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Spectrochimica Acta Part A 57 (2001) 2721–2727

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

Spectrophotometric study on the adduct formation of nickel (II)-di(2,4-dimethylphenyl)carbazonate with heterocyclic nitrogen bases

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Received 8 November 2000; accepted 12 January 2001

Abstract

The study of the adduct formation of Ni(II)di(2,4-dimethylphenyl)cabazonate has been undertaken by synthesising and characterising it by magnetic susceptibility, IR and ^{1}H-NMR spectral measurements. The Ni(II) chelate forms adducts with heterocyclic nitrogen bases, spectrophotometeric method has been employed for the study of the adduct formation in a monophase chloroform. Both bidentate and unsaturated monodenate heteronuclear nitrogen bases form hexa-coordinated adducts with 1:1 stoichiomety (metal chelate, base). However, the saturated nitrogen bases form penta-coordinated adducts with 1:1 stoichiometry. The results are discussed in terms of basicity and steric factors of the bases.

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

1. Introduction

Diphenylcarbazone (DPC) [1], a keto compound can exist in enolic form when dissolved in an organic solvent and react with various metal ions to form intense coloured metal complexes. Therefore it has been used in the determination of Mn^1, Cu^2 and fatty acids [2] in blood serum etc. Though, it was introduced as an analytical reagent [3,4] much earlier than its sulphur analogue, dithizone, it has received considerably less attention as a ligand for metal complexes [5,6]. Comprehensive studies of Ni(II) dithiozonates and their pyridine adducts have revealed the analytical importance of adduct formation in the extraction of trace amounts of metals [7,8]. The associated spectral changes can be employed to determine adduct formation constants and to confirm the structure of the pyridine adduct [9]. Hence, in this work, we have undertaken the synthesis, characterisation and have studied adduct formation of nickel (II)-di(2,4-dimethylphenyl)carbazonate [Ni(2,4DMPC)$_2$], as a continuation of our earlier research [10–12].

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PII: S1386-1425(01)00424-3

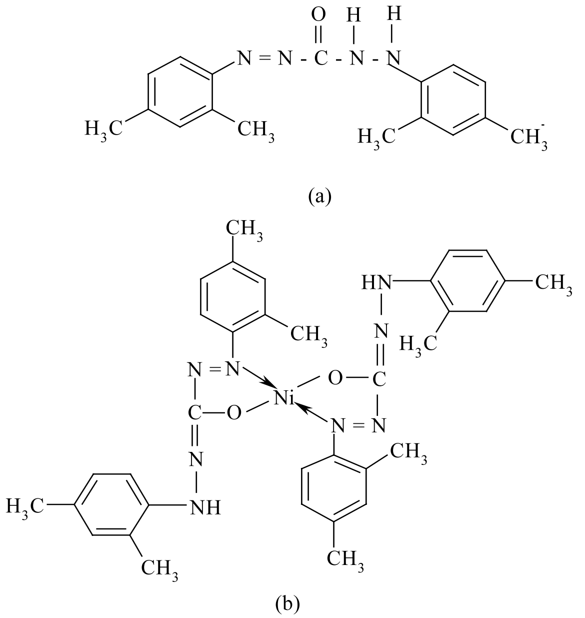
2. Experimental

2.1. Apparatus

Absorbances were measured on a 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 Perkin–Elmer 157 and VXR 300S Varian spectrometers, respectively. The magnetic moment of the nickel complex was determined by the Gouy method. The metal content was estimated by EDTA titration [13].

2.2. Chemicals and reagents

Pyridine (Fisher), picolines (Eastman), lutidines, collidine and ethylenedimmine (BDH) were dried over KOH and redistilled. Pyrrolidine, piperidine and morpholine (BDH) and hexamethylene-imine (Sigma) were purified by refluxing over BaO for 18–24 h followed by fractional distillation. 2,2′bipyridyl (Eastman), 1,10-phenanthroline (G.F. Smith), 2,9-neocuproine (BDH), $CHCl_3$ (Merck) and nickel chloride (Fisher AR grade) were used as supplied.



