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MODE OF COORDINATION AND CHEMICAL REACTIVITY OF α -IMINE HYDRAZONE LIGANDS

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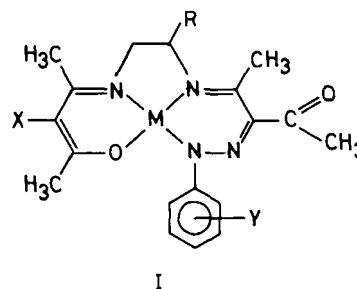
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Interaction of nickel(II) and copper(II) complexes of 4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione, Ni(baen) and 4,6,9-trimethyl-5,8-diazadodeca-4,8-diene-2,11-dione, Ni(bapn), with arene diazonium chlorides in buffered solutions of methanol yielded metal derivatives of glyoxaliminearylhydrazones. This typical electrophilic addition at the 3-carbon of the complex occurs owing to the pseudo aromatic behaviour of the chelate ring. A mechanism which predicts the attack of the diazonium cation through the coordination shell of the metal is well documented from the available experimental evidences. The chemical reactivity of a few complexes with a single residual non-substituted γ -carbon is reasonably manifested by their reaction with phenyl isocyanate.

KEY WORDS: Glyoxaliminearylhydrazones of Ni(II) and Cu(II) – Mode of coordination – mechanism of diazo coupling reaction – Reactivity with phenyl isocyanate.

INTRODUCTION

In recent years considerable effort has been directed towards the development of convenient synthetic routes to macrocyclic polydentate ligands and their metal complexes.¹ In this regard few classes of coordination compounds have served as the focus of such extensive and continuing research efforts as have those prepared from the 1,3-diketones of their nitrogen analogues. The coordinated 1,3-diketone or its nitrogen derivative Schiff base enable a reactive electron rich centre for chemical reactions, more favourably electrophilic additions, to occur. We have recently reported the reactions of the tetradentate Schiff base complexes derived from acetyl acetone and 1,2-diamines with arene diazonium ions.² These reactions yielded a new class of coordination complexes with the introduction of a chelate having $-N=C-C=N-N-$ functionalities. The formation of these potentially polydentate complexes was found to be concentration-controlled.² In this paper we report the reaction of the Schiff base complexes and the arene diazonium ions in one to one stoichiometry. The emphasis is being made on probing pseudo aromatic behaviour of the chelate ring. The readiness with which complex I ($X=H$) undergoes electrophilic addition is adopted for this purpose.



EXPERIMENTAL

Materials

The reagents used as starting materials were obtained commercially and used without further purification, unless noted.

The Schiff bases derived from acetylacetone and ethylene/propylene diamine were prepared according to the procedure reported in the literature.³ They were crystallized from methanol and purity was checked by melting points and spectral properties. The aromatic amines used for the preparation of arene diazonium salts were Fluka products and purified before use. Sodium nitrite, hydrochloric

acid, sodium acetate, nickel acetate, and copper acetate were A.R. grade.

Phenyl isocyanate

Phenyl isocyanate used for the reaction was prepared according to the reported procedure.⁴

Arene diazonium chlorides

Freshly prepared aqueous solutions of aryl diazonium chlorides were used for the reactions. They were prepared by the diazotization of the aromatic amines according to procedure described elsewhere.²

Ni(baen), Ni(bapn), Cu(baen), and Cu(bapn) complexes

These chelates were prepared by a procedure reported in the literature.³ In principle, 1:1 molar ratio of the ligand to metal was taken. The complexes are soluble in all organic solvents. Purification was accomplished by washing with water and crystallized from methanol-chloroform mixture (1:1).

