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Coordination Compounds of Hydrazine Derivatives With Transition Metals. XIV. Nickel(II) Chelates with Bidentate Aroylhydrazones and Their Reactions with Heterocyclic Bases

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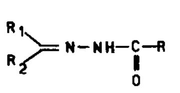
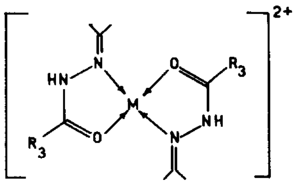
Both cationic and neutral bis(ligand)nickel(II) chelates derived from some bidentate aroylhydrazones have been prepared and characterised. Whenever the solubility permits, the reaction of the neutral bis(ligand) chelates, NiL_2, with some heterocyclic bases were studied spectrophotometrically in benzene solution. The stability constants as well as the thermodynamic parameters (ΔG, ΔH, ΔS) for the adduct formation reaction have been measured. Stable solid mono-, bis- and tetrapyridinate adducts have been isolated from the crystallization of neutral bis(ligand) chelates from pyridine solutions.

Introduction

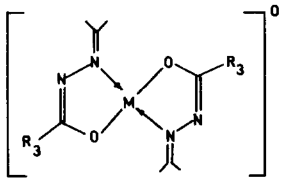
Aroylhydrazones of the type (I) were found to react with divalent transition metal ions forming either neutral (IIa) or cationic (IIb) metal chelates [1–4]. The present work is devoted to a study, in some details, of the reaction of nickel(II) salts with some bidentate aroylhydrazones. Hereafter, HL and L refer to the neutral and mono-negative bidentate ligands, respectively. Two series of nickel(II) chelates of the general formula $Ni(HL)_2X_2$ and NiL_2 have been isolated and characterised. Whenever solubility permitted, the reactions of NiL_2 with some heterocyclic bases were studied spectrophotometrically in benzene solution. Attempts were also made to isolate adducts and stable mono-, bis- and tetrapyridinate adducts were isolated from the crystallisation of neutral bis(-ligand) chelates from pyridine solution.



(I)



(IIa)



(IIb)

Experimental

Preparation of Organic Ligands

The aroylhydrazines were prepared as previously described [7]. The aroylhydrazones (1) were generally prepared by the reaction of aroylhydrazine with the corresponding ketone or aldehyde according to the method reported in the literature [4].

Preparation of Nickel(II) Complexes

Bis(aroylhydrazone)nickel(II) chloride, bromide, thiocyanate and nitrate complexes were prepared using the same procedure previously described for the corresponding cobalt(II) chelates [4]. The prepared cationic bis(ligand) chelates together with their elemental analyses are given in Table I.

Bis(aroylhydrazinato)nickel(II) Complexes

A hot solution of nickel(II) acetate tetrahydrate (0.01 mol) in 50% aqueous ethanol (30 ml) was added to a boiling solution of aroylhydrazone (0.02 mol) in ethanol (30 ml). To this reaction mixture an aqueous solution of concentrated ammonium hydroxide (1 ml) was added and the resulting solution was refluxed for one hour. On cooling, the precipitated complex was filtered, washed with hot ethanol, then dried under vacuum. The isolated chelates are given in Table III.

Preparation of Pyridine Adducts

The neutral bis(ligand)nickel(II) chelate (1 gm) was dissolved in pyridine (10 ml). The solution was heated on a water bath for 1/2 hr, then treated with 10 ml of dry benzene. On cooling the pyridine adduct precipitated out. It was filtered and washed with dry benzene. The analytical data of the prepared adducts are given in Table V.

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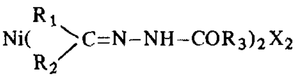
TABLE I. Analytical and Magnetic Data of Nickel(II) Complexes of the General Formula



