

## Studies of Penta-Coordinated Complexes of Nickel(II) with Hydrazones

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The combining ratio is 1 : 1 in all the complexes. The electronic spectra of  $[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4)\text{Cl}]$ ,  $[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}]$ ,  $[\text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_3)\text{Cl}]$  complexes show bands in the region 7000-9000, 10000-12000, 15000-17000 and 22000-23,000  $\text{cm}^{-1}$ , a characteristic of penta co-ordination assigned to  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{B}_2(\text{F})$ ;  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{F})$ ;  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{P})$  and  ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}$  transitions in order of increasing energy, based on  $\text{C}_4\text{v}$  symmetry, and the transitions are related. IR studies indicate the involvement of  $>\text{C}=\text{O}$ ,  $-\text{CH}=\text{N}$  and  $(\text{CONH})$  groups in coordination.

**Key Words:** Penta-coordinated, Complexes, Nickel(II).

### INTRODUCTION

The transition metal complexes of varied coordination number are reported.<sup>1,2</sup> Electronic structure of Ni(II) complexes has been reviewed by sacconi.<sup>3</sup> In the present studies complexes of  $\text{Ni}^{2+}$  have been isolated and characterised by elemental analysis, magnetic, electronic and IR spectral studies to be penta-coordinated.

TABLE-1  
ANALYTICAL DATA OF NICKEL COMPLEXES

Compound	Analysis Found (Caled.)%			
	Ni	C	H	N
$[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4)\text{Cl}]$	15.92 (16.07)	45.90 (46.00)	2.97 (3.01)	6.92 (7.66)
$[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}]$	14.93 (15.40)	43.77 (44.07)	2.63 (2.88)	6.99 (7.34)
$[\text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_3)\text{Cl}]$	14.65 (15.64)	50.93 (51.17)	3.20 (3.46)	7.23 (7.46)

### Preparation of Ni(II) Complexes

Ni(II) hydrazones were obtained by first refluxing ethanolic solution of 2-acetyl furan glyoxal; 2-acetyl thiophene glyoxal and phenyl glyoxal (20 mL, 0.010 mole) and *p*-methoxy benzyl hydrazide (20 mL, 0.10 mole) frequency by

adding an ethanolic solution of  $\text{NiCl}_2$  (25 mL, 0.005 mole). After adjusting the pH with ethanolic sodium hydroxide (0.8%, 2 mL) the mixture was refluxed for about 2 h, and allowed to stand for about 1 h at room temperature. The complexes were filtered as coloured precipitate, washed with water and dried.

TABLE-2  
MAGNETIC AND SPECTRAL DATA OF PENTA-COORDINATED Ni(II) COMPLEXES

Complexes	Bands ( $\text{cm}^{-1}$ )	B	Dq	DQ	DS	DT
$[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4)\text{Cl}]$	3BI(F)	461	1840	23097	7427	4632
	↓					
	7400 ( $\nu_1$ )					
	15080					
	18400( $\nu_2$ )					
	22080					
$[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}]$		369	1030	24457	5200	3250
	0200 ( $\nu_1$ )					
	18300( $\nu_2$ )					
	16800 ( $\nu_2$ )					
	22340					
$[\text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_3)\text{Cl}]$		454	1070	25380	5446	3399
	8500 ( $\nu$ )					
	10900					
	15880					
	22340					
	22700					

Complex	$D_{qz}$	DT/DQ	DS	Dt	$d\sigma$	$d\pi$	$\mu_{\text{eff}}$ (B.M)
$[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4)\text{Cl}]$	442	0.20	-1861	342	1805	2446	2.50
$[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}]$	610	0.132	-744	240	1266	1716	2.65
$[\text{Ni}(\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_3)\text{Cl}]$	630	0.133	-778	251	1323	1794	2.72

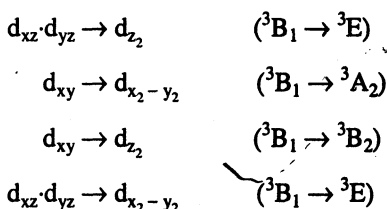
## RESULTS AND DISCUSSION

The magnetic susceptibility of the Ni(II) complexes lie in the range 2.50–2.72 B.M. The postulated range for high spin six-coordinated nickel complexes is 2.80–3.20 B.M. but however distorted nickel complexes are known to have magnetic moment as long as 2.50 B.M. But the possibility of being distorted octahedral has been ruled out on the basis of electronic spectra. Five-coordinated nickel complex with low  $\pi$ -bond forming ability has been found to have magnetic

moments in the range 1.71–2.50 B.M. and in one case a diamagnetic species has been reported.<sup>4,5</sup> In the present complexes all the donor atoms are hard in nature according to concept of Pearson, therefore, the cause of observed low magnetic moments appears to be other than the nature of donor atom. The lower magnetic moment value may be (a) distortion from the regular square-pyramidal or trigonal bipyramidal stereochemistry towards the square-planar structure, (b) presence of a diamagnetic species, (c) a spin state equilibrium, and (d) presence of anti-ferromagnetic interaction.<sup>6,7</sup>