Preparation of complexes M=Cu and X=H

They are prepared according to the reported procedure.²

Preparation of I(M=Ni; X=H) by arene diazonium reactions

1.4 g (0.005 mol) of Ni(baen) was dissolved in 200 ml of methanol containing 10 g of sodium acetate and kept stirred at 5°C. The aqueous benzene diazonium chloride (0.005 mol) was added slowly and dropwise to the methanolic solution in a period of 10 minutes. At the end of the addition, a red crystalline solid precipitated out. It was filtered, washed with 1:2 alcohol-water mixture, and dried in vacuum over Conc. H₂SO₄. The complex was recrystallized from 1:1 methanol-chloroform mixture yield 80%.

Reactions with phenyl isocyanate

Reactions of I (M=Cu, Ni; X=H) with phenyl isocyanate were carried out according to the following general procedure.

To a solution containing 0.01 mol of I(M=Cu, Ni; X=H) in 50 ml of dry benzene, 0.01 mol of

TABLE I
Analytical^a and electronic absorption bands of the complexes.

Complex	M	R	X	V	C(%)	H(%)	N(%)	M(%)	$\lambda_{\max}(\epsilon \times 10^{-3})$
I _a	Ni	H	H	p-OCH ₃	54.39 (54.96)	5.72 (5.80)	13.36 (13.49)	14.76 (14.14)	472(6.6)
I _b	Ni	H	H	m-NO ₂	50.61 (50.89)	5.23 (5.05)	16.38 (16.17)	16.69 (13.56)	480(5.82)
I _c	Ni	CH ₃	H	p-OCH ₃	55.62 (55.97)	6.42 (6.10)	13.61 (13.05)	13.59 (16.67)	470(6.63)
I _d	Ni	CH ₃	H	m-NO ₂	51.39 (51.80)	5.98 (5.57)	15.21 (15.93)	13.90 (13.31)	480(8.41)
I _e	Ni	H	CONHPh	p-CH ₃	60.72 (60.25)	5.72 (5.64)	13.67 (13.52)	11.48 (11.33)	475(6.7)
I _f	Ni	H	CONHPh	p-NO ₂	58.82 (54.67)	4.90 (4.77)	15.62 (15.31)	10.33 (10.69)	478(6.11)
I _g	Ni	H	CONHPh	p-OCH ₃	58.67 (58.45)	5.82 (5.47)	13.62 (13.11)	10.72 (10.99)	480(5.82)
I _h	Ni	CH ₃	CONHPh	p-OCH ₃	59.33 (59.15)	5.92 (5.70)	12.63 (12.77)	10.63 (10.71)	475(6.0)
I _i	Cu	H	CONHPh	p-CH ₃	59.33 (59.69)	5.72 (5.58)	13.62 (13.39)	12.29 (12.15)	400(5.9)
I _j	Cu	H	CONHPh	p-NO ₂	54.60 (54.19)	4.85 (4.70)	15.81 (15.17)	11.63 (11.47)	395(6.1)
I _k	Cu	CH ₃	CONHPh	p-CH ₃	60.61 (60.37)	5.71 (5.82)	13.61 (13.04)	11.40 (11.81)	395(6.3)
I _l	Cu	CH ₃	CONHPh	p-NO ₂	54.39 (54.96)	4.72 (4.90)	14.72 (14.80)	11.38 (11.19)	400(6.7)

^aValues in parentheses correspond to theoretical values.

phenyl isocyanate was added dropwise. The reaction flask was closed with a CaCl_2 tube and stirred for 24 hrs. The precipitated product was filtered, washed with 50 ml of dry benzene followed by 100 ml of hexane and dried in vacuum. The complexes could not be crystallized owing to their insoluble nature in most of the common organic solvents.

Elemental Analysis

Ni(II) and Cu(II) in the complexes were estimated using conventional methods.⁵ Carbon, hydrogen, and nitrogen contents in the complexes were estimated microanalytically. All the elemental analyses data are given in Table I.