$Ni(\overset{R_1}{\underset{R_2}{>}}C=N-NH-COR_3)_2X_2$

No.	R_1	R_2	R_3	X	Ni%	N%	X%	μ_{eff} (°K)
1	H	C_6H_5	C_6H_5	Cl	10.02 (10.60)	9.52 (9.69)	12.11 (12.26)	3.20(292)
2	H	p-$CH_3C_6H_4$	C_6H_5	Cl	9.58 (9.69)	9.41 (9.25)	11.51 (11.72)	3.18(292)
3	H	p-$CH_3OC_6H_4$	C_6H_5	Cl	9.18 (9.21)	8.67 (8.78)	11.00 (11.13)	3.18(293)
4	H	p-ClC_6H_4	C_6H_5	Cl	9.12 (9.08)	8.57 (8.66)	16.36 (16.47)	3.07(293)
5	H	p-$NO_2C_6H_4$	C_6H_5	Cl	8.75 (8.79)	12.42 (12.58)	10.81 (10.63)	3.12(293)
6	H	p-$(CH_3)_2NC_6H_4$	C_6H_5	Cl	8.71 (8.68)	12.32 (12.41)	10.50 (10.49)	3.21(293)
7	H	C_8H_7	C_6H_5	Cl[b]	9.30 (9.32)	8.88 (8.92)	11.22 (11.31)	3.13(293)
8	H	C_6H_5	o-HOC_6H_4	Cl	9.58 (9.61)	9.20 (9.18)	11.60 (11.62)	3.12(292)
9	H	p-$CH_3OC_6H_4$	o-HOC_6H_4	Cl	8.64 (8.75)	8.40 (8.36)	10.43 (10.58)	3.18(292)
10	CH_3	CH_3	C_6H_5	Cl	12.20 (12.20)	11.50 (11.63)	14.56 (14.70)	3.21(293)
11	CH_3	CH_3	C_6H_5	Br	10.80 (10.30)	9.71 (9.82)	27.30 (27.99)	3.10(295)
12	CH_3	CH_3	C_6H_5	SCN	11.30 (11.13)	16.00 (16.12)		3.17(295)
13	CH_3	CH_3	C_6H_5	NO_3	10.70 (10.90)	15.81 (15.92)		3.10(294)
14	CH_3	CH_3	o-HOC_6H_4	Cl	11.40 (11.30)	10.82 (10.90)	14.10 (13.85)	3.28(290)
15	CH_3	CH_3	o-HOC_6H_4	Br	9.90 (9.70)	9.34 (9.29)	26.10 (26.59)	3.31(292)
16	CH_3	CH_3	o-HOC_6H_4	SCN	10.30 (10.40)	14.13 (14.02)		3.28(293)
17	CH_3	CH_3	o-HOC_6H_4	NO_3	10.20 (10.30)	14.52 (14.82)		3.25(292)
18	CH_3	CH_3	p-$CH_3OC_6H_4$	Cl	11.40 (10.80)	10.22 (10.30)	12.90 (13.08)	
19	CH_3	CH_3	p-$CH_3OC_6H_4$	SCN	10.40 (10.03)	14.54 (14.69)		3.20(295)
20	CH_3	CH_3	p-$NO_2C_6H_4$	Cl	10.60 (10.20)	9.63 (9.80)	12.18 (12.39)	3.22(292)
21	CH_3	CH_3	p-$NO_2C_6H_4$	SCN	9.70 (9.50)	18.00 (17.98)		3.20(294)
22	C_5H_{10}		C_6H_5	Cl	10.20 (10.40)	9.73 (9.97)	12.20 (12.60)	3.18(294)
23	C_5H_{10}		C_6H_5	SCN	9.11 (9.18)	12.72 (12.96)		3.17(293)
24	C_5H_{10}		C_6H_5	NO_3[b]	8.82 (9.01)	13.33 (13.65)		3.18(294)
25	C_5H_{10}		o-HOC_6H_4	Cl	9.70 (9.88)	9.37 (9.43)	11.60 (11 98)	3.20(293)
26	C_5H_{10}		o-HOC_6H_4	SCN	9.02 (8.74)	12.62 (12.74)		3.21(293)
27	C_5H_{10}		o-HOC6H_4	NO_3[b]	8.43 (8.59)	12.72 (12.93)		3.13(292)

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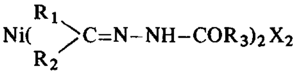
[a] Figures in parentheses indicate the required percentage. [b] Isolated as dihydrate.

