and characterization of a new derivative of dpc, viz D6Cl2MPC and its Ni(II) chelate, viz Ni(II)-di[6-chloro,2-methylphenyl]-carbazonate (abbreviated as $Ni(6Cl2MPC)_2$ and its adduct formation with nitrogen bases. An attempt to study the relative importance of steric hindrance and basicity with methyl substituted pyridines has been made. The saturated heterocyclic bases of almost of equal basicity are also considered in this study to find out the influence of ring size of these bases on the adduct formation.

2. Experimental

2.1. Apparatus

Absorbances were measured on Hitachi 150-20 UV-VIS spectrophotometer. Elemental analysis was carried out on Perkin-Elmer 240 CHN analyser. IR and ^{1}H-NMR spectra were recorded on Nicolet-170 FTIR spectrometer and VXR 300s Varian spectrometer, respectively. The magnetic moment of the Ni(II) complex was found out by Gouy method and the metal estimation was done by EDTA titration method [12].

2.2. Preparation of D6Cl2MPC

D6Cl2MPC was synthesised by a method described earlier [13,14]. Di(6-chloro,2-methylphenyl)carbazide was first prepared by heating a mixture of 6-chloro,2-methylphenylhydrazine and urea (2:1) at 155–160°C for about 3 h. The crude carbazide so obtained was crystallised from alcohol. About 1 g of the carbazide was dissolved in a mixture of 60 ml glacial acetic acid, 20 ml of 1 N sulfuric acid and 2–3 drops of 10% ferric alum and oxidised by adding 20 ml of 0.06 M potassium persulfate ($K_2S_2O_8$) dropwise with vigorous stirring for about 30 min. The resulting carbazone was extracted with ether, washed washed several times with water, evaporated dried and purified by column chromatography using a silica gel (60–120 mesh) column. A mixture of Me_2Co:$CHCl_3$ (1:4) is used as an eluent: yield, 58%; m.p., 142–143°C.

2.3. Reagents

Pyridine (Fisher), picolines (Eastman), lutidines, collidines, ethylenediamine (BDH) were dried over KOH and distilled to get pure samples. Pyrrolidine, piperidine, morpholine (BDH) and hexamethylneimine (Sigma) were purified by refluxing over bariumoxide for 20–24 h. The amines were fractionally distilled to get pure samples. 2,2′-bipyridyl (Eastman). 1,10-Phenanthroline. (G.F. Smith and Co.), 2,9-Neocuprine (BDH), cyanopyridines (Fluka) and nickel chloride (Fisher, AR grade) were used as received.

2.4. Preparation of $Ni(6Cl2MPC)_2$ complex

About 1 g of nickel chloride was dissolved in an acetate buffer (pH 6.2) and added to an alcoholic solution (0.01 M) of D6Cl2MPC dropwise at room temperature. The mixture was stirred for about 30 min and the resulting pre-

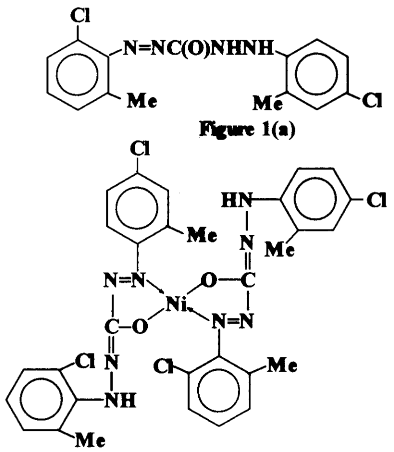

Fig. 1. (a) Structure of the D6Cl2MPC. (b) Structure of Ni(6Cl2MPC)$_2$.

cipitate was collected under suction and washed several times with water. The complex was dried over P_2O_5 under vacuum at room temperature and purified by Soxhlet method [15]: m.p., 229–230°C (decomposes).

2.5. Measurement of absorbances

Known volumes of chloroform solution of the above nickel complex was pipetted into 10 ml standard flasks containing different amounts of nitrogen bases (dissolved in chloroform) of known concentration. The mixtures in the flasks were diluted to the mark with the solvent. The absorbance spectra were measured in the visible region around 400–700 nm with an optical path length of 10 mm and using chloroform as a reference. The absorbance at 634 nm was considered for analysis. A typical spectra of the adduct of Ni(6Cl2MPC)$_2$ with 2,2′-bipyridyl is shown in Fig. 2.