(a)

(b)

Fig. 1. (a) Structure of D2,4DMPC, (b) structure of Ni(D2,4DMPC)$_2$.

2.3. Preparation of D2,4DMPC

It was synthesised by a method described earlier [14,15]. Di(2,4-dimethylphenyl) carbazide was first prepared by heating a mixture of 2,4-dimethylphenyl hydrazine 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 in a mixture of 60 ml glacial acetic acid was oxidised with 20 ml of 0.06 M potassium persulfate ($K_2S_2O_8$) adding dropwise with vigorous stirring for about 30 min. The resulting carbazone was extracted with ether, washed several times with water, evaporated, dried and purified by column chromatography using silica gel (60–120 mesh) column. A mixture of Me_2CO and $CHCl_3$ (1:4) was used as an eluent (yield 42%; m.p. 110°C).

2.4. Nickel (II)-D2,4DMPC complex

A solution of $NiCl_2$ (1 g) in an acetate buffer (pH 6.2) was mixed with 0.01 M EtOH solution of 2,4DMPC at room temperature (Fig. 1). The mixture was stirred and the resulting precipitate was collected by suction and was washed several times with H_2O. The complex was dried over P_4O_{10} in vacuo at room temperature and then purified by Soxhlet method [16], using (1:1) Et_2O:petroleum ether as solvent. The extract contained impurities and failed to give the characteristic colour of the adduct with nitrogen bases. The pure complex was obtained as shining crystalline power in the Soxhlet tube (yield 70%; m.p. 248°C).

2.5. Measurement of absorbances

$CHCl_3$ solutions (1 cm^3 in each case) of the nickel complexes were pipetted into standard flask (10 cm^3) containing different amounts of nitrogen bases (dissolved in $CHCl_3$). Each of the mixtures in the flask were diluted to the mark with solvent. The absorption spectra were measured in the visible region at 400–700 nm with a 10 mm optical path length, using $CHCl_3$ as a reference. The absorption at 640 nm was used for analysis. A typical spectrum of the Ni(D2,4DMPC)$_2$-2,2′bipyridyl adduct is as shown in Fig. 2.