TABLE II. The Electronic Spectral Data of Some Nickel(II) Chelates of the General Formula:



$Ni(R_1R_2C{=}N{-}NH{-}COR_3)_2X_2$

R_1	R_2	R_3	X	Band Maxima (nm)								
CH_3	CH_3	C_6H_5	Cl	440	480	602	685	735		815	930	990
CH_3	CH_3	C_6H_5	Br				634	719			940^a	
CH_3	CH_3	C_6H_5	SCN	400		580	699	699	775	840	920	962
CH_3	CH_3	C_6H_5	NO_3	390		600	667^a		769	820	920	962
CH_3	CH_3	o-HOC_6H_4	Cl			645	690	730		800	900	970
CH_3	CH_3	o-HOC_6H_4	Br			610	670	750			910	960
CH_3	CH_3	o-HOC_6H_4	SCN	415		580	645	700	775	860	930	980
CH_3	CH_3	o-HOC_6H_4	NO_3			625	675	725(sh)		755(sh)	920	990
CH_3	CH_3	p-$CH_3OC_6H_4$	Cl			580	650	700	780		920^a	
CH_3	CH_3	p-$NO_2C_6H_4$	Cl			600	660	710	780	860	950^a	
CH_3	CH_3	p-$NO_2C_6H_4$	SCN		500	570	645	710	785	850	921	976
C_5H_{10}		C_6H_5	Cl	445		615	670	750		800	911	1000
C_5H_{10}		C_6H_5	SCN	420		570	620	675	730	840	880	941
C_5H_{10}		C_6H_5	NO_3	410		570	620	680		870	911	955
C_5H_{10}		o-HOC_6H_4	Cl	450		650		720		800		940
C_5H_{10}		o-HOC_6H_4	SCN	425	540	585	630	685	775	861	921	961
C_5H_{10}		o-HOC_6H_4	NO_3	405	530	615	685	715	780	850	900	961

^{a}Broad band.

Physical Measurements

Magnetic measurements, infrared and nujol mull electronic spectra were obtained using the same procedure previously described [2, 4]. Solution electronic spectra were recorded on a Carl Zeiss PMQ II spectrophotometer fitted with a fluid thermostat cell holder. The actual temperature of the solution under investigation was recorded by a calibrated thermocouple dipped in the cell. Thermogravimetric and differential thermal analyses were performed on a derivatograph Model D-102, manufactured by MOM (Hungary) using Al_2O_3 as standard.

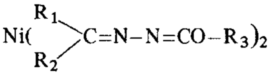
Results and Discussion

The reaction of aroylhydrazones of the type (I) with nickel(II) nitrate or chloride afforded the bis ligand chelates of the general formula $Ni(HL)_2X_2$. The corresponding bromo and thiocyanato chelates were prepared metathetically. The prepared bis ligand chelates together with their elemental analyses are given in Table I. These chelates are insoluble in non polar solvents, sparingly soluble in ethanol but slightly soluble in dimethylformamide and acetonitrile.

The infrared spectra of $Ni(HL)_2X_2$ chelates are similar to those reported for the corresponding cobalt(II) chelates [4] and show bands due to ν(N–H), amide I and ν(C=N) at *ca.* 3200, 1630 and 1618 cm^{-1} respectively. The position of both ν(C=N) and amide I bands are generally lowered by *ca.* 20–30 cm^{-1} as compared to the parent ligand suggesting bidentate nature (IIa) of the ligand [2, 4]. These chelates are paramagnetic with magnetic moments varying from 3.10–3.28 BM (Table I) and their nujol mull electronic spectra (Table II) are quite similar to one another and are clearly diagnostic of pseudo-octahedral structures [5]. Strong tetragonal distortion is evident from the observed splitting in both ν_2 and ν_1 bands [5].

The bis ligand chelates (1, 7, 11, 15 and 22) were readily hydrolysed in boiling 50% aqueous ethanol giving the tris(benzoylhydrazine)nickel(II) dichloride (IIa) with the liberation of the free aldehyde or ketone. The corresponding bis ligand nickel(II) chloride was not isolated [6, 7]. Hydrolysis of the thiocyanato complexes (9, 13, 18, and 20), however, gave the bis ligand chelates (IIIb). In all cases studied, no 1,2-dibenzoylhydrazine was detected [8]. It is noteworthy that the parent organic ligands do not show appreciable hydrolysis under identical experimental conditions. It seems that coordination of Ni(II) ions via the azomethine nitrogen results in the polarization of the C=N bond, rendering the carbon atom much more susceptible to nucleophilic attack [9, 10]. In boiling pyridine, these chelates are readily decomposed giving $Ni(Py)_4Cl_2$ and the free ligand (Scheme 1).