3. Results and discussion

3.1. Characterization of D6Cl2MPC and Ni(6Cl2MPC)$_2$

The elemental analyses of the ligand and the complex, along with the magnetic data are reported in Table 1. The C, H, N and metal analyses confirm that the stoichiometry of the complex is 1:2 for metal to ligand. The complex is air stable, non-hygroscopic and soluble in non-polar solvents. It is dark blue in colour. The subnormal magnetic moment (2.31 BM) of the chelate may be attributed to mixed stereochemistry around nickel(II) [16].

3.2. IR spectra

The IR spectra of the ligand and the complex were recorded in 4000–400 cm^{-1} range. The ligand showed bands at 3301, 3110 and 3035 cm^{-1} which may be attributed to the intermolecular bounded (–N–H) vibrations. The bands at 1684 cm^{-1} and 1573 cm^{-1} are assigned to (–C=O) stretching and (–N–H) deformation, respectively. The disappearance of (–C=O) stretching band at 1684 cm^{-1} in the spectra of the nickel complex indicates that oxygen atom of the ligand is involved in the coordination with the metal through the enolic form. This was further confirmed by the appearance of a band at 1505 cm^{-1} due to (–C=N) stretching in the spectra of the complex. The IR peaks of both the ligand and the complexes are given in Table 2.

Table 1
Analytical magnetic data of the ligand D6Cl2MPC and Ni(6Cl2MPC)$_2$

Compound	Found (calculated) (%)				Molecular formula	μ_{eff} (BM)
	C	H	N	M		
D6C/2MPC	53.34 (53.43)	4.10 (4.18)	16.41 (16.62)	–	$C_{15}H_{14}N_4OCl_2$	–
Ni(6Cl2MPC)$_2$	59.24 (49.28)	3.50 (3.59)	15.40 (15.33)	8.06 (8.03)	Ni($C_{30}H_{26}NO_2Cl_4$)	2.31

Table 2
IR frequencies (cm^{-1}) of the ligand D6Cl2MPC and Ni $(6Cl2MPC)_2$

Compound	υ(N–H)	υ(C=O)	υ(N–H)	υ(C=N)	υ(C=C)ar	υ(C–O)	υ(N–H) (bend)
D6Cl2MPC	3301, 3110, 3035	1684	1578	–	1486	–	763
$Ni(6Cl2MPC)_2$	2937	–	1573	1505	1462	1200, 1165, 1098	780

3.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectrum of the ligand was recorded using $CDCl_3$ as solvent and the TMS as an internal reference. The two sharp singlets at δ 2.35 and 2.76 are due to two non-equivalent $-CH_3$ groups. The two broad peaks at δ 6.13 and 8.2 are due to aniline –NH and amide –NH groups, respectively. The multiplets observed in the region δ 6.76–7.70 may be attributed to six aromatic hydrogen atoms. The data is given in Table 3.

From the elemental and spectral analyses the structures of D6Cl2MPC and $Ni(6Cl2MPC)_2$ may be confirmed as shown in Fig. 1(a and b), respectively.

3.4. Adduct formation study

The spectrum of pure chloroform solution of $Ni(6Cl2MPC)_2$ shows two absorption bands in the visible region at around 464 and 634 nm ($\varepsilon_{464} = 3.2 \times 10^4$ l mol^{-1} cm^{-1} and $\varepsilon_{634} = 4.0 \times 10^4$ l mol^{-1} cm^{-1}), respectively. The spectrum of $Ni(6Cl2MPC)_2$ undergoes a profound change on addition chloroform solution of an heterocyclic bases and the absorption bands of the chelate collapse into a single band at around 518 nm. It was also noticed that greenish blue colour of the chelate solutions in chloroform change to pink upon the adduct formation. Though there are two isosbestic points in the visible region at around 472 and 580 nm for $Ni(6Cl2MPC)_2$ adduct systems, the measurements at 634 nm is more suitable for analysis since the difference in absorbance between the chelate and adduct is the largest at this value. Therefore, absorbance value at 634 nm were plotted as a function of $-\log[B]$ to get sigmoidal curves. A_{ch}, A_{ad}, A and $-\log[B]$, values were used for the calculation of $\log \beta_n^{ad}$ using Eq. (1):

$$\log \beta_n^{ad} = -n \log[B] + \log[(A_{ch} - A)/(A - A_{ad})] \tag{1}$$

where 'n' is the number of base adducts 'B', attached to the chelate. A_{ch} and A_{ad} are the absorbances due to chelates and adducts, respectively while 'A' is the absorbance due to the chelate–adduct equilibrium mixture.