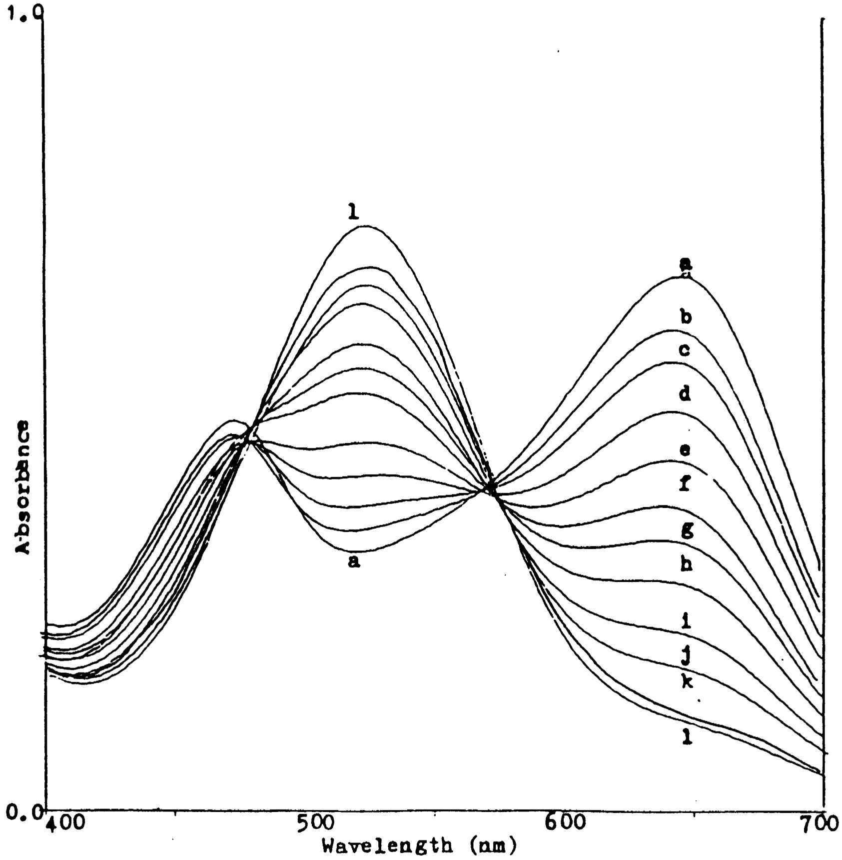


Fig. 2. Absorption spectra of $Ni(D2,4DMPC)_2 + 2,2'$bipyiridyl mixture in $CHCl_3$ ($10\ cm^3$). $[Ni(D2,4DMPC)_2] = 1.478 \times 10^{-5}$ M; [2,2′-bipyridyl] $\times 10^{-6}$ M (a) 0.00; (b) 1.36; (c) 2.71; (d) 4.07; (e) 5.42; (f) 6.78; (g) 9.50; (h) 10.85; (i) 12.20; (j) 14.92; (k) 17.63; (l) 21.70.

Table 1
Physical and analytical data for D2,4DMPC and $[Ni(D2,4DMPC)_2]$

Compound	M.P. (°C)	Found (calculated)%				μ_{eff} (BM)
		C	H	N	M	
D2,4DMPC[a]	110	68.63	6.68	18.70	–	
$C_{17}H_{20}N_4O$		(68.91)	(6.76)	(18.92)		
$[Ni(D2,4DMPC)_2]$[b]	210	62.90	5.83	17.20	9.00	2.28
$Ni(C_{34}H_{38}N_8O_2)$		(62.88)	(5.90)	(17.26)	(9.04)	

[a] D2,4DMPC, di(2,4-dimethylphenyl)carbazone.

[b] $[Ni(D2,4DMPC)_2]$, Ni (II)-di(2,4-dimethylphenyl) carbazonate.

Table 2
IR and ^{1}H-NMR spectral data

Compound	$\gamma_{(N-H)}$ [a]	$\gamma_{(C=O)}$	$\gamma_{(N=N)}$	$\gamma_{(C=N)}$	$\gamma_{(C=C)}$ar	$\gamma_{(C-O)}$	^{1}H-NMR (δ) ppm
D2,4DMPC	3400/3283 3160, 3085	1720	1593	–	1468	–	6.21 (br, –NH–Ar) 7.9 (br, –NH–amide) 6.7–7.6 (m, Ar–H) 2.2, 2.4, 2.5 (S, –CH_3)
[Ni(D2,4DMPC)$_2$]	3307	–	1590	1560	1458	1056 1180 1201	–

[a] Intermolecular/intramolecular.

3. Results and discussion

The physical and analytical data of the ligand and the metal complex are given in Table 1 and confirm that the complex contains 1:2 metal–ligand stoichiometry. The complex is air stable, non-hygroscopic and soluble in non-polar solvents. The sub-normal magnetic moment (2.28 BM) for the Ni (II) chelate requires explanation, since the spin-only value (2.83 BM) is expected for tetrahedral or octahedral geometries. The result is attributed to the mixed stereochemistry around Ni (II) [17,18]. As Ni (II) (D2,4DMPC)$_2$ gives charge transfer transitions with high molar absorptivity, it is often difficult to determine the mixed stereochemistry around Ni (II) ion on the basis of electronic spectral data, as explained earlier [8]. Furthermore, a large magnetic moment is associated with tetrahedral geometry and, in solution bidentate and unsaturated monodentate bases form hexacoordinated adduct with 1:1 and 1:2 metal–ligand stoichiometries respectively, which exclude the possibility of tetrahedral and octahedral geometries. Hence, it is assumed that the chelate undergoes distortion in chloroform to such an extent that it almost conforms to square planar structure. This paves the way for the formation of penta- and hexa-coordinated adduct [19–21].