Physical Measurements

Infrared spectra were taken on a Carl-Zeiss UR-10 grating I.R. spectrometer. KBr pellet and Nujol mull techniques were employed. Electronic spectra were obtained using a Beckman model-25 recording spectrophotometer with 1 cm matched quartz cells. Weighed samples were dissolved in spectroquality CHCl_3 to give approximately 5×10^{-4} M solution. Proton Nuclear Magnetic resonance spectra were obtained by using Varian HA-100D and Varian T-60 spectrometers. TMS was used as an internal standard. The mass spectrum of one of the complexes (I) was recorded on a MS-702 spectrometer using an electron source for molecular fragmentation. Conductivity measurements were obtained using a Siemens' conductivity bridge. Measurements were made at room temperature on approximately 5×10^{-3} M solution using AR solvents. Room temperature magnetic susceptibility was measured by the Guoy method, using Hg Co(SCN)_4 as the calibrant.

RESULTS AND DISCUSSION

Synthesis and characterization of Ia, Ib, Ic and Id

The synthesis of these complexes involves the addition of arene diazonium chlorides to Ni(baen) or Ni(bapn) in methanol buffered with sodium acetate (pH = 5.0). The stoichiometry was maintained strictly 1:1 in order to avoid the formation of the di-substituted products.² Results of elemental analysis (Table I) and molecular weight determination (by mass spectrum) are consistent with the formulation as depicted (I). All these

complexes are soluble in slightly polar organic solvents including ether, chloroform and alcohols but insoluble in water. The molar conductance measurements suggest them to be non-electrolytes in acetone with Λ_M of 5 ($\text{mhos cm}^2 \text{ mol}^{-1}$). The non-electrolytic character and the solubility characteristics are consistent with neutral nature of the complexes, in which the ligand is binding as a binegative entity.

The selected IR frequencies and their possible assignments are given in Table II. Comparison of the frequencies with those of the starting complexes, namely Ni(baen) and Ni(bapn), has been helpful in sorting out the vibrations arising from $\mu(\text{C-H})$, $\mu(>\text{C=O})$, and $\mu(>\text{C=N})$ groups. All these complexes exhibit IR bands around 765 cm^{-1} and 1160 cm^{-1} . These two bands are present in the IR spectra of the starting complexes and arise from the out-of-plane and in-plane deformation modes of $\gamma(\text{C-H})$ respectively. Thus, appearance of these bands in the diazo substituted complexes suggests the presence of $\gamma(\text{C-H})$ groups. The band around 1520 cm^{-1} arising from the coordinated (C-O) in Ni(baen) and Ni(bapn) is also present in the complexes, indicating the coordinated nature of (C-O). The presence of $\gamma(\text{C-H})$ and coordinated carbonyl groups in the diazo coupled complexes suggests that the complexes contain a coordinated β -ketoimine ring.

The fact that diazo coupling had taken place at the other $\gamma(\text{C-H})$ is seen from the absorption in the region $1500\text{--}1700 \text{ cm}^{-1}$. The intense absorption band around 1650 cm^{-1} in the complexes is assigned to free C=O. Similar observations are made by Bose and Patel⁶ in nitrosated complexes. The band around 1580 cm^{-1} is assigned to coordinated $>\text{C=N}$. It is possible that the band around 1600 cm^{-1} could be due to the $>\text{C=N}$ of the hydrazone and the $-\text{C=C}-$ group. The IR spectra of all organic azo compounds exhibit a band around 1480 cm^{-1} with varying intensity and this has been attributed to $\mu(\text{N=N})$.⁷ The absence of this band in all the complexes eliminates the possibility of a $-\text{N=N}-$ group. In other words, the added arene diazonium group undergoes an intramolecular rearrangement subsequent to the coupling reaction.² This would result in the formation of arylhydrazone derivatives.

From the foregoing discussion, the presence of free $>\text{C=O}$, $>\text{C=N}$, and absence of $-\text{N=N}-$ it is seen that the complex contains (a) β -ketoimine and (b) substituted glyoxal iminearylhydrazone part. This is further indicative of the fact that diazo coupling had taken place selectively at one of the $\gamma(\text{C-H})$ groups leading to a mixed ligand Schiff base complex.

TABLE II
 Principal infrared frequencies (cm^{-1}) and magnetic moments (B.M) of the complexes.