For adduct formation from $Ni(6Cl2MPC)_2$ with unsaturated monodentate bases such as pyridine, methyl pyridines and cyanopyridines, the adducts were found to contain two moles of bases per chelate molecule as indicated by the slope 2 in the plots of $\log[(A_{ch} - A)/(A - A_{ad})]$ versus $-\log[B]$. This indicates hexacoordinated adducts with 1:2 chelate:base stoichiometries. It is interesting to note that $Ni(6Cl2MPC)_2$ adducts with pyridine, 3-picoline, 4-picoline and 3,4-lutidine are unstable and decolorize rapidly whereas those with 2-picoline, 2,4-lutidine and 2,4,6-collidine which have sterically hindered groups are stable for at least 1 h. The formation of stable adducts by 2-picoline, 2,4-lutidine and 2,4,6-collidine may

Table 3
^{1}H-NMR spectra of ligands[a]

Compound	Methyl ($-CH_3$)	Phenyl-NH	Amide-NH	Aromatic H
D6Cl2MPC	2.35 (s), 2.76 (s)	6.13 (br)	8.2 (br)	6.76–7.70 (m)

[a] Chemical shifts in ppm (δ).

be attributed to their increased basicity which deminates over steric effects. In the case of bases forming unstable adducts, the adduct formation constants could not be determined. 3-Cyano and 4-cyanopyridine from stable adducts with the nickel chelate (Fig. 4). The log β_n^{ad} values of the 4-cyanopridine adduct, are higher than those of the 3-cyanopyridine adduct, because the cyano group in the fourth position will tend to withdraw electrons from the nickel(II) ion into the ring or, in other words, increase the double bond character. Groups in the three position cannot contribute to this type of resonance [17]. A comparison of the stability of cyanopyridine adducts with those of methylpyridines is not possible, since the bases of the latter form unstable adducts with nickel(II) chelates under study.

The log β_n^{ad} values of $\mathrm{Ni(6Cl2MPC)_2}$–methylpyridine adducts lie in the following order: 2-picoline < 2,4-lutidine < 2.4,6-collidine. Thus the stability of these adducts increases as the basicity of nitrogen base increases.

The monodentate pyridine bases form 1:2 hexacoordinated adducts with $\mathrm{Ni(6Cl2MPC)_2}$ as shown by the slope of 2 in the plots of $\log[(A_{\mathrm{ch}} - A)/(A - A_{\mathrm{ad}})]$ versus $-\log[\mathrm{B}]$. The order of stability of these adducts follows the expected steric hindrance and basicity of the adducting bases. Thus 2-picoline < 2,4-lutidine < 2,4,6-colidine < pyridine < 3-picoline < 4-picoline < 3,4-lutidine. The following is the stability order for cyano- and methylpyridine adducts: 3-cyanopyridine < 4-cyanopyridine < 3-picoline < 4-picoline. This follows the expected resonance and substitution effects of the bases.

Pentacoordinated adducts were obtained with saturated heterocyclic bases with 1:1 stoichiometry. The adduct constant formation constants of Ni(II) chelate decrease when the ring sizes of the nitrogen bases increase from five-membered