3.1. IR spectra

The IR spectra of the ligand and complex were recorded in the 4000–400 cm^{-1} range in KBr pellets (Table 2). The ligand exhibited a band at 3400 cm^{-1} attributed to the intermolecular bonded $\gamma_{(N-H)}$ vibration. Bands at 3283, 3160 and 3085 cm^{-1} have been attributed to the intramolecular bonded $\gamma_{(N-H)}$ vibration [1]. The band at 1720 cm^{-1} is assigned to C=O stretching vibration and a band at 1590 cm^{-1} to N=N stretching vibrations. The disappearance of the $\gamma_{(C=O)}$ stretching a band at 1720 cm^{-1} in the complex indicates that the oxygen atom of the ligand is involved in coordination to the metal through the enolic tautomer. This fact was further

Table 3
Formation constants of [Ni(D2,4DMPC)$_2$] adduct system in chloroform

Base	PK$_a$	Slope (n)[a]	β_n^{ad}
Pyridine	5.20	–	ID
2-Picoline	5.90	2	2.65
3-Picoline	5.86	–	ID
4-Picoline	6.08	–	ID
2,4-Lutidine	6.72	2	3.00
3,4-Lutidine	6.52	–	ID
2,4,Collidine	7.48	2	3.10
3-Cyanopyridine	–	–	ID
4-Cyanopyridine	–	–	ID
Pyrrolidine	11.27	1	3.15
Piperidine	11.00	1	2.75
Hexamethyl-imine	11.07	1	2.25
Morpholine	8.35	1	1.75
2,2′-Bipyridyl	4.40	1[b]	5.30
1,10-Phenanthroline	4.95	1[b]	5.26
2,9-Neocuproine	5.85	1[b]	5.15
Ethylenediamine	6.84	1[b]	5.20

[a] Number of base molecules per chelate.

[b] Value obtained from mole-ratio method. ID, instantaneously decolourised.

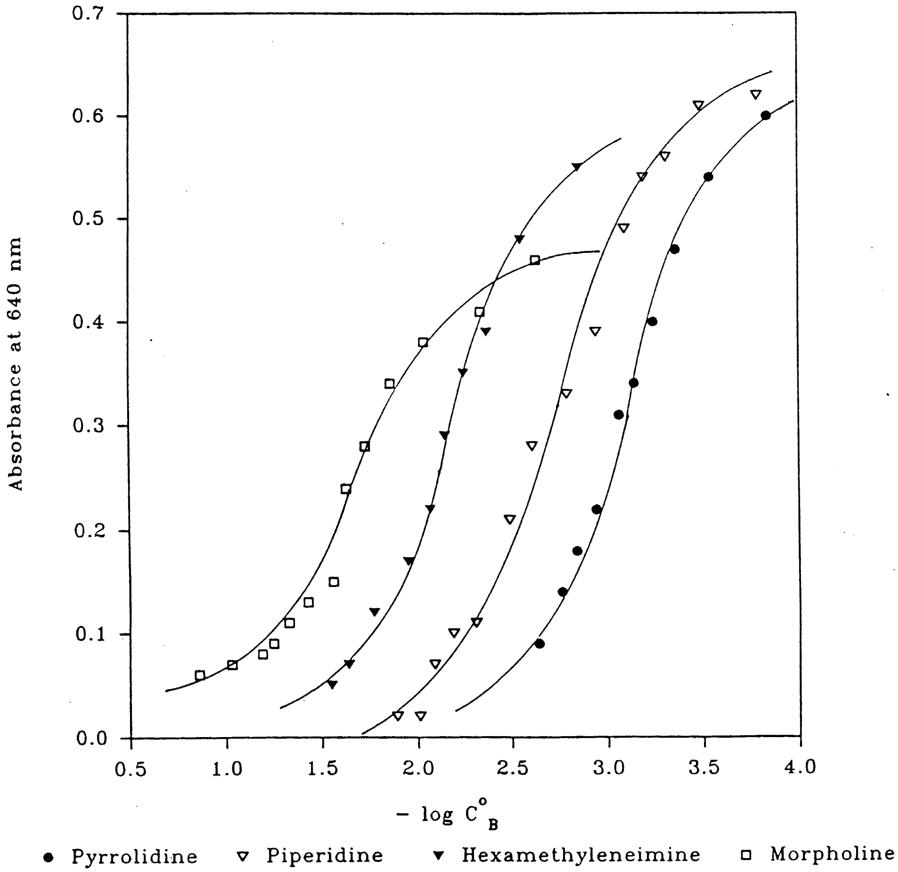


Fig. 3. Sigmoidal plots for the adducts of Ni(D2,4DPMC)$_2$ monodentate bases in chloroform.