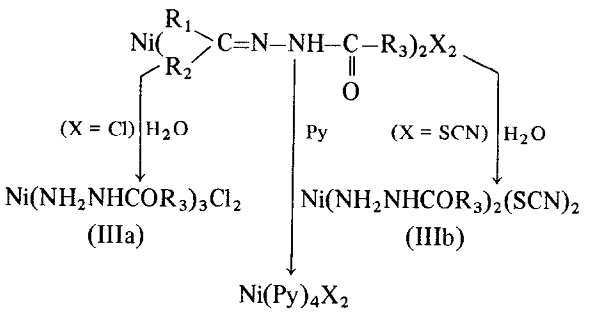
TABLE III. Analytical Data of Nickel(II) Chelates of the General Formula:



$\mathrm{Ni}(\overset{R_1}{\underset{R_2}{>}}C{=}N{-}N{=}CO{-}R_3)_2$

No.	R_1	R_2	R_3	Nickel[a] (%)	Nitrogen[a](%)
28	H	C_6H_5	C_6H_5	11.64 (11.62)	11.14 (11.09)
29	H	*p*-$CH_3OC_6H_4$	C_6H_5	10.65 (10.39)	10.65 (10.92)
30	H	*m*-$CH_3OC_6H_4$	C_6H_5	10.21 (10.39)	9.87 (9.92)
31	H	*p*-$CH_3C_6H_4$	C_6H_5	11.00 (11.02)	10.32 (10.51)
32	H	*p*-ClC_6H_4	C_6H_5	10.06 (10.23)	9.77 (9.76)
33	H	*p*-$(CH_3)_2NC_6H_4$	C_6H_5	10.32 (9.93)	14.11 (14.22)
34	H	C_6H_5	*o*-HOC_6H_4	10.87 (10.92)	10.50 (10.43)
35	H	*p*-$CH_3OC_6H_4$	*o*-HOC_6H_4	9.82 (9.83)	9.27 (9.38)
36	H	C_8H_7	C_6H_5[b]	10.28 (10.21)	9.58 (9.74)
37	CH_3	CH_3	*p*-$MO_2C_6H_4$	12.10 (11.70)	16.51 (16.76)
38	CH_3	C_2H_5	*p*-$NO_2C_6H_4$	10.84 (11.13)	15.82 (15.95)
39	C_2H_5	C_2H_5	*p*-$NO_2C_6H_4$	10.79 (10.58)	15.10 (15.14)
40	CH_3	C_6H_5	*p*-$NO_2C_6H_4$	9.70 (9.40)	13.25 (13.45)
41	C_5H_{10}		*p*-$NO_2C_6H_4$	10.06 (10.14)	14.32 (14.52)
42	C_5H_{10}		C_6H_5[c]	11.16 (11.21)	16.01 (16.01)

[a] Figures in parentheses indicate the required percentage. [b] Isolated as monohydrate. [c] Isolated as diammine.



Scheme 1.

Reaction of the aroylhydrazones with nickel(II) acetate in boiling ethanol, on the other hand, gave orange or red crystalline products of the general formula NiL_2 (Table III). In some cases the formation of these neutral chelates required the addition of a base such as ammonia or sodium acetate to enhance deprotonation. In case of cyclohexanone benzoylhydrazone only the green diamine complex (42) was isolated. In hot benzene this complex gave a red solution and attempts to isolate the red chelate NiL_2 were unsuccessful. Using cinnamaldehyde benzoylhydrazone (I, R_1 = H, R_2 = $C_6H_5CH{=}CH$ and R_3 = C_6H_5) the reaction proceeded with the formation of a yellow monohydrate (36) which crystallized from benzene giving the brown anhydrous chelate.

The i.r. spectra of NiL_2 chelates lack absorption due to both (N–H) and amide I, but show a strong band at *ca.* 1610 cm^{-1} due to C=N–N=C residue [2, 4]. These spectra suggest the coordination mode (IIb) in which the hydrazone molecule acts as a mononegative bidentate ligand.

