

## Organo nickel complexes of Schiff bases

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### ABSTRACT

The present paper deals with the study of synthesis and characterization of Ni(II) complexes as organo nickel complexes of Schiff's base. The study is supported by transitional energy measurement, magnetic susceptibility, infrared spectral study etc.

**Key words:** Organo nickel complexes, Schiff base, infrared study.

### INTRODUCTION

Considerable interest has been shown in the synthesis and physicochemical properties of the transition metal complexes of poly amine ligands. Studies on the reaction of coordinated imino group e.g. amine exchange reactions are of considerable interest not only because of preparative significance<sup>1,2</sup> but also for the understanding of the biological processes of transamination and determination<sup>3</sup>. Often these reactions continue unique methods for the synthesis of coordination compounds, which are otherwise not obtainable by the routine procedure. It was therefore thought worthwhile to react the metal with the hetrochelates and study their structures in an environment of hetero atomic ligands field around the cation.

### MATERIAL AND METHODS

Organic complexes were isolated by reported methods(4) . Molecular formulae of the complexes were given in table 1.

### RESULTS AND DISCUSSION

**Magnetic susceptibility measurement of**  
 $[\text{Ni}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{SO})_2]$ ,  $[\text{Ni}(\text{C}_{18}\text{H}_{14}\text{NSO}_4)_2]$ ,  
 $[\text{Ni}(\text{C}_{15}\text{H}_{17}\text{ON}_2)_2] (\text{H}_2\text{O})_2$ ,  $[\text{Ni}(\text{C}_{12}\text{H}_{11}\text{NO})_2 \text{Cl}_2]$ ,  
 $[\text{Ni}(\text{C}_{17}\text{H}_{17}\text{N}_4\text{SO})_3]$

The octahedral Ni(II) Complexes should have magnetic moments ranging from 2.9 to 3.9 B.M. depending upon the magnitude of orbital contribution and tetrahedral nickel complexes have moment ranging from 3.5 to 4.2 B.M. In the present complexes magnetic moment lie in between 3.36-3.30 B.M. which is well in the range for octahedral complex<sup>5-6</sup>.

### Electronic spectral studies

$[\text{Ni}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{SO})_2]$

The electronic spectra of the complex is helpful in assigning the geometry around the metal ion, if the Ni<sup>+2</sup> complex show two bands around 15630 and 9000 cm<sup>-1</sup> with a sharp band at 400 nm, then the geometry around the Ni<sup>+2</sup> is tetrahedral<sup>7-9</sup>. These bands have therefore assigned to the

transition  ${}^3T_1(E) \rightarrow {}^3T_1(P)$  and  ${}^3T_1(E) \rightarrow {}^3T_2$  respectively.

In the octahedral Ni (II) complexes, three bands due to the transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ),  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) and  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  ( $\nu_1$ ) are possible. In our complexes the bands due to  $\nu_3$ ,  $\nu_2$  and  $\nu_1$  are observed at 27300, 15470 and 9480  $\text{cm}^{-1}$  respectively. The bands in the region 10000-5000  $\text{cm}^{-1}$  are split showing distortion of octahedral symmetry to lower symmetry. Furlani<sup>10</sup> Maki<sup>11</sup> Ballhausen<sup>(12)</sup> independently calculated the energy level of Nickel in distorted octahedral environment and have shown that departure from cubic octahedral symmetry results in the splitting of orbital triplets  ${}^3T_{1g}$  and  ${}^3T_{2g}$  producing a large number of electronic transitions.

The value of 10 Dq and B have been calculated using the transition equations, and included in the table.

$$10 Dq = 9/34 [ E_1 + E_2 \% \{ ( E_1 \% E_2 )^2 \% 16/81 E_1 E_2 \} ]^{1/2}$$

$$15 B = E_1 + E_2 \% 30 Dq$$

### [Ni(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)<sub>2</sub>]

For complex with d<sup>8</sup> configuration in octahedral symmetry, three bands are expected in the electronic spectrum attributed to the transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  ( $\nu_1$ ),  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ).