confirmed by the appearance of a band at 1560 cm^{-1} due to $\gamma_{(C=N)}$ stretching. Based on analytical and spectral data, the structures of ligand and complex are assigned as shown in Fig. 2.

3.2. Adduct formation

The absorption spectra were measured in the visible region at 400–700 nm using chloroform (10^{-3} M) as the reference (Table 3). The chloroform solution of [Ni(D2,4DMPC)$_2$] (in the absence of a heterocyclic nitrogen base) has two absorption bands in the visible region at 640 nm, $\varepsilon = 4.5 \times 10^4$ lmol^{-1} cm^{-1}) and a shoulder at 468 nm, $\varepsilon = 3.81 \times 10^4$ lmol^{-1} cm^{-1}). The spectrum of [Ni(D2,4DMPC)$_2$] undergoes an intense change on addition of a chloroform solution of the heterocyclic bases and the deep violet chelate solutions in chloroform change to pink upon adduct formation. Two isosbestic points in the visible region occur at around 574 and 476 nm for the adduct system. Measurements at 640 nm were plotted as a function of $-\log[\mathrm{B}]$ in order to generate sigmoidal curves as shown in Fig. 3. The data obtained from the extrapolation of these curves are used in the calculation of stability constant log β_n^{ad} values using the equation

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

Here n is the number of base adducts B attached to the chelate, A_{ch} and A_{ad} are respective absorbances due to chelates and adducts and A is the absorbance due to the chelate adduct equilibrium mixture. The log β_n^{ad} values for [Ni(D2,4DMPC)$_2$] with saturated bases such as pyrrolidine, piperidine, hexamethylene-imine and

