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SYNTHESIS AND STUDY OF SOME NEW FLUORINATED GLYOXALIMINEHYDRAZONES AND THEIR NICKEL COMPLEXES

KRISHNA C. JOSHI AND BIDYA S. JOSHI

Department of Chemistry, University of Rajasthan,
Jaipur-302004(India)

SUMMARY

Spectral studies of some fluorinated glyoxaliminehydrazones reveal that in these compounds the hydrazoneimino tautomer with hydrogen bonding via the imino-N predominates. The complexation of these ligands with nickel involves the N-atoms of the observed tautomeric form.

INTRODUCTION

Glyoxaliminehydrazones are reported to exist in the hydrazoneimino (A) and azoamino (B) tautomeric forms [1]. Although the mode of coordination of these ligands is well documented there is not much information about the structure of these ligands [2-5]. In this communication the synthesis and detailed systematic studies on the structural aspects of some fluorinated glyoxaliminehydrazones and their nickel complexes are reported.

$R^1NHN{:}CC(O)R^2CR^3{:}NR^4$ (A) $R^1N{:}NCC(O)R^2CR^3NHR^4$ (B)

(R^1 = m-$CF_3C_6H_4$; R^2 = p-HC_6H_4, p-BrC_6H_4, p-ClC_6H_4 and p-FC_6H_4; R^3 = CH_3; R^4 = C_6H_5)

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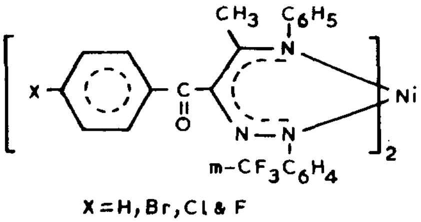
RESULTS AND DISCUSSION

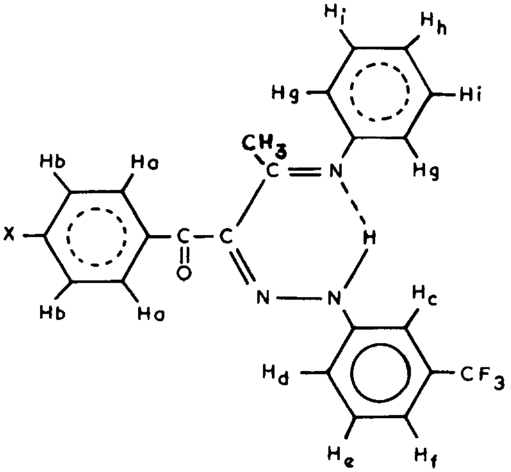
Spectral studies of the compounds give evidence that they exist exclusively in the hydrazoneimino form (A). In the IR spectra the N–H vibration is observed as a broad band around 3400 cm^{-1}; two well defined bands in the region 1650 cm^{-1} and 1590 cm^{-1} are assigned to a C=O stretching mode of a non-hydrogen bonded arylketo and a hydrogen bonded azomethine, C=N, stretching vibration [6,7] . The C–F and CF_3 stretching modes are observed between 1330–1000 cm^{-1}. The following changes were noticed after the formation of nickel complexes. Firstly, the intramolecularly hydrogen bonded (N–H...N=C) absorption band disappeared from the region 3400 cm^{-1}; secondly the azomethine vibration band was lowered to 1560 cm^{-1} due to coordination of the nitrogen atom and finally the non-coordinated carbonyl stretching was observed around 1630 cm^{-1} due to electron delocalization in the adjacent chelate ring [6–9] , (Scheme 1).



Scheme 1.

The high field ^1H NMR spectral data of the compound is given in Table 1. A detailed interpretation of the spectrum of compound (4), (Scheme 2) is discussed below.

Olefinic methyl protons appeared as a broad singlet at δ 2.3 ppm; while the N–H proton was observed in the downfield region at δ 15.66 ppm as a broad signal. Various aromatic protons are assigned as : H_g, H_g' as dbr at δ 6.94 ppm; H_h, H_h' as dd at δ 7.5 ppm; H_i as dd at δ 7.23 ppm; H_a, H_a' as



X = (1) H; (2) Br; (3) Cl; (4) F

Scheme 2

dbr at δ 8.04 ppm; H_b, H_b' as dd at δ 7.15 ppm; H_c as sbr at δ 7.40 ppm; H_d as dd at δ 7.38 ppm; H_e as dd at δ 7.30 ppm and H_f as dbr at δ 7.28 ppm. Assignments of various protons have been confirmed by sequential decoupling experiments.

Several possible structures can be alternately written for the hydrazoneimino tautomer (A) keeping in view the various possible modes of hydrogen bonding. However, in the compounds under study, it has been confirmed by nuclear Overhauser effect experiments and Dreiding Models that the hydrogen bonding occurs via the imino-nitrogen i.e. N-H...N=C.

Irradiation of CH_3 protons (Fig. 2) gave a clear NOE with H_g, H_g' and H_a, H_a' protons, while irradiation of N-H proton gave a strong NOE with H_c and H_d protons and a weak NOE with H_g, H_g' protons.