The electronic spectra of the complexes do not show bond characteristics of square-planar geometry, hence the possibility of diamagnetic impurity is ruled out.

The electronic spectra of the complexes show bands in the region 7000–9000, 10000–12000, 15000–17000 and 22000–23000  $\text{cm}^{-1}$ , a characteristic of pentacoordination assigned to  ${}^3B_1(F) \rightarrow {}^3B_2(F)$ ;  ${}^3B_1(F) \rightarrow {}^3E(F)$ ;  ${}^3B_1(F) \rightarrow {}^3A_2(P)$  and  ${}^3B_1(F) \rightarrow {}^3E$ , transitions in order of increasing energy, based on  $C_{4v}$  symmetry and the transitions are related<sup>8</sup>.



The transitions are used in evaluating radial parameters DS and Dt as well as B (the separation between  ${}^9F$  and  $3p = 15B$ ). Making use of normalised spherical harmonic (NSH) Hamiltonian theory, the values of DQ, DS and DT also have been calculated.

The ratio DQ/DT gives the amount of distortion whereas Meclure<sup>10</sup> parameters ( $d\sigma$  and  $d\pi$ ) indicate the donating abilities of ligands to metal ion in axial and equatorial position.<sup>11</sup>

$$d\sigma = \sigma_z - \sigma_L \quad \text{and} \quad d\pi = \pi_z - \pi_L$$

The relationship between crystal field parameter and molecular orbital parameter are as follows:

$$8d\sigma = -12DS - 15Dt$$

$$2d\pi = -3DS + 5Dt$$

The values of  $d\sigma$  and  $d\pi$  have been calculated and the values are 1805, 1266, 1323 and 2446, 1716, 1794 respectively.

### IR Studies

The presence of aromatic ring indicated by the usual peaks, *i.e.*, a (C—H) stretching at  $3000 \text{ cm}^{-1}$ ,  $\nu(\text{C—C})$  stretching at *ca.*  $1460 \text{ cm}^{-1}$ , a (C—H) in-plane bending *ca.*  $1170 \text{ cm}^{-1}$  and  $1040 \text{ cm}^{-1}$  and (C—H) out-of-plane deformation at  $860 \text{ cm}^{-1}$ .

The peak observed at  $1610 \text{ cm}^{-1}$  (for C=N) vibration suggest the hydrazone

formation. The doublet at  $3,200\text{ cm}^{-1}$  represents  $\text{—NH}$  stretching and for (CONH) and that at  $1300\text{ cm}^{-1}$  to other linkage. The (N—H) bending absorption appeared at  $1560\text{ cm}^{-1}$ . The spectra also show a broad band at  $1700\text{—}1650\text{ cm}^{-1}$  region be due to which may include stretching frequency of free (C=O) and  $\text{—(CH=N)}$ . The perturbed (C=O) or  $\text{—(CH=N)}$  stretching frequency of free (C=O) and  $\text{—(CH=N)}$  stretching vibration appear as a broad band near  $1680\text{ cm}^{-1}$  can be attributed to the coordinated  $\text{—(CH=N)}$  and (C=O) stretch involving coordination through the nitrogen atom of the azomethine group.<sup>12,13</sup>

A broad band obtained at  $3000\text{ cm}^{-1}$  in the spectrum of the ligands is due to the enolic  $\text{—OH}$  which on complexation presumably deprotonates.

In conclusion, it is suggested that complexation leads to the bonding through enolic  $\text{—OH}$  nitrogen atom of ( $\text{—CH=N}$ ) and ketonic  $\text{>C=O}$  (oxygen)<sup>14</sup>. Evidence in favour of three bonding sites is further substantiated by observation of  $\nu(\text{Ni—O})$ ,  $\nu(\text{Ni—N})$  and  $\nu(\text{Ni—S})$  stretching bands in the far IR spectrum of the complexes<sup>15–17</sup>.

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