The electronic spectrum of [Ni(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)<sub>2</sub>] complex exhibits band in the region 1000 ( $\nu_1$ ), 16700 ( $n_2$ ) and 27380  $\text{cm}^{-1}$  ( $n_3$ ) and weak shoulder at 13360  $\text{cm}^{-1}$ . These are d-d transitions. B-value 938  $\text{cm}^{-1}$  for [Ni(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)<sub>2</sub>] is calculated from  $n_1$ ,  $n_2$  and  $n_3$  band energies using the diagonal sum rule ( $15 B = \nu_1 + \nu_2 - 3 \nu_3$ ). This result is comparable to the other octahedral Ni (II) complexes. The transition  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  ( $\nu_1$ ) directly give the value of 10 Dq. The position of theoretical bands  $\nu_2$  and  $\nu_3$  were calculated from the secular<sup>13</sup> determinant are in good agreement with the observed values.

$$\nu_2 = 15B/2 + 3/2 (10 Dq)^{-1/2} [(9B^2 - 10Dq)^2 + 144B^2]^{1/2}$$

$$\nu_3 = 15B/2B + 3/2 (10 Dq) + 1/2 [(9B^2 - 10Dq)^2 + 144B^2]^{1/2}$$

**Table 1: Analytical data of the nickel (II) complexes**

S. No.	Complexes	% Analytical data found (calc.)						
		C	H	N	S	Cl	Ni	$\mu_{\text{eff}}$
1.	[Ni(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> SO <sub>2</sub> ) <sub>2</sub> ]	60.66 (60.73)	3.66 (3.71)	9.38 (9.44)	9.98 (10.79)	—	9.72 (9.90)	3.50
2.	[Ni(C <sub>18</sub> H <sub>14</sub> NSO <sub>4</sub> ) <sub>2</sub> ]	58.10 (58.48)	3.70 (3.79)	3.71 (3.79)	8.56 (8.66)	—	7.85 (7.94)	3.48
3.	[Ni(C <sub>15</sub> H <sub>17</sub> ON <sub>2</sub> ) <sub>2</sub> ] (H <sub>2</sub> O) <sub>2</sub>	62.36 (62.42)	6.52 (6.58)	9.66 (9.71)	—	—	10.63 (10.71)	3.51
4.	[Ni(C <sub>12</sub> H <sub>11</sub> NO) <sub>2</sub> Cl <sub>2</sub> ]	57.56 (57.63)	4.32 (4.40)	5.52 (5.60)	—	13.74 (14.20)	11.68 (11.74)	3.58
5.	[Ni(C <sub>17</sub> H <sub>17</sub> N <sub>4</sub> SO <sub>3</sub> ) <sub>3</sub> ]	59.06 (59.20)	4.86 (4.93)	16.03 (16.25)	9.96 (9.28)	—	5.56 (5.67)	3.45

1. 2-( $\beta$ -Hydroxyl acetyl naphthalimine) Thiazole Nickel (II) complex
2. O-( $\beta$ - Hydroxyl-1- acetyl naphthalimine) Benzene sulphonic acid Nickel (II)sulphate
3. 2- Hydroxyl acetyl naphthalene propane -1,2- diamine Nickel (II) complex
4. O-Tolyl furfuralimine Nickel (II) complex
5. 3-Propyl-4-amino-5-mercapto-2'- Hydroxyl acetyl naphthalidene Nickel (II) complex