From these results it is evident that hydrogen bonding in the hydrazoneimino tautomer is via imino-nitrogen, (N-H... N=C).

The ^1H NMR spectra of the nickel complexes shows no N-H proton signal, the methyl protons are observed around δ 2 ppm and the aromatic protons at δ 6.5-8 ppm.

TABLE 1

^1H NMR Spectral data of 2-arylhydrazones (values in ppm) in $CDCl_3$ with TMS as internal standard.

$PhN{:}C(CH_3)C{:}NNH(m\text{-}CF_3Ph)\ C(O)(P\text{-}XPh)$ (Scheme 2)

Protons	Compounds				coupling constant (J)
	X=H	X=Br	X=Cl	X=F	
H_a	8.00dbr	7.85dbr	7.50dbr	8.04dbr	$H_a, H_b = H_b, H_a$
H_b	7.15dd	7.62dd	7.45dd	7.15dd	$H_h, H_g = H_g, H_h$ = 8 Hz
H_c	7.42sbr	7.38sbr	7.38sbr	7.38sbr	
H_d	7.44dd	7.40dd	7.40dd	7.40dd	
H_e	7.24dd	7.30dd	7.30dd	7.26dd	H_d, H_e = 8 Hz
H_f	7.28dbr	7.31dbr	7.31dbr	7.30dbr	
H_g	6.94dbr	6.94dbr	6.95dbr	6.94dbr	$H_d, H_c = H_d, H_f$ = 1.5Hz
H_h	7.49dd	7.45dd	7.42dd	7.45dd	
H_i	7.20dd	7.22dd	7.23dd	7.23dd	$H_e, H_d = H_e, H_f$ = 8 Hz
H_j	7.27dd	-	-	-	
CH_3	2.30sbr	2.30sbr	2.30sbr	2.30sbr	
N-H	15.64sbr	15.72sbr	15.70sbr	15.66sbr	

abbreviations : s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet;
br, broad.

TABLE 2

Melting point and analytical data of 1-(4-Xphenyl)-3-phenylimino-1,2-butanedione-2-(3-trifluorophenyl)hydrazones (a) and bis 2-(3-trifluorophenylazo)-3-(phenylimino)-1-(4-Xphenyl)-1-butanato nickel(II)(b).

	X	M.P. (°C)	C %		H %		F %		N %		Ni %	
			Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
(a)	Ligands											
1.	H	127	67.4	67.5	4.4	4.4	13.9	13.9	10.2	10.2	-	-
2.	Br	150	56.5	56.5	3.4	3.4	11.6	11.7	8.6	8.6	-	-
3.	Cl	156	62.2	62.2	3.8	3.8	12.8	12.8	9.4	9.4	-	-
4.	F	170	64.6	64.6	3.9	4.0	13.3	13.3	9.8	9.8	-	-
(b)	Complexes											
1.	H	119	63.1	63.0	3.8	3.8	13.0	13.0	9.8	9.5	6.7	6.6
2.	Br	145	53.4	53.4	3.0	2.9	11.0	11.0	8.1	8.1	5.6	5.6
3.	Cl	124	58.4	58.5	3.3	3.3	12.0	11.9	8.9	8.8	6.2	6.2
4.	F	130	60.6	60.5	3.5	3.5	16.6	16.7	9.2	9.1	6.4	6.4

In the mass spectra of glyoxaliminohydrazones a molecular ion peak was observed for all species. Some of the characteristics observed during mass degradation are : (i) presence of $Ar{=}CO^+$, (ii) formation of fragments $M{-}CH_3C{:}NC_6H_5^+$ and $M{-}NHC_6H_4CF_3{-}m^+$. These characteristics give additional evidence for the existence of the hydrazoneimino tautomeric form (A).

EXPERIMENTAL

Fluorobenzene [10], 4-substituted acetophenones [10,11], 1,3-diketones [12,13], 1,3-ketoamines [14], 3-aminobenzotrifluoride [15,16] and its diazonium chloride [17] were prepared by literature methods.

The fluorinated glyoxaliminehydrazones were prepared by modifying the earlier reported methods [1,4]. The condensation of m-trifluoromethylphenyldiazonium chloride (0.01M) and the ketoamine (0.01M) was carried out at 0-5°C in pyridine. The compounds were precipitated by the addition of water and recrystallized from ethanol. The compounds prepared and their analytical data are recorded in Table 2.

The nickel complexes were prepared by the method of Hirsch [1] by refluxing a mixture of nickel chloride hexahydrate (0.005M), the hydrazone (0.01M) and triethylamine (0.01M) in absolute alcohol. They were purified by recrystallization from ethanol and dried in vacuum over P_2O_5.

The complexes prepared and their analytical data are recorded in Table 2.

IR spectra were recorded using a Perkin-Elmer-577 spectrometer in KBr pellets; ^1H NMR spectra by a Bruker WH-400 in $CDCl_3$ solution with TMS as an internal standard; MS were recorded on a Jeol JMS-D 300 instrument. Melting points are uncorrected.

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