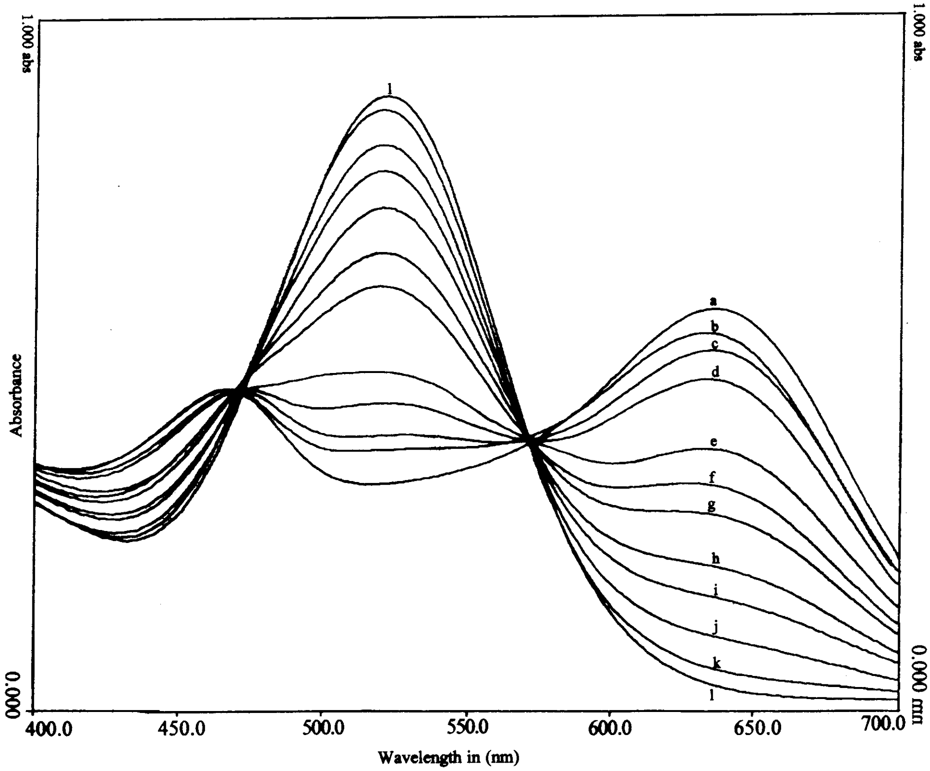

Fig. 2. Absorption spectra of $\mathrm{Ni(6Cl2MPC)_2}$ + 2,2′-bipyridyl mixture in $\mathrm{CHCl_3}$[Ni(6Cl2MPC)] 1.4325×10^{-5} M:[2,2′-bipyridyl] 10^{-6} M. (a) 0.00; (b) 0.10; (c) 0.20; (d) 0.30; (e) 0.40; (f) 0.50; (g) 0.60; (h) 0.70; (i) 0.80; (j) 0.90; (k) 1.00; (l) 1.20.

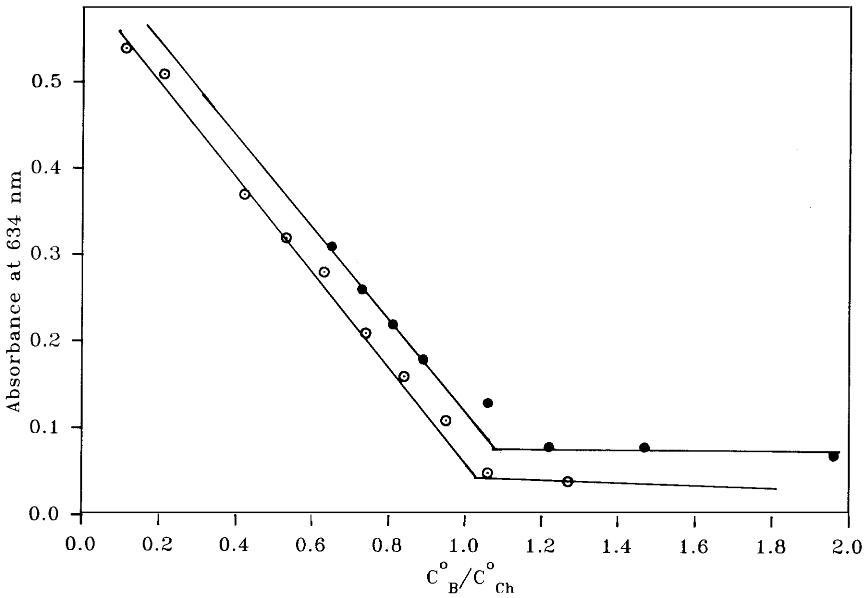

Fig. 3. Mole ratio plots of the adduct of $Ni(6Cl2MPC)_2$ + 2,2′-bipyridyl 2,9-neocuprine bases in $CHCl_3$.