Table 2: Experimental transition energies and calculated values for parameters

Complexes	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ( $\nu_3$ )	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ( $\nu_2$ )	${}^3A_{2g}(F) \rightarrow {}^3E_g(P)$ ( $\nu_1$ )	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ ( $\nu_1$ )	B	10 Dq	Calcd. ( $\nu_2$ )	Calcd. ( $\nu_3$ )	L.F.S.E. K.Cals/mole	$\beta$
[Ni(C <sub>15</sub> H <sub>17</sub> N <sub>2</sub> SO) <sub>2</sub> ]	27300	15470	9830	9480	363	9480	9760	15184	22.2857	0.34
[Ni(C <sub>18</sub> H <sub>14</sub> NSO) <sub>2</sub> ]	27380	16700	-	10000	938	10000	19005	25065	34.2857	0.90
[Ni(C <sub>15</sub> H <sub>17</sub> ON <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	28360	15870	9700	12340	547	12340	18901	26323	42.3085	0.52
[Ni(C <sub>12</sub> H <sub>11</sub> NO) <sub>2</sub> Cl <sub>2</sub> ]	31400	17340	10600	11890	871	11890	22617	26117	40.7657	0.83

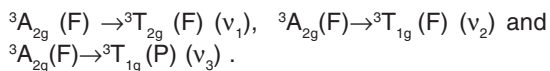
Table 3: Infrared spectral data of the Nickel (II) complexes

[C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> SO]	[Ni(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> SO) <sub>2</sub> ]	[C <sub>18</sub> H <sub>15</sub> NSO <sub>4</sub> ]	[Ni(C <sub>18</sub> H <sub>14</sub> NSO) <sub>2</sub> ]	[C <sub>15</sub> H <sub>18</sub> ON <sub>2</sub> ]	[Ni(C <sub>15</sub> H <sub>17</sub> ON <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Assignments
1620(s)	1600(str)	1640(s)	1620(s)	1640(s)	1605(s)	-CH=N
3480(s)	3440(m)	3500(w)	-	3480	-	-OH
1320(wag)	1290(mw)	1300(tw)	1280(m)	1280(w)	1337(m)	(-C%O)Phenolic
2600(str)	2550(mw)	-	-	-	-	(C%S%O)
-	-	3170	-	-	-	(SO <sub>2</sub> OH)
3050(m)	3010	3040(w)	3050(str)	3050(str)	3070(str)	(C%H) Aromatic
-	1100	-	1070(w)	1080(s)	1080(s)	Ring formation

(m) = medium ; (mw) = medium weak ; (s) = strong ; (sh) = shoulder ; (str) = stretch ; (tw) = twisting ; (w) = weak ; (wag) = wagging

**[ Ni(C<sub>15</sub>H<sub>17</sub>ON<sub>2</sub>)<sub>2</sub> ] (H<sub>2</sub>O)<sub>2</sub>**

The electronic spectrum of [Ni(C<sub>15</sub>H<sub>17</sub>ON<sub>2</sub>)<sub>2</sub>] (H<sub>2</sub>O)<sub>2</sub> complex shows two broad bands at 11000 and 17460 cm<sup>-1</sup> indicating a pseudo octahedral stereochemistry around the Ni(II) ion in the complex.<sup>(14,15)</sup> There are three spin allowed d-d transitions predicted for Ni(II) ion in a regular octahedral field represented by



The octahedral coordination sphere of Ni(II) ion in the complex is distorted by the band splitting in the spectra of the complex. Various values of ligand field parameters Dq, B, L.F.S.E. and E<sub>1</sub> and E<sub>2</sub> have been calculated using following matrix.

$$10 Dq = 9/34 [ E_1 + E_2 \% \{ ( E_1 \% E_2 )^2 \% 16/81 E_1 E_2 \} ]^{1/2}$$

$$15 B = E_1 + E_2 - 30 Dq$$

**[ Ni(C<sub>12</sub>H<sub>11</sub>NO)<sub>2</sub> Cl<sub>2</sub> ]**

The electronic spectra of [Ni(C<sub>12</sub>H<sub>11</sub>NO)<sub>2</sub> Cl<sub>2</sub>] complex exhibits characteristic bands associated with octahedral stereochemistry. In octahedral symmetry the <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>T<sub>1g</sub>(F) level of an octahedral complex splits into (<sup>3</sup>B<sub>2g</sub>+E<sub>g</sub>), (<sup>3</sup>A<sub>2g</sub>+<sup>3</sup>E<sub>g</sub>). The ligand field parameter calculated by using the lever<sup>(16)</sup> method. Confirm the octahedral coordination for the complex B, n<sub>2</sub> and n<sub>3</sub> as follows.