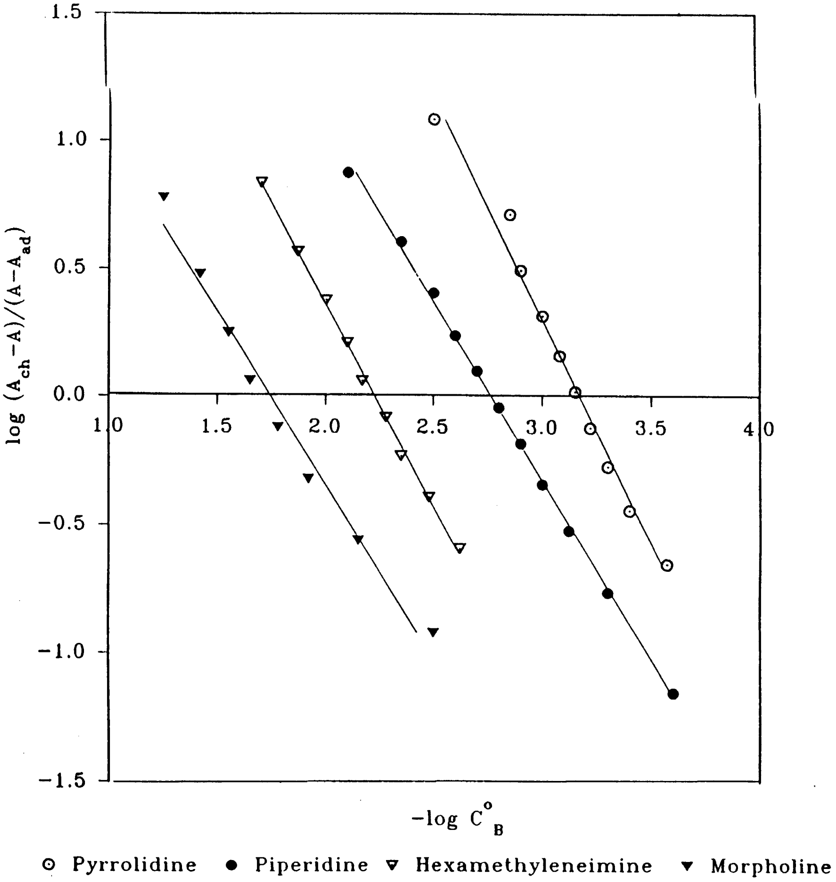


Fig. 4. Linear plots for the adducts of Ni(D2,4DPMC)$_2$ monodentate bases in chloroform.

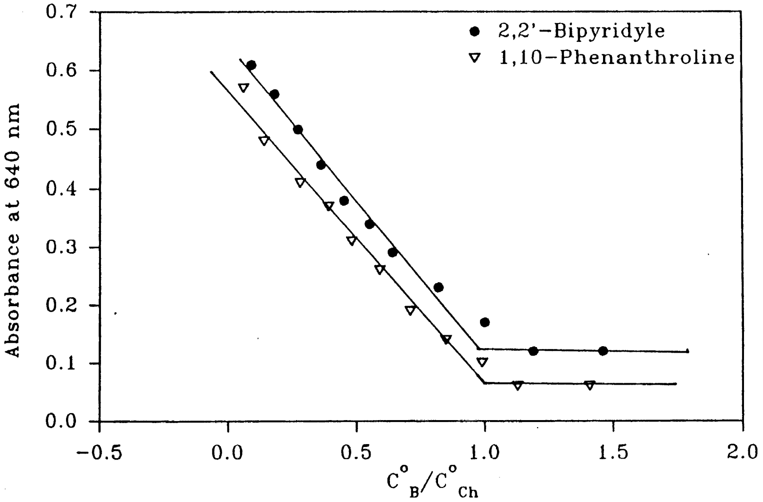


Fig. 5. Mole-ratio plots for the adducts Ni(D2,4DPMC)$_2$ bidentate bases in chloroform.

morpholine form pentacoordinate adducts of 1:1 stoichiometry. The stability of the adducts decreases from 5-membered pyrrolidine to the 7-membered hexamethylene-imine ring membered hexamethylene-imine ring (pyrrolidine > piperidine > hexamethylene-imine > morpholine) indicating the influence of ring size on adduct formation. The formation of a less stable adduct with morpholine may be due to the decreased basicity of the nitrogen atom in the morpholine ring [22].

The monodentate pyridine bases form 1:1 penta-coordinated adduct with [Ni(D2,4DMPC)$_2$] as shown by the unit slope for plots of $\log [(A_{\mathrm{ch}} - A)/A - A_{\mathrm{ad}})]$ versus $-\log$ [B], (Fig. 4). The stability order for these adducts follows the expected steric hindrance and basicity of the adducting bases: 2-picoline < 2,4-lutidine < 2,4,6-collidine < pyridine < 3-picoline < 4-picoline. This follows the expected resonance and substituent effects order for the bases [23,24].

For the [Ni(D2,4DMPC)$_2$] chelate adduct with bidentate bases such as 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-neocuprine and ethylenediamine, in addition to the unit slope found from Eq. (1), the mole ratio method was also used to confirm the chelate base ratio. The mole ratio method shows that the stoichiometry for the chelate-bidentate base is 1:1, accounting for the six coordination sites around the nickel atom, forming the octahedral structure. The mole ratio plot for the Ni(D2,4DMPC)$_2$-2,2′bipyridyl and 1,10-phenanthroline adduct systems is shown in Fig. 5. Here, the formation of adducts might be due to rearrangement of the chelate rings in order to provide a cis disposition for the bidentate bases. The *cis* adduct thus formed was of almost equal stability. This result shows that adduct formation with bidentate bases is not much influenced by steric effects.

The considerable increase in absorbance due to adduct formation constitutes the bases for the extraction of nickel with chloroform and hence, the ligand D2,4DMPC can be used as analytical reagent for this purpose.

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