Magnetic susceptibility measurements showed that all the neutral chelates of the type NiL_2 are dia-

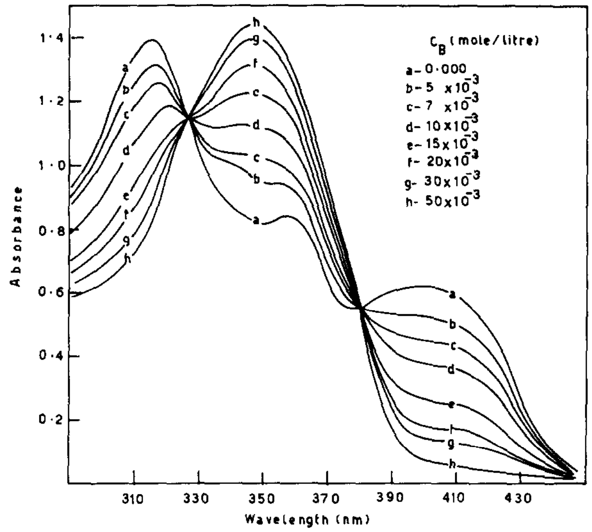


Fig. 1. Spectrophotometric titration of 3.57 X 10^{-5} *M* bis(benzaldehyde benzoylhydrazonato)nickel(II) with pyridine in benzene solutions. C_{Py}, *M*: (a) 0.000, (b) 0.005, (c) 0.007, (d) 0.010, (e) 0.015, (f) 0.020, (g) 0.030 and (h) 0.050.

magnetic implying a square planar environment around the Ni(II) ion. This assignment was confirmed from their Nujol mull as well as solution spectra in benzene. The spectra do not show any absorption beyond 700 nm but exhibit a strong band at *ca.* 410 nm of charge transfer origin.

The green diammine complex (42) was found to be paramagnetic, μ_{eff} = 3.22 BM (299 °K), and its Nujol mull electronic spectrum suggests an octahedral structure with two ammonia molecules probably occupying the *trans* axial position. The monohydrate (36), on the other hand, is also of high spin type (μ_{eff} = 2.99 BM (298 °K)), which on dehydration afforded the diamagnetic anhydrous chelate. The change of spin multiplicity on dehydration suggests that the water molecule is directly attached to the central Ni(II) ion forming a five coordinate structure. The relatively low magnetic moment observed for this complex as compared to those reported for five coordinate nickel(II) chelates may be due to partial dehydration during the preparation of the sample for magnetic measurements. The Nujol mull electronic spectra of the monohydrate shows a broad maximum absorption band at 780 nm besides a strong band at 400 cm^{-1}, confirming the five coordinate geometry [5, 10].

Similar to other NiO_2N_2 chelates [11–14], the neutral bis-ligand chelates react with nitrogen bases giving different adducts. The nature of these adducts depends on the substituents in R_1, R_2 and R_3 of the ligand molecule. In benzene solutions, the reaction of some heterocyclic bases, *viz.* pyridine (Py), 3-methylprydine (3-MePy), 4-methylpyridine (4-MePy) and isoquinoline (Isoqu), with the bis-ligand chelates derived from substituted benzaldehyde benzoylhydrazones (25–29) was followed spectrophotometrically.

Typical spectral changes on adding different pyridine concentrations are shown in Fig. 1. The successive absorption curves pass through two fixed sharp isobestic points at 327 and 380 nm implying the existence of only one equilibrium in these solutions, Eq. (1). Similar spectral variations were also observed with other square planar Ni(II) chelates using different heterocyclic bases.

Analysis of the data obtained from these spectrophotometric titrations in the range 380–450 nm, using the Coleman, Verga and Mastin graphical method [15], revealed the presence of only two light absorbing species in equilibrium, namely the parent NiL_2 and the formed $NiL_2 \cdot nB$ adduct, Eq. (1). The formation constant (K) of each adduct is given by Eq. (2). In all the systems studied a large excess of the base was used as compared to the initial concentration of the parent NiL_2 (C_B/C_{NiL_2} varies from 50–2000), thus the analytical concentration C_B will be taken as the equilibrium concentration [B] and the logarithmic Eq. (3) was applied to confirm the stoichiometry and to calculate logK [16].

$$NiL_2 + nB \rightleftharpoons NiL_2B_n \tag{1}$$

$$K = \frac{[NiL_2B_n]}{[NiL_2]\,[B]^n} \tag{2}$$

$$\log \frac{A_0 - A}{A - A_\infty} = \log K + n \log C_B \tag{3}$$

A linear least squares computer program [17] was used to fit the absorbance data in Eq. (3) and plots of $\log(A_0 - A)/(A - A_\infty)$ *vs.* $\log C_B$ gave straight lines [18], with n = 2, through the whole range of base concentrations. The values of ΔH were calculated from the slopes of the least squares lines for a plot of logK *vs.* 1/T. The temperature was varied in the range 20–40 °C. The calculated values of log K together with the thermodynamic functions ΔG, ΔH and ΔS for all systems studied are collected in Table IV.