Complex	$\mu(\text{C}=\text{O})$ free	$\mu(\text{C}=\text{O})$ bonded	$\mu(\text{C}=\text{N}) +$ $\mu(\text{C}=\text{C})$	δCH	$\mu(\text{C}-\text{N})$	$\pi(\text{C}-\text{H})$	$\mu(\text{N}-\text{H})$	$\mu_{\text{eff}}(\text{B.M})$
I _a	1655s	1520s	1600m 1580s	1180w	1200s	770s	—	diamagnetic
I _b	1650s	1523s	1600m 1580s	1180w	1203s	765m	—	diamagnetic
I _c	1658s	1525s	1595m 1560s	1180w	1200s	770s	—	diamagnetic
I _d	1653s	1525s	1600m 1590s	1182sh	1205s	770s	—	diamagnetic
I _e	1658s	1510s	1580s 1605s	—	1200s	—	3310s	diamagnetic
I _f	1660s	1626s	1580s 1600s	—	1205s	—	3315s	diamagnetic
I _g	1670s	1510s	1575s 1610s	—	1200s	—	3320s	diamagnetic
I _h	1668s	1510s	1570s 1602s	—	1205s	—	3310s	diamagnetic
I _i	1655s	1525s	1575s 1610s	—	1220s	—	3320s	1.83
I _j	1678s	1520s	1585s 1600s	—	1215s	—	3310s	1.85
I _k	1660s	1510s	1570s 1610s	—	1210s	—	3300s	1.80
I _l	1675s	1520s	1585s 1605s	—	1210s	—	3325s	1.88

The donor sites around Ni(II) are N,O (of the ketoimine) and N,N' (of the imine hydrazone) atoms. The N' atom can be either the α or β nitrogen of the hydrazone. Coordination of β -nitrogen to Ni(II) would lead to a residual positive charge on the complex. The neutral behaviour of the complex as observed from the conductivity measurements rules out this possibility. Hence the coordination is from the α -nitrogen. The presence of MN_3O chromophoric system is further substantiated from our recent e.s.r studies of the related copper complexes.²

The 60-MHz p.m.r. spectrum of the present complex Ni(baen) indicates that the methyl groups are equivalent. On examining the p.m.r. spectra of I_a, I_b, I_c, and I_d the presence of 3 methyl signals is seen corresponding to 6 : 3 : 3 protons (Table III). The signal at 2.4 δ corresponds to six protons and it is assigned to the two methyl groups on the non-substituted β -ketoimine ring. The resonance of one of the methyl groups, the $-\text{CH}_3$ of the noncondensed COCH_3 end of the β -diketone, at a slightly higher field suggests its orientation in the shielding zone of the aromatic ring.

The mass spectrum of I_b is dominated by an intense peak at m/e 429 (base peak) which corresponds to the parent ion having the molecular formula $\text{C}_{18}\text{H}_{21}\text{N}_5\text{O}_4\text{Ni}^+$. The appearance of a peak

at m/e 401 corresponding to the molecular formula $\text{C}_{17}\text{H}_{21}\text{N}_5\text{O}_3\text{Ni}^+$ in the mass spectrum suggests that the parent ion undergoes fragmentation through the loss of CO from the CH_3CO group and subsequently the methyl group migrates to the nucleus of the chelate ring. We have reported such methyl migrations in related complexes.⁸

The electronic absorption spectra of the starting complexes Ni(baen) or Ni(bapn) show a band at 565 nm. This band has earlier been assigned^{9,10} to the $^1\text{A}_1 \rightarrow ^1\text{B}_2$ transition of the square planar chromophore. None of the complexes of I shows any absorption in this region. Instead, an intense band at 475 nm is observed for the complexes (Table I). The possibility that this band may arise from the d-d transition of square planar ni(II) seems unlikely since the intensity of the band is rather high. We attribute this band as a composite one arising from both the d-d transition and a charge transfer transition, possibly of MLCT type.