$$15 B = (\nu_2 + \nu_3 - 3\nu_1).$$

And the theoretical transitions  $\nu_2, \nu_3$  by the following equation :

$$\nu_2 = 15B/2 + 3/2 (10 Dq)^{-1/2} [(9B^{-1}10Dq)^2 + 144B^2]^{1/2}$$

$$\nu_3 = 15B/2B + 3/2 (10 Dq) + 1/2 [(9B^{-1}10Dq)^2 + 144B^2]^{1/2}$$

For a d8 system in an octahedral field the first transition <sup>3</sup>A<sub>2g</sub>(F)→<sup>3</sup>T<sub>2g</sub>(F) represents 10 Dq. The parameter B can also be calculated by the method

Complexes	Transitions	10 Dq	Dt	B	β	L.F.S.E.K. Cals/mole	
[ Ni(C <sub>17</sub> H <sub>17</sub> N <sub>4</sub> SO) <sub>3</sub> ]	<sup>3</sup> B <sub>1g</sub> → <sup>3</sup> E' <sub>g</sub> (ν <sub>1</sub> )	9900	12400	240	713	42.51	21.25
	<sup>3</sup> B <sub>1g</sub> → <sup>3</sup> B <sub>2g</sub> (ν <sub>2</sub> )	14500					
	<sup>3</sup> B <sub>1g</sub> → <sup>3</sup> A <sub>2g</sub> (ν <sub>3</sub> )	25900					
	<sup>3</sup> B <sub>1g</sub> → <sup>3</sup> E <sub>g</sub> (ν <sub>1</sub> )	12300					
	<sup>3</sup> B <sub>1g</sub> → <sup>3</sup> A <sub>2g</sub> (ν <sub>1</sub> )	16800					

**Table 4: Infrared spectral data of some Ni (II) complexes**

(C <sub>12</sub> H <sub>11</sub> NO)	[ Ni(C <sub>12</sub> H <sub>11</sub> NO) <sub>2</sub> Cl <sub>2</sub> ]	(C <sub>17</sub> H <sub>18</sub> N <sub>4</sub> SO)	[ Ni(C <sub>17</sub> H <sub>18</sub> N <sub>4</sub> SO) <sub>3</sub> ]	Assignments
1600	1640	1640	1600(s)	-CH=N
1250	1210	—	—	(C%O%C)
—	—	3450(s)	3380(s)	(NH <sub>2</sub> )
—	—	3320(m)	3300(m)	ν (NH)
—	—	1380	1370	(SO <sub>2</sub> -NH)
—	—	1380(sh)	1300(sh)	
—	—	1150	1150	δ NH
—	—	1050(sh)	1080(sh)	
—	—	1490(s)	1265(s)	δ NH <sub>2</sub>
—	—	1520(s)	1410(m)	-CH <sub>3</sub>
1170(w)	1190(sh)	1180(m)	1170(s)	(C-H)
1150(m)	1180(s)	1150(w)	1140(s)	

of Underhill and Billing<sup>17</sup>. The value of B calculated is lowered than the free ion value reflecting the extent of covalent character of the metal ligand bond.