The available results suggest that reaction of NiL_2 with heterocyclic bases in benzene solutions afforded bis adducts (n = 2 ± 0.02) and the measured logK values exhibit the expected linear increase with increasing donor power of the base [11, 12]. It is also observed that substitution in R_1 (I, R_2 = H and R_3 = C_6H_5) greatly influences the acceptor power of the parent NiL_2 chelates. This is evident from the linear correlation between logK and Hammett sigma value (σ) [19] for various substituents. The presence of an electron withdrawing group results in an increase in the formal charge on the nickel(II), thereby increasing the metal base interaction and *vice versa.*

TABLE VI. Equilibrium Constants and Thermodynamic Parameters for Bis Adduct Formation of $Ni(R_1R_2C{=}N{-}N{=}COR_3)_2$ Chelates With Some Heterocyclic Bases in Benzene at 25 °C.

R_2[a]	Base	LogK	$-\Delta G$ Kcal/mol	$-\Delta H$ Kcal/mol	$-\Delta S$ Cal/mol/deg
p-$CH_3C_6H_4$	Py	3.75	5.11	22.50	58.40
	3MePy	3.98	5.43	24.10	62.30
	4MePy	4.38	5.97	22.00	53.80
	Iso.Quin	3.52	4.80	21.00	54.40
m-$OCH_3C_6H_4$	Py	4.31	5.88	22.80	56.80
	3MePy	4.59	6.25	24.20	60.20
	4MePy	4.89	6.67	22.50	53.10
	Iso.Quin	4.18	5.70	22.10	55.00
C_6H_5	Py	4.02	5.48	23.00	58.80
	3MePy	4.23	5.77	22.58	56.40
	4MePy	4.60	6.27	24.80	62.20
	Iso.Quin	4.00	5.45	20.70	51.20
p-$CH_3OC_6H_4$	Py	3.62	4.94	20.00	50.50
	3MePy	3.70	5.05	23.80	62.90
	4MePy	4.03	5.49	22.30	56.40
	Iso.Quin	3.42	4.66	19.87	51.04
p-ClC_6H_4	Py	4.56	6.22	25.50	64.69
	3MePy	4.71	6.42	25.80	65 03
	4MePy	5.00	6.82	24.90	60 70
	Iso.Quin	4.40	6.00	22.74	56.20

[a] I, R_1 = H and R_3 = C_6H_5.

In presence of a large excess of pyridine concentration ($C_{Py}/C_{NiL_2} > 5000$) the spectra of NiL_2 chelates in benzene become time dependent. The observed spectral changes and the presence of a sharp isosbestic point at 340 nm suggest that the initially formed bis adduct NiL_2B_2 slowly undergoes further reaction with base molecules giving species with n > 2. In fact, crystallization of NiL_2 chelates (1–5) from either neat pyridine or benzene solutions containing large excess of pyridine afforded stable solid tetrapyridinate adducts NiL_2B_4. Attempts to isolate the bis-adducts NiL_2Py_2 which were identified spectrophotometrically in benzene solutions with C_{Py}/C_{NiL_2} varying from 50–2000 were unsuccessful.

The isolated tetrapyridine adducts (Table V) are of high spin type with magnetic moments falling in the range 3.00–3.18 BM. Their Nujol mull electronic spectra are consistent with octahedral structure. It is evident from the previous results that in presence of a large excess of pyridine the chelate rings are opened and an octahedral tetrapyridine adduct is formed with the aroylhydrazone molecule acting as a monodentate ligand.