pyrrolidine to seven-membered hexamethyleneimine ring although their pK_a values are almost the same. Therefore, steric effects are found to be more important in the formation of adducts in these cases. The smaller formation constant of the adduct of Ni(II) chelate with morpholine may be attributed to the decreased basicity of the nitrogen atom in the morpholine ring. Strong bases however will form 1:1 adducts and the formation of 1:2 adducts is not possible due to steric hindrance by the substituents on the chelate rings which are no longer planar [18]. Further, the chelate rings will be disrupted due to the higher basicity of donor nitrogen atom. There is a strong interaction between the nickel atom in $[Ni(6Cl2MPC)_2]$ and pyrrolidine, piperidine, hexamethylnimine, and morpholine as a result of which the available positive charge on the nickel atom decreases and there by the tendency for the axial addition of a sixth ligand to the nickel atom is reduced (Fig. 5). 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 additions of another axial ligand [19]. Hence, when strong bases are used to form adducts with planar metal chelates, 1:1 adducts will be formed almost exclusively (Fig. 6).

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 [20]. Fernando [21] 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 [22]. For example, piperdine, 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. The order of stability of these adducts is: morpholine < hexa-methyleneimine < pyrrolidine < piperidine. Thus, the order follows the electrostatic and steric variance of the bases [18].

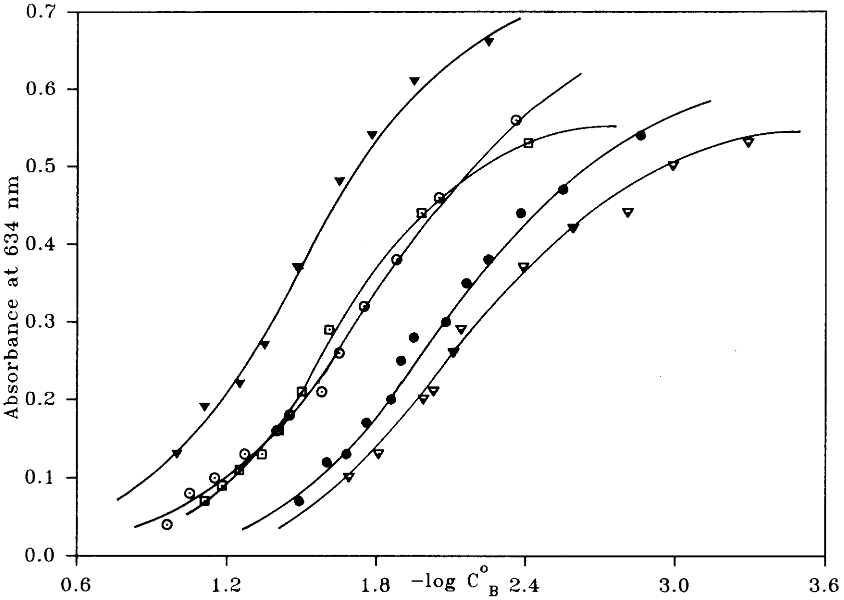

Fig. 4. Sigmoidal plots for the adducts of Ni(6Cl2MPC)$_2$ monodentate bases in CHCl$_3$: 2-picolene, 2,4-lutidine, 2,4,6-colidine, 3-cyanopyridine, 4-cyanopyridine.