#### [Ni(C<sub>17</sub>H<sub>17</sub>N<sub>4</sub>SO)<sub>3</sub>]

The electronic spectra of the nickel complex shows bands at 9900 cm<sup>-1</sup>(v<sub>1</sub>), 12300 cm<sup>-1</sup>(v<sub>1</sub>'), 14500 cm<sup>-1</sup>(v<sub>2</sub>), 16800 cm<sup>-1</sup>(v<sub>1</sub>'') and 25900 cm<sup>-1</sup>(n<sub>3</sub>) a characteristic of distorted octahedral environment which are assigned to transitions (<sup>3</sup>B<sub>1g</sub>→<sup>3</sup>E<sub>g</sub>'), (<sup>3</sup>B<sub>1g</sub>→<sup>3</sup>B<sub>2g</sub>), (<sup>3</sup>B<sub>1g</sub>→<sup>3</sup>A<sub>2g</sub>), (<sup>3</sup>B<sub>1g</sub>→<sup>3</sup>E<sub>g</sub>) and (<sup>3</sup>B<sub>1g</sub>→<sup>3</sup>A<sub>2g</sub>). The energy of the component obtained by splitting of the (v<sub>1</sub>) band is given by

$$E(^3B_{1g} \rightarrow ^3B_{2g}) = 10 Dq$$

$$E(^3B_{1g} \rightarrow ^3E_g) = 10 Dq - 35/4 Dt.$$

The value of 10 Dq can be obtained directly while Dt is calculated from the splitting of the first band, 35/4 Dt. However the field strength is asserted by Dt (d<sub>4h</sub>) = 4/7 (Dq<sub>xy</sub> - Dq<sub>z</sub>)

Other calculated parameters are Dq, Dt, B and β. Further the ratio of v<sub>2</sub>/v<sub>1</sub>. Is also significant in pointing the stereochemistry<sup>18,19</sup> which comes to showing octahedral coordination in the complex.

#### Infrared spectral studies

[Ni(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>SO)<sub>2</sub>], [Ni(C<sub>18</sub>H<sub>14</sub>NSO<sub>4</sub>)<sub>2</sub>], [Ni(C<sub>15</sub>H<sub>17</sub>ON<sub>2</sub>)<sub>2</sub>] (H<sub>2</sub>O)<sub>2</sub>, [Ni(C<sub>12</sub>H<sub>11</sub>NO)<sub>2</sub> Cl<sub>2</sub>], [Ni(C<sub>17</sub>H<sub>17</sub>N<sub>4</sub>SO)<sub>3</sub>]

I R-spectra were recorded of the solids in KBr discs in the range 4000-400 cm<sup>-1</sup> region . All

the spectra show medium weak absorptions at 3050, 3010 cm<sup>-1</sup> due to aromatic C-H stretching. A prominent CH=N stretch is seen at 1620 in the complex. Aromatic C=C stretches give absorptions at 1610-1590 and 1530 cm<sup>-1</sup>. The C-N and C-O stretching absorptions are seen at 1200 cm<sup>-1</sup> and 1290 cm<sup>-1</sup> for this derivative.

The IR-spectrum of ligand exhibits bands at 3250, 2800, 1670, 1625 and 1540 cm<sup>-1</sup> due to v(C=N) and v(C=O) phenolic modes respectively. The v(NH) and v(C=O) bands disappear in the spectra of all the complexes, indicating the destruction of carbonyl moieties as a result of enolisation and subsequent coordination of enolic oxygens to the metal ion.

A new band appeared at 1280 cm<sup>-1</sup> is assigned to v(C=O) phenolic mode<sup>20-23</sup>. The shift of v(C=N) azomethine to lower frequency by 10-20 cm<sup>-1</sup> while shift of v(C=O) phenolic mode to higher frequency by 5-10 cm<sup>-1</sup> in the complexes, indicating the participation of azomethine nitrogen and phenolic oxygen atoms in coordination<sup>24-26</sup>. Thus Schiff base unit behave as monobasic bi/tridentate ligand.

The band of medium intensity observed in the region 2600-2500 cm<sup>-1</sup> is assigned to the (C=S) stretch. This band does not shift in spectra of complexes, showing its non participation in bond formation. The bands appeared at 3170 cm<sup>-1</sup> in the ligand, disappeared on chelation, show that SO<sub>2</sub>-OH also part in complexation.

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