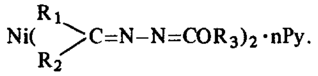
Thermogravimetric (t.g.) and differential thermal analyses of the tetrapyridine adducts (43), (44) and (45) showed that the pyridine molecules were lost in two successive steps. In each, the percentage loss in weight corresponds to two pyridine molecules, while in (46) and (47) three endothermic peaks were observed where two pyridine molecules were lost in the first step, while the remaining two molecules were evolved successively in two steps.

The present results clearly show that depyridination of the tetrabase adducts proceeds *via* the formation of stable bis adducts NiL_2Py_2. In some cases, however, the formation of mono adducts NiL_2Py is also evident. Complete depyridination affords the parent square planar chelate.

Stable crystalline bis adducts of the type NiL_2Py_2 were also isolated from the reaction of (33), (36), (41) and (42) with pyridine. These adducts are paramagnetic, Table V, and their mull spectra show bands at *ca.* 560, 800(sh) and 1000 nm, characteristic of octahedral stereochemistry. The thermogravimetric analysis of these adducts indicates that one of the pyridine molecules is lost at relatively lower temperature giving the intermediate mono pyridine adduct which on further heating reverts to NiL_2. The formation of bis adducts (48) and (49) rather than tetrabase adducts can be related to the electronic effects of R_2 groups, *viz.* $N(CH_3)_2$ and $C_6H_5CH{=}CH$, which increase the basicity of azomethine nitrogen and consequently make these chelates much more reluctant to bond rupture. Steric effects of cyclohexyl group in (50) and (51) may play an essential role in the stability of the formed bis adducts.

Reaction of square planar chelates (37), (38) and (40) with pyridine gave mono base adducts. Both

TABLE V. Analytical and Magnetic Data of the Base Adducts of the General Formula



$\mathrm{Ni}(\begin{smallmatrix}R_1\\ R_2\end{smallmatrix}{>}C{=}N{-}N{=}COR_3)_2\cdot n\mathrm{Py}.$

No.		R_1	R_2	R_3	Ni(%)[a]	N(%)[a]	Py(%)[a]	μ_{eff}(°K)
(i)	$NiL_{2}.4Py$							
	43	H	C_6H_5	C_6H_5	7.01 (7.15)	13.35 (13.65)	38.32 (38.50)	3.07(294)
	44	H	p-$CH_3C_6H_4$	C_6H_5	6.89 (6.91)	13.02 (13.20)	36.93 (37.24)	3.18(294)
	45	H	p-ClC_6H_4	C_6H_5	6.43 (6.58)	12.42 (12 59)	35.21 (35.52)	3.15(295)
	46	H	p-$CH_3OC_6H_4$	C_6H_5	6.87 ((6.67)	12.61 (12.72)	35.52 (35.88)	3.09(293)
	47	H	m-$CH_3OC_6H_4$	C_6H_5	6.75 (6.67)	12 51 (12.72)	35.41 (35.88)	3.10(293)
(ii)	$NiL_2 2Py$							
	48	H	p-$(CH_3)_2NC_6H_4$	C_6H_5	7.93 (7.84)	15.00 (15.10)	21.00 (21.10)	3.18(292)
	49	H	C_8H_7	C_6H_5	18.19 (18.22)	11.43 (11.75)	22.10 (22.11)	3.21(292)
	50	C_5H_{10}		C_6H_5	9.43 (9.11)	12.87 (12.98)	24.21 (24.43)	3.18(292)
	51	C_5H_{10}		p-$NO_2C_6H_4$	8.19 (7.96)	15.10 (15.20)	24.05 (21.45)	3.01(292)
(iii)	NiL_2Py							
	52	CH_3	CH_3	p-$NO_2C_6H_4$	10.15 (10.16)	16.65 (16.96)	13.70 (13.67)	3.31(295)
	53	CH_3	C_2H_5	p-$NO_2C_6H_4$	9.70 (9.69)	16.21 (16.18)	13.20 (13.04)	3.28(294)
	54	CH_3	C_6H_5	p-$NO_2C_6H_4$	8.40 (8.37)	13.76 (13.97)	11.11 (11.26)	3.31(294)

[a] Figures in parentheses indicate the required percentages.

magnetic and spectral data confirm the five coordinate geometry, probably of a distorted square pyramidal structure. The steric effect imposed by R_1 and R_2 groups in the aroylhydrazone ligand is the major factor determining the formation of these five coordinate monobase adducts.

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