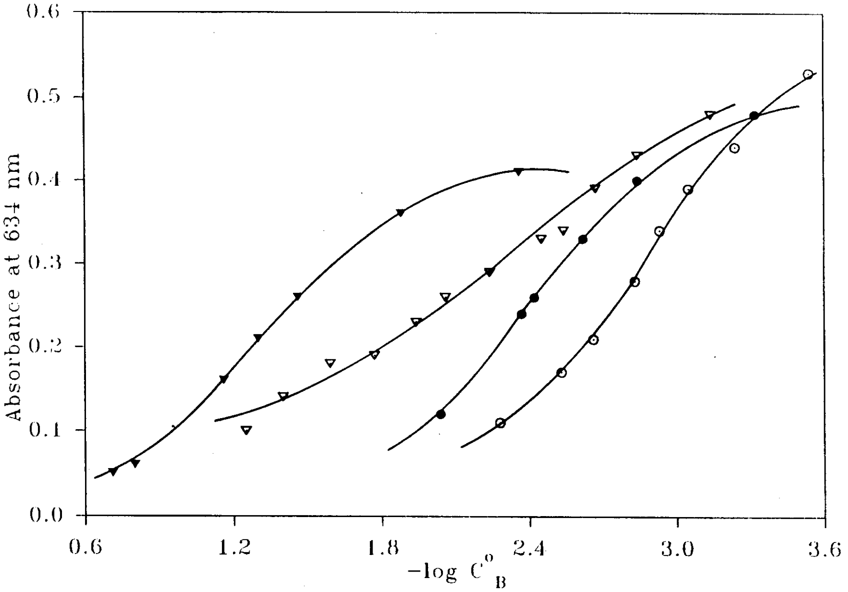

Fig. 5. Sigmoidal plots for the adducts of Ni(6Cl2MPC)$_2$ monodentate bases in CHCl$_3$: pyrrolidine, piperidine, hexamethyleneimine, morpholine.

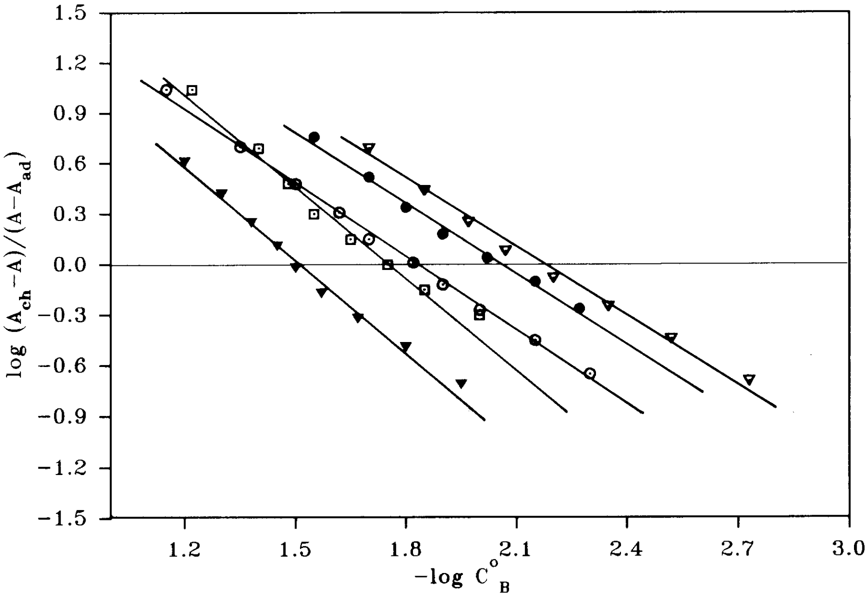

Fig. 6. Linear plots for the adducts of Ni(6Cl2MPC)$_2$ monodentate bases in CHCl$_3$.

Table 4
Adduct formation constants of nitrogen bases with Ni(II) chelate of D6Cl2MPC

Base	pK_a	Slope (n)[a]	Log β_n^{ad}
Pyridine	5.20	ID	–
2-Picoline	5.90	2	1.82
3-Picoline	5.68	ID	–
4-Picoline	6.08	ID	–
2,4-Lutidine	6.72	2	1.90
3,4-Lutidine	6.52	ID	–
2,4,6-Collidine	7.48	2	2.18
3-Cyanopyridine	–	2	1.57
4-Cyanopyridine	–	2	1.78
Pyrrolidine	11.27	1	2.90
Piperidine	11.00	1	2.50
Hexamethyleneimine	11.07	1	2.30
Morpholine	8.35	1	1.47
2,2′-Bipyridyl	4.40	1[b]	5.05
1,10-Phenanthroline	4.95	1[b]	5.00
2,9-Neocuproine	5.85	1[b]	4.96
Ethylenediamine	6.84	1[b]	5.10

[a] n is the number of base molecules per chelate.

[b] The value obtained from mole ratio plot. Slope = 1 means 1:1 ratio and slope = 2 means 1:2 ratio for Ni chelate to base. ID, instantaneously decolourized.

From the formation of almost equally stable adducts in the case of bidentate bases such as 2,2′-bipyridyl, 1,10-phenanthroline 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 [23]. 2,9-Neocuproine forms a less stable adduct due to the steric hindrance offered by the methyl groups. The stoichiometry of these adducts were confirmed by mole ratio method. The mole ratio plots for Ni(6Cl2MPC)$_2$–2,2′-bipyridyl 2,9-neocuproine adducts system are shown in Fig. 3. The experimental results given in Table 4.

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