Chemical Reactivity of Complex I ($M=\text{Ni}, \text{Cu}; X=\text{H}$)

The isolation of complex I provides a $\gamma\text{-C}-\text{H}$ grouping for further electrophilic substitution reactions. It is likely that in the mono-diazo coupled Cu(II) and

TABLE III
 PMR data (δ ppm) of the complexes^a

Complex	Ring $-\text{CH}_3$	Terminal $-\text{CH}_3$	γ -CH	Diamine protons	Phenyl and its substituent protons
I_a	1.37(s, 3)	2.43(s, 6)	4.97(s, 1)	3.2(sext, 4)	7.2(q, 4)
	1.91(s, 3)				3.83(s, 3)
I_b	1.36(s, 3)	2.46(s, 6)	4.9(s, 1)	3.3(sext, 4)	7.7(m, 4)
	1.89(s, 3)				
I_c	1.36(s, 3)	2.5(s, 6)	4.9(s, 1)	1.62(d, 3)	7.3(q, 4)
	1.84(s, 3)			2.92(m, 2)	3.8(s, 3)
I_d	1.33(s, 3)	2.31(s, 3)	4.9(s, 1)	3.7(m, 1)	7.7(m, 4)
	1.82(s, 3)	2.42(s, 3)		1.63(d, 3)	
				2.9(m, 2)	

^aThe letters in the parentheses denote the nature of the signal and the numbers indicate the total number of protons involved in the resonance.
 s = singlet; d = doublet; m = multiplet; q = quartet

Ni(II) complexes, the acidic nature of the γ -CH and hence its reactivity may be considerably altered due to the presence of diazo substitution at one of the chelates. We have studied before¹¹ the bromination reactions of these Ni(II) complexes. Recently a study of the reaction with phenyl isocyanate was undertaken to explore the electronic effects imposed on the reactivity of the γ -CH in these complexes. It was found that the yields of the phenyl amido substituted complexes are high in both Ni(II) and Cu(II) complexes. In all cases the reaction took place readily and it was found that the reaction was over within 10 minutes. The infrared spectra of these complexes do not give absorption around 765 ($\pi_{\text{C}-\text{H}}$) and 1190 cm^{-1} ($\delta_{\text{C}-\text{H}}$). This is a good evidence for the introduction of the PhNHCO at C-3. The i.r. absorption at 3420–3210 cm^{-1} is assigned to γ (N–H) arising from the amide group. This is in accordance with the observation of Nelson *et al.*¹² in the reaction of Ni(baen) and Ni(bapn) with organic isocyanates. Only one band is observed around 1640 cm^{-1} which has been assigned to free γ (C=O) arising from both amide C=O and acetyl C=O groups, though one would expect two different bands for these groups. The positions of the coordinated γ (C=O) (1525 cm^{-1}) and γ (C=N) (15960 cm^{-1}) remain the same as observed for the mono-diazo coupled complexes (Table II).

Mechanism of the Diazo coupling Reactions: It is clear from the present work and our previous studies² that the azo coupling of Ni(baen) or Cu(baen) complexes occurs in a stepwise fashion though two equally accessible γ -CH groups are available for

simultaneous attack by the arene diazonium cation. A possible mechanism for this reaction would be the attack of the arene diazonium cation through the coordination shell of the metal complex. It is reasonable to expect that the proximity of the positively charged bulky diazonium ions in this shell will be highly unfavourable both from the coulombic and steric interactions. The initial interaction between the diazonium cation and the metal results in charge delocalization through the metal centre and the ligand. This would presumably activate the C-3 for a electrophilic displacement of the azo group and subsequent formation of the C–N bond. We have measured qualitatively the rate of formation of the azo coupled complexes. It is found that Cu(baen) reacts 100 times faster than Ni(baen). Also the reaction in aqueous methanol is faster (~100 times) than in pyridine medium. This is not surprising since the square planar Cu(II) (d^9) forms an adduct readily whereas square planar nickel complex (d^8) does not prefer a fifth ligand.

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